Inorg. Chem. **1986**, *25*, 413-416 **413**

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Synthesis, Characterization, Structure, and Magnetic Properties of the Novel Trinuclear Copper(II) Hydroxo Complex $[(AE)_3Cu_3OH](ClO_4)_2$ (AEH = 7-Amino-4-methyl-5-aza-3-hepten-2-one)

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Received May 16, 1985

The synthesis, structure, and main properties of the (μ_3-hydroxo)tris(μ-7-amino-4-methyl-5-aza-3-hepten-2-onato)tricopper(2+) perchlorate complex $[(AE)_3Cu_3OH](ClO_4)_2$ are described. The cation is trinuclear with a Cu_3OH core held by peripheral bridging ligands. The compound crystallizes in the triclinic space group C_i^1-$P\bar{1}$ with two formula weights in a cell having the dimensions $a = 12.448$ (1) Å, $b = 12.698$ (1) Å, $c = 11.765$ (1) Å, $\alpha = 90.26$ (1)°, $\beta = 113.36$ (1)°, and $\gamma = 80.66$ (1)°. Magnetic susceptibility measurements point to a weak antiferromagnetic interaction ($J = -12$ cm^{-1}). These data are compared with those reported in the literature for similar (L_3Cu_3OH and L_3Cu_3O) trinuclear complexes derived from oximato ligands.

Introduction

There are numerous accounts in the literature describing the chemistry of metal complexes of Schiff base ligands containing two, four, five, and six donor atoms.[1-3] Particular attention has been paid to complexes of tetradentate diimino bases that result from the condensation of two molecules of a keto precursor with one molecule of diamine. Very few of the ligands reported so far have arisen from the condensation of the carbonyl function with only one end of the diamine.[4,5] We have recently shown[6] that it is possible to effect such a single condensation in the case of acetylacetone and ethylenediamine to obtain a potentially terdentate (N_2O) Schiff base, 7-amino-4-methyl-5-aza-3-hepten-2-one (abbreviated as AEH in the following). During the course of a general study of its complexing ability[7,8] we succeeded in preparing a novel trinuclear copper(II) complex involving a Cu_3OH core.

The existence of an M_3O core held by peripheral bridging ligands is well documented in the chemistry of iron(III) and chromium(III).[9] In the case of copper(II) the fully characterized examples are based on oxime ligands and involved either a central oxygen O^{2-} or a hydroxyl OH^-.[10-12] Recently a trinuclear copper(II) complex involving a central hydroxo group and bridging pyrazolates has been reported.[13] The data reported in the present paper show that the AEH ligand can lead to a similar (but not identical) structural framework.

Experimental Section

Compound Preparation. To a 7 × 10^{-3} M solution of AEH[6] in ethanol was first added triethylamine (2 mL) and, a few minutes later, the equivalent amount of copper perchlorate hexahydrate (2.6 g) dissolved in ethanol, giving a deep blue solution upon stirring at room temperature. Precipitation occured slowly. Two hours later, filtration gave a deep blue product, which was washed with ethanol and diethyl ether and then dried. Anal. Calcd for $C_{21}H_{40}Cl_2Cu_3N_6O_{12}$: C, 30.48; H, 4.82; Cl, 8.56; Cu, 22.96; N, 10.13. Found: C, 30.46; H, 4.82; Cl, 8.76; Cu, 22.49; N, 10.04. Slow crystallization from an acetone-water solution gave deep blue crystals suitable for X-ray diffraction study.

