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Synthesis and Relation between Magnetism and Structure of a Trinuclear Copper(II) Hydroxo Complex $[Cu_3OHL_3(ClO_4)]ClO_4$ and a Hexanuclear Copper(II) Oxo Complex $[Cu_3OL'_3(ClO_4)]_2$ (LH = 3-(Phenylimino)butanone 2-Oxime, L′H = 1,2-Diphenyl-2-(methylimino)ethanone 1-Oxime)

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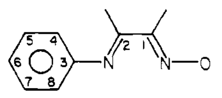
The synthesis, structure, and properties of the title complexes are described. The cation of the complex $[Cu_3OHL_3(ClO_4)]ClO_4$ is trinuclear with a Cu_3OH skeleton which has one oxime N–O bridge between each pair of copper atoms. By contrast, previous studies had identified Cu_3O species. The existence of the Cu_3OH fragment is confirmed by a pseudotetrahedral oxygen environment and by detection of the OH hydrogen atom and the extra perchlorate required by stoichiometry. $[Cu_3OL'_3(ClO_4)]_2$ is a centrosymmetric hexanuclear molecule containing two equivalent Cu_3O units, the central oxygens of which are bonded to a copper from the other Cu_3O unit via a relatively weak Cu–O bond (2.334 (3) Å). The central oxygens of the Cu_3O groups are very flattened tetrahedra, whose apices point along the Cu–O bonds linking the two Cu_3O units. The Cu_3O units in $[Cu_3OL'_3(ClO_4)]_2$ have stronger Cu–O bonds (av. 1.868 Å) than those in the Cu_3OH units of $[Cu_3OHL_3(ClO_4)]ClO_4$ (1.964 Å), in keeping with the greater negative charge on the central oxygen atom. $[Cu_3OHL_3(ClO_4)]ClO_4$ exhibits relatively strong intramolecular antiferromagnetic interactions ($J = -122$ cm^{-1}). At very low temperature (~5 K), a weak interionic interaction is evident so that the magnetic moment falls below that expected for one unpaired electron. In $[Cu_3OL'_3(ClO_4)]_2$ the antiferromagnetic interaction within the Cu_3O units is far stronger, so that only a single unpaired electron per Cu_3O unit is observed even at high temperatures. At low temperatures a further (weaker) interaction is observed, presumably between the two Cu_3O units of the hexanuclear complex to promote a further decrease in magnetic moment. Crystal data for $[Cu_3OHL_3(ClO_4)]ClO_4$: space group $P2_1/n$, $Z = 4$, $a = 15.630$ (8) Å, $b = 14.354$ (3) Å, $c = 17.255$ (4) Å, $\beta = 93.39$ (5)°, $V = 3864$ Å^3, $R = 6.4\%$ for 1840 reflections. Crystal data for $[Cu_3OL'_3(ClO_4)]_2$: space group $P2_1/n$, $Z = 2$, $a = 14.063$ (6) Å, $b = 19.449$ (5) Å, $c = 17.131$ (9) Å, $\beta = 97.62$ (4)°, $V = 4644$ Å^3, $R = 5.0\%$ for 4591 reflections.

Introduction

Trinuclear copper(II) compounds of various kinds have generated great interest. They may have three different types of copper environments for the three copper atoms,[1] one unique and a pair of equal environments,[2] or all three copper environments identical.[3] For the cases with three equal and unequal copper atoms, a compound containing a central hydroxyl OH^- and oxygen O^{2-} has been reported. The Cu_3O–oxime series recently reported is therefore of special magnetic, structural, and theoretical interest as is the possible existence of the Cu_3OH analogues. We examine here the trinuclear copper complexes **1** and **2** of L and L′, where LH = 3-(phenylimino)butanone 2-oxime and L′H = 1,2-diphenyl-2-(methylimino)ethanone 1-oxime. Complex **1** turns out to have the formulation $[Cu_3OHL_3(ClO_4)]ClO_4$ and does not have a central Cu_3O unit as expected from earlier literature,[4] while complex **2** is $[Cu_3OL'_3(ClO_4)]_2$.



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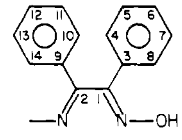

L′

Experimental Section

Preparation of the Complexes. $[Cu_3OHL_3(ClO_4)]ClO_4$. A 1 mmol sample of butane-2,3-dione oxime and 1 mmol of $Cu(ClO_4)_2 \cdot 6H_2O$ were dissolved in a mixture of methanol (ca. 50 mL) and triethyl orthoformate (5–10 mL) to yield a light green solution. An excess of aniline (2–3 mmol) was added, causing a color change to deep green. The resulting solution was heated and stirred for 10–15 min and then filtered into a flask and allowed to crystallize (usually within 2–3 days). Large green-black well-formed needlelike crystals resulted which were isolated by filtration.

$[Cu_3OL'_3(ClO_4)]_2$. Benzil oxime was synthesized from benzil via standard methods.[5] The same procedure was then followed as for the above compound with benzil oxime substituted for butane-2,3-dione oxime and methylamine substituted for aniline. Large green-black well-formed needlelike crystals resulted which were isolated by filtration.