Table I. Summary of Crystal and Intensity Collection Data

compd: $[Cu_3(OH)(AE)_3](ClO_4)_2$
formula: $C_{21}Cl_2H_{40}N_6O_{12}Cu_3$
fw = 829.52
$a = 12.448$ (1) Å
$b = 12.698$ (1) Å
$c = 11.765$ (1) Å
$\alpha = 90.26$ (1)°
$\beta = 113.36$ (1)°
$\gamma = 80.66$ (1)°
$V = 1680.9$ Å^3
$Z = 2$
$F(000) = 850$
$D_{\text{measd}} = 1.64$ g/cm^3 [a]
$D_{\text{calcd}} = 1.639$ g/cm^3

space group: C_i^1-$P\bar{1}$
radiation: Mo Kα from graphite monochromator
linear abs coeff: $\mu = 21.1$ cm^{-1}
temp: 20 °C
receiving aperture: 4.0 × 4.0 mm; 30 cm from cryst
takeoff angle: 3.0°
scan mode: ω
scan range: $(0.80 + 0.35 \tan \theta)$°
2θ limits: 54°

[a] Measured by flotation in $C_2H_2Br_4/CH_2Cl_2$.

Caution! The compound reported here was isolated as the perchlorate salt. We have worked with this compound in a number of organic solvents without incident, and as a solid, it seems to be reasonably stable to shock and heat. In spite of these observations, the unpredictable behavior of perchlorate salts[14] necessitates extreme caution in their handling.

Physical Measurements. Infrared spectra of KBr disks were measured with a Perkin-Elmer 983 instrument. Electronic spectra were obtained with a Cary 14 spectrometer. EPR spectra were recorded at X-band and Q-band frequencies with a Bruker 200 TT spectrometer operating at 9.4-9.5 GHz and 34-34.5 GHz.

Magnetic susceptibility data were collected on powdered samples of the title compound with use of a Faraday type magnetometer fitted with a helium continuous-flow cryostat. Independence of the magnetic susceptibility vs. magnetic field was checked at each temperature. Mercury tetrakis(thiocyanato)cobaltate (susceptibility at 20 °C 16.44 × 10^{-6} cgsu) was used as a susceptibility standard. All data were corrected for diamagnetism (estimated at -328×10^{-6} cgsu for the title compound) and TIP (taken as 60 × 10^{-6} cgsu/Cu atom).

Collection and Reduction of X-ray Data. Crystals belong to the triclinic system, space group $P1$ or $P\bar{1}$. The structure was successfully solved in the C_i^1-$P\bar{1}$ space group. The selected dark blue crystal of dimensions 0.283 × 0.250 × 0.636 mm was sealed on a glass fiber and

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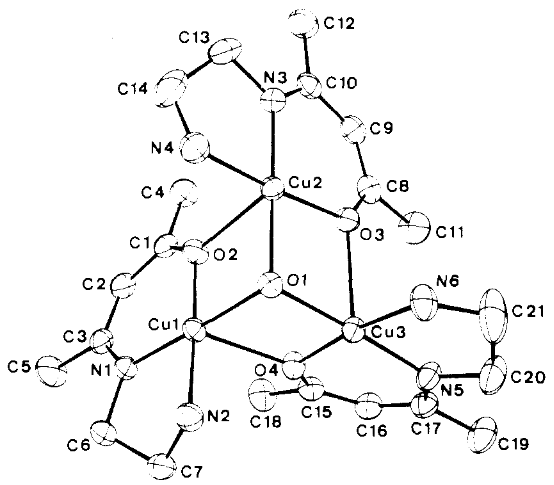

Figure 1. ORTEP plot of $[(AE)_3Cu_3OH](ClO_4)_2$ with the ellipsoids drawn at the 40% probability level.

mounted on an Enraf-Nonius CAD4 diffractometer. Cell constants were obtained from a least-squares fit of the setting angles of 25 reflections. A summary of crystal and intensity collection data are given in Table I. A total of 7300 independent reflections were recorded to a 2θ (Mo) maximum of 54° by procedures described elsewhere.[15] Intensity standards, recorded periodically, showed only random, statistical fluctuations. Intensity data were corrected for Lorentz, polarization, and absorption[16] ($\mu = 21.1$ cm^{-1}, calculated transmission range 0.58–0.69). A total of 4598 reflections for which $F_o^2 > 4\sigma(F_o^2)$ were used in subsequent calculations.

Structure Solution and Refinement. The structure was solved[17] by the heavy-atom method and difference Fourier maps. ClO_4 oxygen atoms appeared to be disordered. Their occupancy factor was first allowed to vary and then kept fixed to 50% in the final cycles of refinement. All non-hydrogen atoms, except the disordered one, were refined anisotropically.

The hydrogen atoms were located on a difference Fourier map and introduced in calculations in idealized positions (C–H = N–H = O–H = 0.95 Å) with an isotropic temperature factor $U = 0.063$ Å^2 kept fixed.

The atomic scattering factors used were those proposed by Cromer and Waber[18] with anomalous dispersion effects.[19] Scattering factors for the hydrogen atoms were taken from Stewart et al.[20]

The final full-matrix least-squares refinement, minimizing the function $\sum w(|F_o| - |F_c|)^2$, converged to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.027$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.031$ with unit weights. The error in an observation of unit weight was $S = [\sum w(|F_o| - |F_c|)^2/(n - m)]^{1/2} = 1.06$ with $n = 4598$ observations and $m = 389$ variables. In the last cycle of refinement the shifts for all parameters were less than 0.02σ. A final difference Fourier map showed no excursion of electron density greater than 0.3 e/Å^3.

Final fractional coordinates for non-hydrogen atoms are listed in Table II. An ORTEP plot[21] of the molecule with the atomic labeling scheme is shown in Figure 1.

Results and Discussion

The complex $[(AE)_3Cu_3OH]^{2+}$ has been first isolated from a reaction mixture containing copper(II) ions, the "half-unit" AEH, and pyridine. The expected complex, i.e. $[(AE)CuPy]^+$, was isolated in a low yield of ca. 20% due to a precipitation at the very early stage of the reaction.[22] Preliminary investigation of the nature of this precipitate pointed to the absence of pyridine. Furthermore, the ratio of ClO_4^- anions per metal atom was noninteger (2/3), suggesting a polynuclear structure that, on the basis of infrared data, could involve OH bridging.