Crystal Data for $[Cu_3OHL_3(ClO_4)]ClO_4$: $Cu_3Cl_2O_{12}N_6C_{30}H_{33}$, mol wt 832, space group $P2_1/n$, $Z = 4$, $a = 15.630$ (8) Å, $b = 14.354$ (3) Å, $c = 17.255$ (4) Å, $\beta = 93.39$ (5)°, $V = 3864$ Å^3, $\rho_{calcd} = 1.43$ g cm^{-3}, $\rho_{obsd} = 1.40$ g cm^{-3}, μ(Mo Kα) = 18.2 cm^{-1}, black crystal. Crystal dimensions (distances in mm of faces from centroid): (100) 0.12, $(\bar{1}00)$ 0.12, (010) 0.09, $(0\bar{1}0)$ 0.09, (001) 0.11, $(00\bar{1})$ 0.11. Maximum, minimum transmission coefficients 0.94, 0.92.

Crystal Data for $[Cu_3OL'_3(ClO_4)]_2$. $Cu_6Cl_2O_{16}N_{12}C_{90}H_{78}$, mol wt 1018, space group $P2_1/n$, $Z = 4$, $a = 14.063$ (6) Å, $b = 19.449$ (5) Å, $c = 17.131$ (9) Å, $\beta = 97.62$ (4)°, $V = 4644$ Å^3, $\rho_{calcd} = 1.46$ g cm^{-3}, $\rho_{obsd} = 1.42$ g cm^{-3}, μ(Mo Kα) = 15.3 cm^{-1}. Crystal dimensions (mm from centroid): (100) 0.13, $(\bar{1}00)$ 0.13, (010) 0.17, $(0\bar{1}0)$ 0.17, (011) 0.135, $(0\bar{1}\bar{1})$ 0.135, $(01\bar{1})$ 0.135, $(0\bar{1}1)$ 0.135. Maximum, minimum transmission coefficients 0.92, 0.87.

For each crystal, the Enraf-Nonius program SEARCH was used to obtain 25 accurately centered reflections that were then used in the program INDEX to obtain approximate cell dimensions and an orientation matrix for data collection. Refined cell dimensions and their standard deviations were obtained from least-squares refinement of 28 accurately centered reflections. The mosaicity of each crystal was examined by the ω-scan technique and judged to be satisfactory.

Collection and Reduction of Data. Diffraction data were collected at 292 K on an Enraf-Nonius four-circle CAD-4 diffractometer controlled by a PDP8/M computer, using Mo Kα radiation from a highly oriented graphite crystal monochromator. The θ–2θ scan technique was used to record the intensities for all nonequivalent reflections for which 1° < 2θ < 45° for $[Cu_3OHL_3(ClO_4)]ClO_4$ and 1° < 2θ < 48° for $[Cu_3OL'_3(ClO_4)]_2$. Scan widths (SW) were calculated from the formula SW = $A + B \tan\theta$, where A is estimated from the mosaicity of the crystal and B allows for the increase in width

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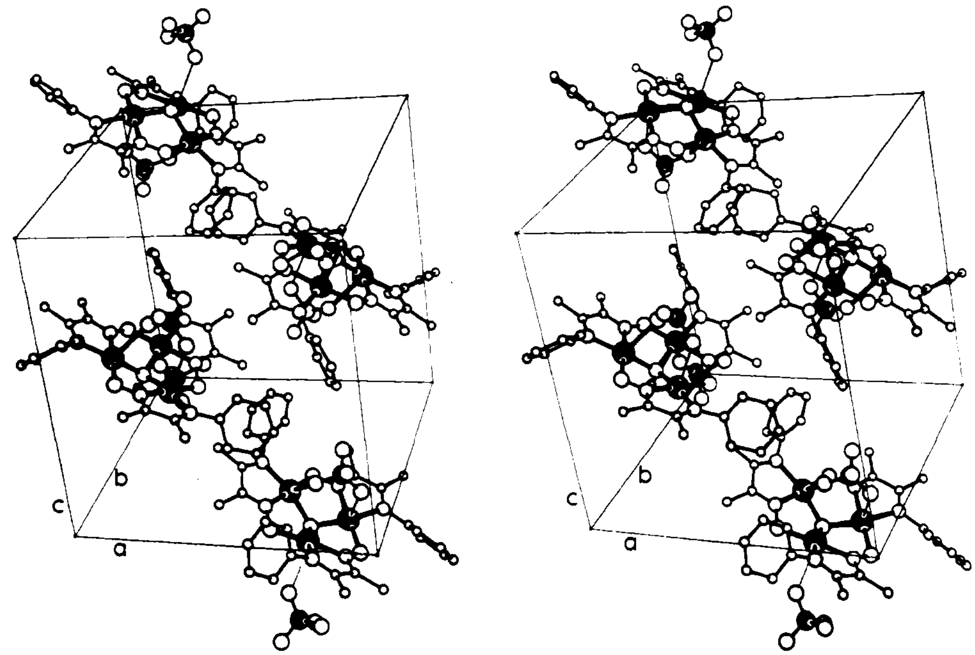