Table II. Fractional Atomic Coordinates with Esd's in Parentheses

atom	x/a	y/b	z/c
Cu(1)	0.35516 (4)	0.21743 (4)	0.25964 (4)
Cu(2)	0.23262 (4)	0.34089 (4)	0.42621 (4)
Cu(3)	0.11619 (4)	0.15666 (4)	0.26111 (4)
O(1)	0.2724 (2)	0.1951 (2)	0.3730 (2)
O(2)	0.3079 (2)	0.3663 (2)	0.2696 (2)
O(3)	0.0733 (2)	0.3360 (2)	0.3138 (2)
O(4)	0.1568 (2)	0.1972 (2)	0.1286 (2)
N(1)	0.4399 (3)	0.2401 (3)	0.1574 (3)
N(2)	0.4137 (3)	0.0624 (3)	0.2554 (3)
N(3)	0.1936 (3)	0.4823 (3)	0.4759 (3)
N(4)	0.3946 (3)	0.3378 (3)	0.5592 (3)
N(5)	−0.0290 (3)	0.1130 (3)	0.1513 (3)
N(6)	0.0841 (3)	0.0920 (3)	0.3961 (3)
C(1)	0.3189 (4)	0.4432 (3)	0.2047 (3)
C(2)	0.3842 (4)	0.4289 (4)	0.1337 (4)
C(3)	0.4477 (4)	0.3319 (4)	0.1167 (4)
C(4)	0.2517 (4)	0.5518 (3)	0.2086 (4)
C(5)	0.5239 (5)	0.3393 (4)	0.0449 (6)
C(6)	0.5028 (4)	0.1378 (3)	0.1350 (4)
C(7)	0.4328 (4)	0.0524 (3)	0.1398 (4)
C(8)	−0.0117 (4)	0.4191 (3)	0.2774 (4)
C(9)	−0.0055 (4)	0.5154 (3)	0.3278 (4)
C(10)	0.0930 (4)	0.5463 (3)	0.4259 (4)
C(11)	−0.1231 (4)	0.3992 (4)	0.1715 (4)
C(12)	0.0746 (5)	0.6576 (4)	0.4660 (5)
C(13)	0.2943 (4)	0.5135 (4)	0.5781 (5)
C(14)	0.4048 (5)	0.4474 (5)	0.5841 (6)
C(15)	0.0820 (4)	0.2154 (3)	0.0136 (3)
C(16)	−0.0266 (4)	0.1861 (4)	−0.0339 (4)
C(17)	−0.0780 (4)	0.1320 (4)	0.0300 (4)
C(18)	0.1250 (4)	0.2721 (4)	−0.0674 (4)
C(19)	−0.1931 (4)	0.0957 (5)	−0.0460 (5)
C(20)	−0.0796 (5)	0.0538 (5)	0.2161 (5)
C(21)	−0.0370 (5)	0.0780 (6)	0.3444 (5)
Cl(1)	0.29396 (12)	0.15771 (11)	0.71575 (11)
O(5)	0.3871 (8)	0.2131 (7)	0.7889 (8)
O(6)	0.2744 (9)	0.0808 (9)	0.7801 (10)
O(7)	0.3367 (7)	0.0962 (7)	0.6362 (8)
O(8)	0.2044 (6)	0.2333 (6)	0.6332 (7)
O(5)′	0.2954 (12)	0.2625 (10)	0.7501 (11)
O(6)′	0.3122 (9)	0.0965 (8)	0.8277 (9)
O(7)′	0.3656 (9)	0.1204 (8)	0.6494 (9)
O(8)′	0.1576 (10)	0.1570 (9)	0.6521 (10)
Cl(2)	0.67361 (11)	0.15581 (11)	0.54917 (12)
O(9)	0.5884 (9)	0.2394 (8)	0.4671 (9)
O(10)	0.7185 (12)	0.1953 (12)	0.6508 (13)
O(11)	0.7720 (12)	0.1405 (11)	0.5235 (13)
O(12)	0.6339 (9)	0.0614 (8)	0.5495 (9)
O(9)′	0.5600 (10)	0.1363 (10)	0.5020 (10)
O(10)′	0.6786 (10)	0.2557 (9)	0.5975 (11)
O(11)′	0.7271 (9)	0.1349 (8)	0.4614 (10)
O(12)′	0.7341 (9)	0.0725 (8)	0.6470 (9)

Among the various types of copper(II) complexes prepared from AEH, $[(AE)_3Cu_3OH]^{2+}$ is actually the most readily accessible. Furthermore, it is easily purified by recrystallization from methanol or acetone, although the trimeric structure is retained in acetone but not in methanol (vide infra).

Spectroscopic Characterization. The infrared spectrum of $[(AE)_3Cu_3OH]^{2+}$ shows three absorbances in the O–H, N–H stretching frequencies area. A reasonably sharp band at 3551 cm^{-1}, which moves to 2628 cm^{-1} upon deuteration, is attributable to the bridging OH. Indeed, this band is lacking in the spectra of previously reported AEH complexes[7,8,22] and it appears in the correct energy region for O–H stretches as revealed by comparing to known monohydroxo-bridged copper(II) complexes.[23] There is thus little doubt that the complex contains a bridging hydroxo and not oxo group. The bands at 3339 and 3286 cm^{-1} are attributed to the NH_2 group of AEH. The other characteristic bands of this ligand are easily located at 1609 cm^{-1} ($\nu_{C=O}$, $\nu_{C=C}$), 1516

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Table III. Interatomic Distances (Å) and Angles (deg) Characterizing the Environment of the Copper Atoms and the Cu_3OH Core