Figure 1. Stereoview of the $[Cu_3OHL_3(ClO_4)]^+$ fragment.

of peak due to $K\alpha_1$–$K\alpha_2$ splitting. The values of A and B were 0.60 and 0.30 and 0.60 and 0.35 for the two complexes, respectively. The calculated scan angle is extended at each side by 25% for background determination (BG1 and BG2). The net count is then calculated as NC = TOT − 2(BG1 + BG2), where TOT is the integrated peak intensity. Reflection data were considered insignificant if intensities registered less than 10 counts above background on a rapid prescan, such reflections being rejected automatically by the computer.

The intensities of four standard reflections, monitored for each crystal at 100-reflection intervals, showed no greater fluctuations during the data collection than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz–polarization effects (including the polarization effect of the crystal monochromator) and then for absorption. After the intensities of equivalent reflections were averaged, the data were reduced to 2456 independent intensities for $[Cu_3OHL_3(ClO_4)]ClO_4$ and 5991 for $[Cu_3OL'_3(ClO_4)]_2$ of which 1840 and 4591 for the two complexes, respectively, had $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics.[6] These data were used in the final refinement of the structural parameters.

Determination and Refinement of the Structures. The positions of the three independent copper atoms were determined for each crystal from three-dimensional Patterson functions calculated from all intensity data. These positions phased the data sufficiently well to permit location of all other nonhydrogen atoms from subsequent Fourier difference syntheses. One of the perchlorate anions of $[Cu_3OHL_3(ClO_4)]ClO_4$ was found to be significantly positionally disordered, the other slightly so.

Full-matrix least-squares refinement was based on F, and the function minimized was $\sum w(|F_o| - |F_c|)^2$. The weights w were then taken as $[2F_o/\sigma(F_o^2)]^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The atomic scattering factors for nonhydrogen atoms were taken from Cromer and Waber[7] and those for hydrogen from Stewart et al.[8] The effects of anomalous dispersion for all nonhydrogen atoms were included in F_c by using the values of Cromer and Ibers[9] for $\Delta f'$ and $\Delta f''$. Agreement factors are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|)^{1/2}$.

Anisotropic temperature factors were introduced for all nonhydrogen atoms. Further Fourier difference functions permitted location of the hydrogen atoms, which were included in the refinement for three cycles of least squares (with fixed temperature factors for $[Cu_3OHL_3(ClO_4)]ClO_4$). The models converged with $R = 6.4$ and $R_w = 7.3\%$ for $Cu_3OHL_3(ClO_4)]ClO_4$ and $R = 5.0$ and $R_w = 7.7\%$ for $[Cu_3OL'_3(ClO_4)]_2$. Structure factor calculations with all observed and unobserved reflections included (no refinement) gave $R = 8.1$ and 8.0% for the two complexes, respectively; on this basis it was decided that careful measurement of reflections rejected automatically during data collection would not significantly improve the results. The errors in an observation of unit weight were 1.2 and 1.7, respectively. A final Fourier difference function was featureless. Tables of the observed and calculated structure factors are available.[10] The principal programs used are as described previously.[11]

Results and Discussion

Final positional and thermal parameters $[Cu_3OHL_3(ClO_4)]ClO_4$ are given in Table Ia. Tables IIa and IIIa contain the bond lengths and angles. The digits in parentheses in the tables are the estimated standard deviations in the least significant figures quoted and were derived from the inverse matrix in the course of least-squares-refinement calculations. Figure 1 shows a stereoview of the $[Cu_3OHL_3(ClO_4)]^+$ fragment. The atom numbering corresponds to that given in **1**. The strongly bound perchlorate which forms a bridge between two of the copper atoms, Cu(A)–O(1)–Cl–O(2)–Cu(C), is shown in front of the Cu_3OHL_3 fragment. The more weakly bound perchlorate (Cu(B)–O(5)) is located behind the fragment as shown and is omitted from the diagram for clarity. The second perchlorate is better seen in Figure 2, which shows the packing in the unit cell. This perchlorate very weakly bridges adjacent $[Cu_3OHL_3(ClO_4)]^+$ fragments, with a Cu(B)–O(5) interaction (2.70 (2) Å) with one fragment and a Cu(A)–O(6) interaction (2.97 (2) Å) with a neighboring one. The hydroxyl hydrogen of the Cu_3OH unit is also readily seen in Figure 2 with the aid of a stereoviewer. The "strongly bonded" perchlorate has bonds Cu(A)–O(1) = 2.552 (9) Å and Cu(C)–O(2) = 2.428 (6) Å. The oxygen involved in the stronger coordination bond has the most elongated bond to the chlorine Cl–O(2) = 1.460 (5) Å, and the other is elongated to Cl–O(1) = 1.426 (5) Å, compared with a 1.254-Å average for the other two Cl–O bonds. The difference is significant,

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[9] Cromer, D. T.; Ibers, J. A. Reference 7.

[10] Supplementary material.

[11] Freyberg, D. P.; Mockler, G. M.; Sinn, E. *J. Chem. Soc., Dalton Trans.* **1976**, 447.

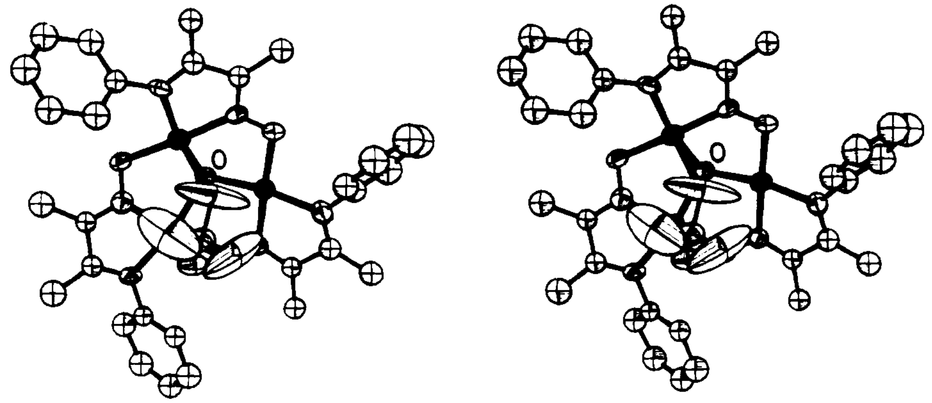

Figure 2. Molecular packing in the $[Cu_3OHL_3(ClO_4)]ClO_4$ lattice.

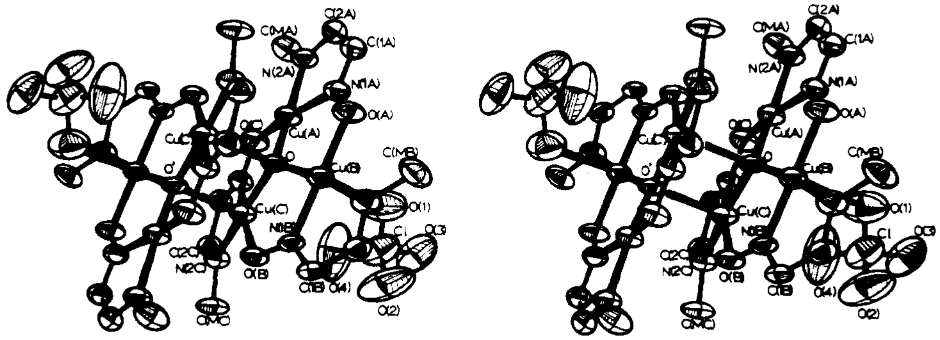

Figure 3. Stereoview of $[Cu_3OL'_3(ClO_4)]_2$ with the six phenyl groups on the ligand omitted for clarity.

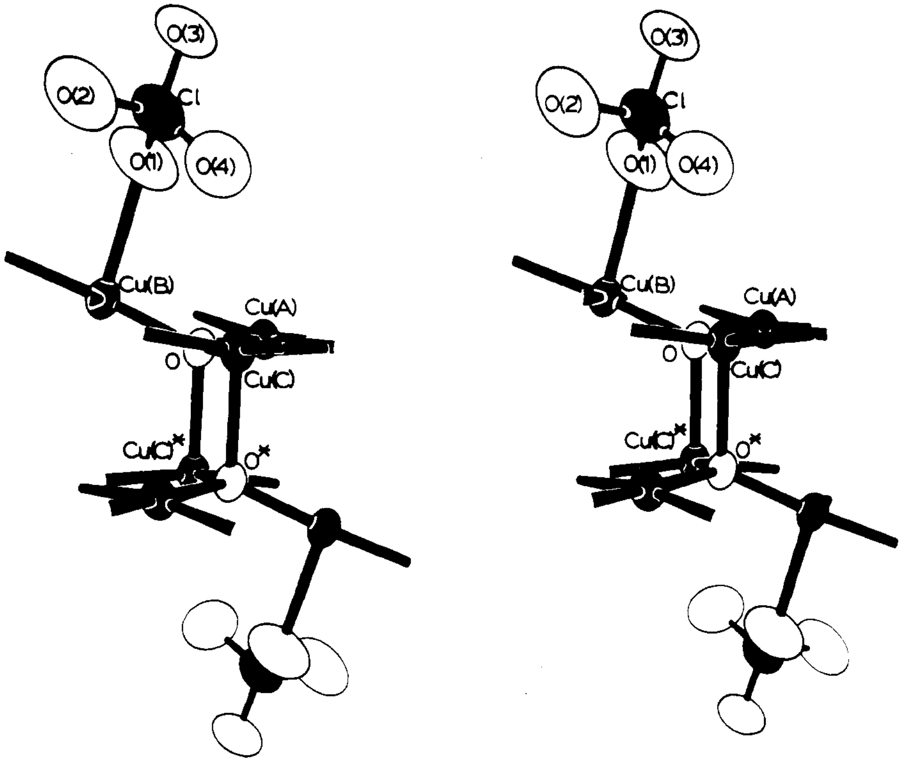

Figure 4. Stereoview of the $[Cu_3O]_2$ unit of $[Cu_3OL'_3(ClO_4)]_2$.

despite the fact that the slight positional disorder reduces the accuracy.