Cu(1)–O(1)	2.028 (3)	Cu(1)–N(1)	1.937 (4)
Cu(1)–O(2)	1.904 (3)	Cu(1)–N(2)	1.992 (3)
Cu(1)–O(4)	2.393 (2)		
O(1)–Cu(1)–O(2)	85.8 (1)	N(1)–Cu(1)–N(2)	85.3 (2)
O(1)–Cu(1)–N(1)	177.6 (1)	O(4)–Cu(1)–O(1)	73.3 (1)
O(1)–Cu(1)–N(2)	95.1 (1)	O(4)–Cu(1)–O(2)	92.3 (1)
O(2)–Cu(1)–N(1)	93.8 (1)	O(4)–Cu(1)–N(1)	109.1 (1)
O(2)–Cu(1)–N(2)	176.8 (1)	O(4)–Cu(1)–N(2)	90.9 (1)
Cu(2)–O(1)	2.001 (3)	Cu(2)–N(3)	1.933 (4)
Cu(2)–O(3)	1.910 (2)	Cu(2)–N(4)	1.997 (3)
Cu(2)–O(2)	2.419 (4)		
O(1)–Cu(2)–O(3)	85.4 (1)	N(3)–Cu(2)–N(4)	85.9 (1)
O(1)–Cu(2)–N(3)	179.5 (2)	O(2)–Cu(2)–O(1)	73.9 (1)
O(1)–Cu(2)–N(4)	94.5 (1)	O(2)–Cu(2)–O(3)	96.4 (1)
O(3)–Cu(2)–N(3)	94.4 (1)	O(2)–Cu(2)–N(3)	105.7 (1)
O(3)–Cu(2)–N(4)	173.1 (2)	O(2)–Cu(2)–N(4)	90.2 (1)
Cu(3)–O(1)	2.006 (2)	Cu(3)–N(5)	1.926 (3)
Cu(3)–O(4)	1.915 (3)	Cu(3)–N(6)	1.994 (4)
Cu(3)–O(3)	2.389 (3)		
O(1)–Cu(3)–O(4)	85.2 (1)	N(5)–Cu(3)–N(6)	85.0 (2)
O(1)–Cu(3)–N(5)	176.8 (1)	O(3)–Cu(3)–O(1)	73.6 (1)
O(1)–Cu(3)–N(6)	95.6 (1)	O(3)–Cu(3)–O(4)	94.5 (1)
O(4)–Cu(3)–N(5)	93.7 (1)	O(3)–Cu(3)–N(5)	109.4 (1)
O(4)–Cu(3)–N(6)	171.3 (1)	O(3)–Cu(3)–N(6)	94.0 (1)
Cu(1)···Cu(2)	3.1924 (8)	Cu(2)···Cu(3)	3.1895 (8)
Cu(1)···Cu(3)	3.1985 (8)		
Cu(2)–Cu(1)–Cu(3)	59.88 (2)	Cu(1)–Cu(2)–Cu(3)	60.16 (2)
Cu(1)–Cu(3)–Cu(2)	59.97 (2)		
O(1)–H(O1)	0.950		
Cu(1)–O(1)–Cu(2)	104.8 (1)	Cu(1)–O(1)–H(O1)	113.9 (3)
Cu(1)–O(1)–Cu(3)	104.9 (1)	Cu(2)–O(1)–H(O1)	113.4 (2)
Cu(2)–O(1)–Cu(3)	105.5 (1)	Cu(3)–O(1)–H(O1)	113.3 (3)

cm^{-1} ($\nu_{C=N}$), and 755 cm^{-1} (δ_{C-H}). An absorbance at 529 cm^{-1}, which disappears upon deuteration, is likely related to ν_{Cu-OH}. Concerning the ClO_4^- anions, the ν_3 mode at 1090 cm^{-1} is somewhat broadened but the ν_4 band at 623 cm^{-1} is devoid of any splitting, suggesting that these anions are not coordinated to the copper atoms.[24]

Similar electronic spectra are obtained in Nujol mull and in acetone solution, both showing a single absorption at 600 and 596 nm, respectively. These values are consistent with a square-based geometry for the copper(II) ions.[25]

Description of the Structure. The complex consists of $[(AE)_3Cu_3OH]^{2+}$ fragments and nonbonded ClO_4^- anions in the ratio of two anions per cation. It may be emphasized that, in contrast with the trinuclear complexes derived from oxime ligands,[13] the anions do not contribute to the coordination spheres of the metal centers and the structure does not include any solvent molecule.

A view of the trinuclear cation is given in Figure 1. The relevant distances and angles are listed in Tables III, IV,[26] and V.[26]

A rough description of the structure can be done in terms of three mononuclear units, [(AE)Cu], interconnected through two types of oxygen bridges afforded by the oxygen atoms of the AE ligands and the central OH group, respectively. However, the resulting trinuclear species is devoid of any threefold symmetry axis.

The geometry at each copper(II) ion is best described as a distorted (4 + 1) square-based pyramid. The basal plane consists of two nitrogen and one oxygen atom from AE and the hydroxy OH^- while the apical site is occupied by one oxygen of another AE ligand, which, in turn, is basal to a second copper atom. As expected, the axial Cu–O bond is longer than the equatorial one. It may be underlined that the oxygen involved in this basal–equatorial bridge pertains to a carbonyl function, which is generally considered as a nonbridging group. In addition to these ligand-mediated bridges, the three copper atoms are held together by bonding to the central hydroxo group. These bonds are of slightly different lengths, i.e. 2.001 (3) Å for Cu(2), 2.006 (2) Å for Cu(3), and 2.028 (3) Å for Cu(1). The presence of Cu_3OH is confirmed by the trigonal pyramid formed by the Cu_3O fragment, the oxygen forming the apex of the pyramid, and the three copper atoms falling at the corners of an approximate equilateral triangle of sides 3.1924 (8), 3.1985 (8), and 3.1895 (8) Å. The apical oxygen is located at 0.804 (2) Å above the Cu_3 plane. The final evidence of the pyramidal structure is afforded by location of the hydrogen at the expected position for completing a pseudotetrahedral environment of the central oxygen atom.

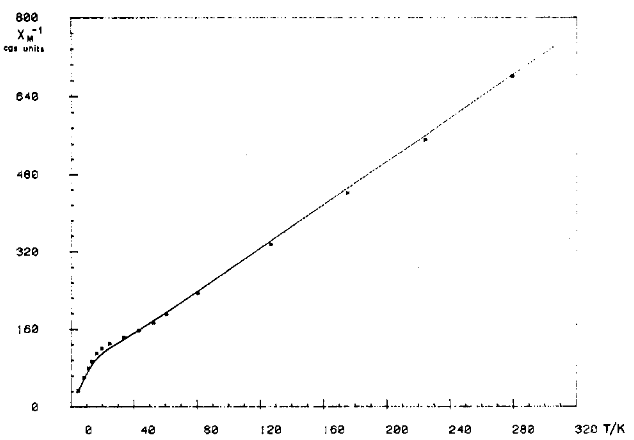

Figure 2. Inverse of the molar susceptibility (*) vs. temperature for $[(AE)_3Cu_3OH](ClO_4)_2$. The solid line represents the least-squares fit to the Curie–Weiss law.

Within each mononuclear unit the copper atom does not lie in the basal plane. As usual, it is displaced toward the apical ligand by 0.0458 (5) Å for Cu(1), 0.0506 (5) Å for Cu(2), and 0.0977 (5) Å for Cu(3). The lengths of the bonds between the copper atoms and the donor sites (O,N,N) of the AE ligands are within the range of values normally found for such bonds.[7,8] Furthermore, they only show small variations in going from one unit to the other. Similarly, interatomic distances and angles in the acetylacetone moiety are roughly identical in the three mononuclear units.

Slightly more important differences (up to 0.07 Å for distances and 6.9° for angles) are observed among the ethylenediamine moieties. Therefore, although (as a reviewer has noted) these variations could result from disorder in the $N-CH_2-CH_2-N$ chain, it is most likely that rearrangements of the ligands to accommodate the pseudotetrahedral geometry of the central oxygen and the formation of three axial Cu–O bonds are practically limited to these five-membered rings. Examination of the details of the structural study does not reveal any indication pointing to disorder. For instance, the fact that the hydrogen atoms in the ethylenediamine chains are clearly located on a difference Fourier map at the expected positions is hardly consistent with the occurrence of disorder.