The complex consists of $[Cu_3OHL_3(ClO_4)]^+$ cationic fragments and weakly bonded ClO_4^- anions in the ratio of one anion per cation. In view of the dramatic departure, from the literature observations of $[Cu_3OL_3]^+ClO_4^-$ complexes, the unique features of the present complex were examined closely. Although the semicoordinated second ClO_4^- is attached to Cu(B) via one oxygen atom and has large thermal parameters on the other oxygens, it is clearly present, where indicated. The presence of Cu_3OH is confirmed by the trigonal pyramid formed by the Cu_3O fragment: here the oxygen forms the apex of the trigonal pyramid. The final evidence of this structure was provided by the location of a hydrogen atom at the expected position to complete a pseudotetrahedral environment around the central oxygen atom. The three phenyl rings are

Table I. Positional and Thermal Parameters[a] and Their Estimated Standard Deviations

a. $[Cu_3OHL_3(ClO_4)]ClO_4$

atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(A)	0.1633 (1)	0.3081 (1)	−0.0915 (1)	0.034 (1)	0.035 (1)	0.049 (1)	0.002 (1)	−0.0190 (9)	−0.001 (1)
Cu(B)	0.2482 (1)	0.1116 (1)	−0.0449 (1)	0.030 (1)	0.036 (1)	0.058 (1)	0.001 (1)	−0.0189 (9)	0.001 (1)
Cu(C)	0.3438 (1)	0.2954 (1)	0.0097 (1)	0.030 (1)	0.040 (1)	0.054 (1)	0.000 (1)	−0.0180 (9)	−0.000 (1)
Cl	0.1502 (3)	0.2450 (3)	0.1078 (2)	0.038 (2)	0.054 (3)	0.051 (2)	0.000 (2)	−0.012 (2)	0.008 (2)
Cl(2)	0.2661 (4)	0.0229 (5)	−0.2340 (3)	0.086 (4)	0.178 (6)	0.065 (3)	0.079 (4)	−0.019 (3)	−0.026 (4)
O	0.2724 (6)	0.2389 (7)	−0.0756 (6)	0.037 (6)	0.034 (6)	0.061 (6)	−0.004 (5)	−0.026 (5)	0.004 (6)
O(A)	0.2987 (6)	0.4175 (7)	−0.0097 (6)	0.026 (6)	0.042 (6)	0.048 (6)	−0.005 (5)	−0.007 (6)	0.003 (6)
O(B)	0.1044 (6)	0.1998 (7)	−0.1342 (6)	0.044 (6)	0.041 (6)	0.056 (6)	−0.005 (6)	−0.023 (5)	−0.007 (6)
O(C)	0.3626 (6)	0.0942 (7)	0.0026 (6)	0.020 (6)	0.045 (6)	0.056 (7)	0.003 (5)	−0.001 (6)	−0.004 (6)
O(1)	0.1014 (7)	0.2640 (9)	0.0371 (6)	0.042 (7)	0.081 (8)	0.030 (6)	0.001 (7)	0.003 (6)	0.019 (7)
O(2)	0.2365 (10)	0.2223 (18)	0.0857 (11)	0.047 (10)	0.356 (26)	0.083 (13)	0.083 (13)	0.059 (12)	0.069 (16)
O(3)	0.1176 (12)	0.1873 (16)	0.1521 (12)	0.179 (13)	0.387 (19)	0.384 (15)	−0.199 (15)	−0.186 (12)	0.357 (11)
O(4)	0.1720 (14)	0.3154 (16)	0.1470 (10)	0.219 (19)	0.228 (20)	0.136 (11)	0.014 (17)	−0.081 (12)	−0.106 (11)
O(5)	0.1971 (9)	0.5153 (13)	0.6670 (8)	0.104 (9)	0.175 (16)	0.108 (10)	−0.025 (11)	−0.066 (7)	0.024 (11)
O(6)	0.1912 (12)	0.4058 (15)	0.7601 (11)	0.130 (14)	0.162 (17)	0.131 (14)	−0.021 (14)	−0.020 (13)	−0.025 (14)
O(7)	0.2393 (19)	0.0375 (18)	0.7155 (11)	0.493 (32)	0.306 (23)	0.090 (14)	0.277 (18)	−0.017 (19)	0.005 (16)
O(8)	0.3199 (15)	0.4310 (27)	0.7151 (16)	0.198 (18)	0.881 (43)	0.571 (23)	−0.294 (26)	−0.233 (17)	0.632 (19)
N(1A)	0.2184 (8)	0.4181 (9)	−0.0431 (7)	0.041 (7)	0.038 (7)	0.035 (7)	−0.008 (7)	−0.017 (6)	0.003 (6)
N(2A)	0.0692 (7)	0.4015 (9)	−0.1089 (7)	0.030 (7)	0.056 (9)	0.044 (7)	0.010 (7)	−0.022 (6)	0.007 (7)
N(1B)	0.1341 (7)	0.1212 (8)	−0.0971 (7)	0.031 (6)	0.024 (7)	0.043 (7)	0.001 (6)	−0.015 (6)	0.005 (6)
N(2B)	0.2010 (8)	−0.0105 (9)	−0.0188 (7)	0.039 (7)	0.038 (7)	0.051 (8)	−0.007 (7)	−0.024 (6)	0.007 (7)
N(10)	0.3936 (8)	0.1722 (8)	0.0325 (8)	0.032 (7)	0.031 (7)	0.054 (8)	−0.014 (6)	−0.013 (7)	0.006 (7)
N(20)	0.4402 (8)	0.3323 (8)	0.0829 (7)	0.027 (7)	0.035 (7)	0.044 (8)	0.005 (6)	−0.006 (7)	0.001 (7)