The two perchlorate anions are disordered over two positions, and apparently they do not form even weak association with the copper ions. Some O(AE)–O(perchlorate) or N(AE)–O(perchlorate) contacts are suggestive of hydrogen-bonding interactions. However, these interactions must be weak and unable to prevent the disorder in both perchlorate ions.

Magnetic Properties. Magnetic susceptibility was determined as a function of temperature in the range of 4.5–280 K. The experimental data in the form of χ_M^{-1} vs. T are illustrated in Figure 2. They point to an overall antiferromagnetic interaction. At 4.5 K the moment per Cu_3 unit is practically equal to 1.8 μ_B so that the ground state has one unpaired electron per unit. As

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[26] Supplementary material.

the temperature rises, there is an increase of μ_{eff} consistent with a gradual occupation of a thermally accessible excited state. From the value of μ_{eff} at ca. 280 K one may conclude that this excited state is a quartet which is almost entirely populated at this temperature.

The magnetic-exchange interaction in a triangular arrangement of three $S = {}^1/_2$ ions may be treated with one exchange parameter if the three ions form an equilateral triangle.[27] This interaction results in three electronic states for the trinuclear complex, i.e. a quartet state and two doublet states. Within the simple model of an isotropic exchange interaction both of the doublet states have the same energy, which differs by $3J$ from the energy of the quartet state. A closed form of the magnetic susceptibility has been derived:[28]

$$\chi = \frac{Ng^2\beta^2}{4kT}\,\frac{1 + 5e^{3J/kT}}{1 + e^{3J/kT}}$$

The experimental data corrected for diamagnetic contributions and TIP (180×10^{-6} cgsu) for the trinuclear unit were analyzed with this equation to give $J = -12.0$ cm^{-1} and $g = 2.11$ so that the quartet state is 36.0 cm^{-1} at higher energy than the two doublets. In Figure 2, the best-fitted curve is represented by a solid line and it can be seen that the fit to experimental data is good.

EPR spectra of the trinuclear complex may be analyzed in terms of three EPR-active states more or less populated according to temperature. On the basis of susceptibility measurements a quartet spectrum is expected at room temperature. From literature data,[29-31] the quartet-state spectrum for an axial triradical consists of five main lines related to $\Delta m = \pm 1$ transitions. Lines of much lower intensities at "half- and third-field" may be also observed. They correspond to $\Delta m = 2$ and $\Delta m = 3$ transitions, respectively. At low temperature ($\sim$4.5 K) two doublets may be observed. However, it is not unreasonable to think that the two doublet states would have very similar g values so that the two expected spectra would merge into one. In practice, spectra of powdered samples do not show any signal from 300 to ca. 40 K. At 30 K, a broad signal devoid of any structure is observed at $g = 2.025$ while a much weaker adsorption is seen at $g \simeq 4.2$. At ca. 10 K, the main signal displays two features at $g = 2.186$ and 2.010, which may be attributed respectively to the $g_{\parallel}$ and $g_{\perp}$ parts of a doublet spectrum. The perpendicular component is somewhat structured, weaker signals being superimposed on the feature. From the corresponding g values (1.973, 1.928) these bumps are likely attributable to transitions within the quartet state. Furthermore the weak signal at $g = 4.2$, which is due to $\Delta m = 2$ transitions, is still observed. A relaxation mechanism due to the anisotropic dipolar coupling could account for the failure to detect resonance at higher temperatures.

It is noteworthy that a similar behavior has been observed for the pyrazolato-bridged complex.[13]

Methanolic solutions of the trinuclear complex yield spectra characteristic of mononuclear copper(II) complexes. The following parameters are deduced from the analysis of spectra obtained at 300 and 100 K: 300 K, $g_{\text{iso}} = 2.111$, $A_{\text{iso}} = 76$ G; 100 K, $g_{\parallel} = 2.236$, $g_{\perp} = 2.045$, $A_{\parallel} = 184$ G.

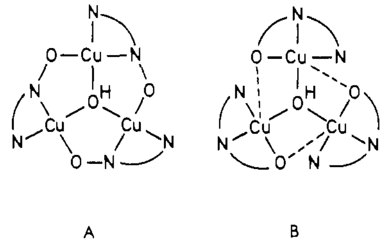

Figure 3. Schematic comparison between (A) $[L_3Cu_3OH(ClO_4)]^+$ (L being an oximato ligand) and (B) $[(AE)_3Cu_3OH]^{2+}$. In A, the perchlorate involved in coordination to the metal center has been omitted for clarity.

It is not unexpected that g values related to the mononuclear species existing in dilute methanolic solutions are different from the g values that characterize the doublet state of the trinuclear species.

In conclusion it may be recognized that $[(AE)_3Cu_3OH]^{2+}$ displays a much weaker magnetic interaction than the previously reported triangular copper(II) complexes. For instance, $|J|$ values of 122 and $\geq$300 cm^{-1} have been reported for $[L_3Cu_3OH(ClO_4)]^+$ (LH = 3-(phenylimino)butanone 2-oxime) and $[L'_3Cu_3O(ClO_4)]_2$ (L'H = 1,2-diphenyl-2-(methylimino)ethanone 1-oxime), respectively.[13]

The most prominent structural differences between $[(AE)_3Cu_3OH]^{2+}$ and the oximato complexes originate in the bonding frameworks, which are schematically represented in Figure 3.

First of all, in oximato complexes each bridge involves a pair of atoms (N,O) while in $[(AE)_3Cu_3OH]$ one atom (O) is involved.

Not considering the perchlorate anions, each copper atom in the oximato complex has a square-planar geometry, which includes the ligand-mediated bridge so that the three coordination planes tend to be coplanar. However, some degree of noncoplanarity is induced by the central O (or OH) bridge. In $[(AE)_3Cu_3OH]$ each AE ligand bridges two pentacoordinated copper atoms in an axial–equatorial arrangement, which together with the constraint of the central O (or OH) bridge forces the coordination planes to be orthogonal to each other. This is an oversimplified description but not inconsistent with the actual structural features.

In $[(AE)_3Cu_3OH]^{2+}$ the OH oxygen is located 0.804 (2) Å above the Cu_3 plane whereas in the oximato complexes the central oxygen is pushed much closer to the Cu_3 plane: 0.695 Å in $[L_3Cu_3OH(ClO_4)]^+$ and 0.352 Å in $[L'_3Cu_3O(ClO_4)]_2$. The coordination planes (O(1), O(4), N(5), N(6); O(1), O(2), N(1), N(2); O(1), O(3), N(3), N(4)) in $[(AE)_3Cu_3OH]^{2+}$ make angles of 98.4, 79.3, and 94.6° with each other. The angles reduce to 40.3, 28.5, and 31.1° in $[L_3Cu_3OH(ClO_4)]^+$ and 14.6, 20.4, and 26.6° in $[L'_3Cu_3O(ClO_4)]_2$. Thus it is clear that the magnitude of the magnetic coupling in these triangular copper(II) complexes strongly depends on the overall degree of coplanarity of the molecular framework.

Acknowledgment. We thank Dr. A. Mari for his contribution to the part of this work dealing with the magnetic measurements.

Registry No. $[(AE)_3Cu_3OH](ClO_4)_2$, 99687-33-9.

Supplementary Material Available: Listings of structure factors, anisotropic thermal parameters, hydrogen parameters, least-squares plane equations, hydrogen bonds and intermolecular contacts, and interatomic distances and angles characterizing the AE ligands and the two disordered perchlorate ions (29 pages). Ordering information is given on any current masthead page.

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