atom	*x*	*y*	*z*	*U*, Å^2	atom	*x*	*y*	*z*	*U*, Å^2
C(1A)	0.1778 (10)	0.492 (1)	−0.0491 (9)	2.7 (3)	C(4C)	0.3834 (12)	0.462 (1)	0.1568 (10)	3.8 (4)
C(2A)	0.0908 (10)	0.483 (1)	−0.0855 (9)	2.7 (3)	C(5C)	0.3891 (13)	0.550 (1)	0.1894 (11)	4.6 (4)
C(3A)	−0.0165 (10)	0.372 (1)	−0.1430 (9)	2.8 (3)	C(6C)	0.4676 (13)	0.601 (1)	0.1707 (12)	5.0 (5)
C(4A)	−0.0553 (10)	0.302 (1)	−0.1152 (9)	2.9 (3)	C(7C)	0.5328 (13)	0.566 (1)	0.1282 (11)	4.6 (4)
C(5A)	−0.1355 (12)	0.275 (1)	−0.1497 (11)	4.3 (4)	C(8C)	0.5232 (12)	0.477 (1)	0.0991 (11)	4.2 (4)
C(6A)	−0.1628 (12)	0.316 (1)	−0.2197 (11)	4.4 (4)	C(9C)	0.5151 (11)	0.083 (1)	0.0879 (10)	3.7 (4)
C(7A)	−0.1197 (11)	0.384 (1)	−0.2515 (10)	3.9 (4)	C(10C)	0.5611 (10)	0.270 (1)	0.1708 (9)	2.7 (3)
C(8A)	−0.0414 (12)	0.418 (1)	−0.2153 (11)	4.1 (4)	H(0)	0.30 (1)	0.24 (1)	−0.13 (1)	5 (5)
C(9A)	0.2129 (13)	0.585 (1)	−0.0168 (11)	4.8 (4)	H(4A)	−0.03 (1)	0.27 (1)	−0.07 (1)	5 (5)
C(10A)	0.0327 (13)	0.568 (1)	−0.0920 (11)	4.8 (4)	H(5A)	0.33 (1)	0.27 (1)	0.37 (1)	5 (5)
C(1B)	0.0909 (10)	0.049 (1)	−0.1007 (9)	2.4 (3)	H(6A)	0.29 (1)	0.21 (1)	0.25 (1)	5 (5)
C(2B)	0.1297 (11)	−0.030 (1)	−0.0538 (9)	3.0 (3)	H(7A)	0.36 (1)	0.09 (1)	0.20 (1)	5 (5)
C(3B)	0.2482 (11)	−0.076 (1)	0.0322 (10)	3.5 (4)	H(8A)	−0.01 (1)	0.47 (1)	−0.24 (1)	5 (5)
C(4B)	0.2564 (12)	−0.055 (1)	0.1081 (10)	4.0 (4)	H(4B)	0.23 (1)	0.00 (1)	0.13 (1)	5 (5)
C(5B)	0.3068 (13)	−0.105 (1)	0.1606 (12)	5.2 (5)	H(5B)	0.31 (1)	−0.09 (1)	0.22 (1)	5 (5)
C(6B)	0.3445 (15)	−0.178 (2)	0.1310 (13)	6.0 (5)	H(6B)	0.38 (1)	−0.22 (1)	0.17 (1)	5 (5)
C(7B)	0.3441 (15)	−0.205 (2)	0.0559 (14)	6.7 (6)	H(7B)	0.38 (1)	−0.26 (1)	0.04 (1)	5 (5)
C(8B)	0.2888 (13)	−0.150 (1)	0.0024 (12)	5.1 (5)	H(8B)	0.28 (1)	−0.16 (1)	−0.05 (1)	5 (5)
C(9B)	0.0027 (11)	0.039 (1)	−0.1476 (10)	3.5 (4)	H(4C)	0.33 (1)	0.43 (1)	0.16 (1)	5 (5)
C(10B)	0.0779 (11)	−0.120 (1)	−0.0491 (10)	3.9 (4)	H(5C)	0.35 (1)	0.58 (1)	0.22 (1)	5 (5)
C(1C)	0.4635 (9)	0.169 (1)	0.0757 (9)	2.2 (3)	H(6C)	0.47 (1)	0.66 (1)	0.19 (1)	5 (5)
C(2C)	0.4885 (10)	0.266 (1)	0.1059 (9)	3.0 (3)	H(7C)	0.58 (1)	0.61 (1)	0.12 (1)	5 (5)
C(3C)	0.4494 (10)	0.423 (1)	0.1153 (9)	2.7 (3)	H(8C)	0.57 (1)	0.45 (1)	0.07 (1)	5 (5)

b. $[Cu_3O(ON_2C_{15}H_{13})_3]ClO_4$

atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(A)	−0.12863 (6)	0.60907 (5)	0.46642 (5)	0.0279 (4)	0.0515 (5)	0.0388 (4)	0.0086 (4)	0.0030 (4)	−0.0020 (4)
Cu(B)	0.03043 (6)	0.60916 (5)	0.61653 (5)	0.0251 (4)	0.0514 (5)	0.0391 (4)	0.0028 (4)	−0.0002 (4)	−0.0102 (4)
Cu(C)	0.07456 (6)	0.53950 (5)	0.45779 (5)	0.0259 (4)	0.0540 (5)	0.0354 (4)	0.0044 (4)	0.0038 (3)	−0.0050 (4)
Cl	0.3375 (2)	0.2309 (1)	0.9028 (1)	0.071 (1)	0.092 (2)	0.081 (1)	0.019 (1)	−0.007 (1)	−0.025 (1)
O	−0.0181 (3)	0.5707 (2)	0.5200 (2)	0.018 (2)	0.051 (3)	0.039 (2)	0.004 (2)	−0.001 (2)	−0.008 (2)
O(A)	−0.0946 (3)	0.6461 (3)	0.6338 (3)	0.026 (2)	0.078 (3)	0.039 (3)	0.009 (3)	−0.004 (2)	−0.010 (3)
O(B)	0.1777 (3)	0.5317 (3)	0.5496 (3)	0.023 (2)	0.062 (3)	0.040 (2)	0.006 (2)	−0.001 (2)	−0.012 (2)
O(0)	−0.1007 (3)	0.5867 (3)	0.3605 (3)	0.037 (3)	0.065 (3)	0.042 (3)	0.013 (3)	0.002 (2)	−0.003 (3)
O(1)	0.4226 (5)	0.2234 (4)	0.9453 (5)	0.076 (4)	0.123 (6)	0.136 (6)	−0.002 (4)	0.030 (4)	−0.047 (5)
O(2)	0.2597 (6)	0.2189 (5)	0.9245 (5)	0.075 (5)	0.170 (7)	0.179 (7)	0.029 (5)	−0.053 (5)	−0.082 (6)
O(3)	0.3323 (5)	0.2989 (4)	0.0146 (4)	0.115 (5)	0.088 (4)	0.110 (5)	0.036 (4)	−0.009 (4)	−0.043 (4)
O(4)	0.3414 (9)	0.1821 (5)	0.0436 (5)	0.285 (12)	0.114 (6)	0.095 (5)	0.053 (7)	0.046 (6)	0.025 (5)
N(A1)	−0.1543 (4)	0.6510 (3)	0.5676 (3)	0.027 (3)	0.047 (4)	0.046 (3)	0.003 (3)	0.005 (3)	−0.005 (3)
N(A2)	−0.2587 (4)	0.6460 (3)	0.4320 (3)	0.026 (3)	0.054 (4)	0.048 (3)	0.005 (3)	0.001 (3)	−0.002 (3)
N(B1)	0.1589 (4)	0.5687 (3)	0.6097 (3)	0.017 (3)	0.050 (3)	0.038 (3)	−0.001 (3)	−0.003 (2)	−0.008 (3)
N(B2)	0.0964 (4)	0.6395 (3)	0.7194 (3)	0.032 (3)	0.061 (4)	0.038 (3)	0.005 (3)	−0.005 (3)	−0.010 (3)
N(C1)	−0.0118 (4)	0.5631 (3)	0.3592 (3)	0.033 (3)	0.047 (4)	0.041 (3)	0.005 (3)	0.006 (3)	−0.003 (3)
N(C2)	0.1597 (4)	0.5198 (3)	0.3773 (3)	0.030 (3)	0.056 (4)	0.037 (3)	0.004 (3)	0.006 (2)	−0.003 (3)
C(1A)	−0.2392 (5)	0.6761 (4)	0.5684 (4)	0.033 (4)	0.047 (4)	0.047 (4)	0.003 (4)	0.005 (3)	−0.008 (4)
C(2A)	−0.2980 (5)	0.6753 (4)	0.4882 (4)	0.040 (4)	0.041 (4)	0.050 (4)	0.003 (4)	0.009 (3)	−0.001 (4)
C(3A)	−0.2791 (5)	0.6970 (4)	0.6411 (4)	0.050 (4)	0.054 (5)	0.044 (4)	0.020 (4)	0.001 (4)	−0.005 (4)
C(4A)	−0.3709 (6)	0.6720 (5)	0.6558 (5)	0.048 (4)	0.084 (6)	0.065 (5)	0.016 (5)	0.020 (4)	−0.000 (5)
C(5A)	−0.4050 (7)	0.6875 (6)	0.7240 (5)	0.071 (6)	0.143 (9)	0.063 (5)	0.018 (7)	0.025 (5)	−0.007 (6)

Table I (*Continued*)

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(6A)	−0.3552 (7)	0.7262 (6)	0.7788 (6)	0.078 (6)	0.146 (9)	0.078 (6)	0.041 (6)	0.028 (5)	−0.015 (6)
C(7A)	−0.2656 (9)	0.7509 (6)	0.7685 (6)	0.123 (8)	0.111 (7)	0.061 (6)	0.046 (7)	−0.027 (6)	−0.035 (5)
C(8A)	−0.2250 (7)	0.7356 (5)	0.6976 (5)	0.070 (6)	0.072 (6)	0.066 (5)	0.020 (5)	0.001 (5)	−0.019 (5)
C(9A)	−0.3956 (5)	0.7078 (4)	0.4768 (4)	0.032 (4)	0.057 (5)	0.046 (4)	0.012 (4)	0.003 (3)	0.006 (4)
C(10A)	−0.4769 (6)	0.6705 (5)	0.4510 (5)	0.037 (4)	0.071 (6)	0.077 (6)	0.004 (4)	−0.003 (4)	−0.015 (5)
C(11A)	−0.5644 (6)	0.7013 (6)	0.4453 (6)	0.030 (4)	0.109 (8)	0.104 (7)	0.005 (5)	−0.002 (5)	0.002 (7)
C(12A)	−0.5734 (6)	0.7687 (5)	0.4644 (6)	0.044 (5)	0.105 (7)	0.106 (7)	0.035 (5)	0.017 (5)	0.019 (6)
C(13A)	−0.4932 (6)	0.8066 (5)	0.4917 (6)	0.052 (5)	0.066 (6)	0.117 (7)	0.026 (4)	0.028 (5)	0.002 (6)
C(14A)	−0.4054 (6)	0.7760 (4)	0.4979 (5)	0.045 (5)	0.058 (5)	0.073 (5)	0.007 (4)	0.012 (4)	0.000 (5)
C(MA)	−0.3042 (6)	0.6439 (5)	0.3483 (4)	0.050 (5)	0.079 (6)	0.034 (4)	0.021 (4)	−0.007 (4)	0.001 (4)
C(1B)	0.2213 (4)	0.5778 (4)	0.6713 (4)	0.019 (3)	0.046 (4)	0.046 (4)	0.000 (3)	0.001 (3)	−0.001 (4)
C(2B)	0.1877 (5)	0.6236 (4)	0.7301 (4)	0.033 (4)	0.052 (5)	0.039 (4)	−0.007 (3)	0.004 (3)	−0.009 (3)
C(3B)	0.3209 (5)	0.5480 (4)	0.6820 (4)	0.034 (4)	0.052 (5)	0.050 (4)	−0.003 (4)	0.001 (3)	−0.016 (4)
C(4B)	0.3562 (6)	0.5153 (5)	0.7520 (5)	0.050 (5)	0.079 (6)	0.054 (5)	0.014 (5)	−0.012 (4)	−0.007 (5)
C(5B)	0.4502 (7)	0.4875 (6)	0.7597 (6)	0.060 (6)	0.109 (8)	0.078 (6)	0.027 (5)	−0.025 (5)	−0.001 (6)
C(6B)	0.5033 (6)	0.4924 (6)	0.7006 (6)	0.031 (5)	0.143 (9)	0.111 (7)	0.025 (6)	−0.011 (5)	−0.036 (7)
C(7B)	0.4716 (6)	0.5243 (5)	0.6326 (6)	0.030 (4)	0.110 (7)	0.096 (6)	−0.001 (5)	0.012 (4)	−0.034 (6)
C(8B)	0.3788 (6)	0.5520 (5)	0.6225 (5)	0.041 (4)	0.071 (6)	0.063 (5)	−0.001 (4)	0.002 (4)	−0.010 (5)
C(9B)	0.2591 (5)	0.6528 (4)	0.7957 (4)	0.026 (4)	0.057 (5)	0.046 (4)	−0.000 (4)	−0.000 (3)	−0.012 (4)
C(10B)	0.2600 (6)	0.6345 (5)	0.8738 (5)	0.045 (5)	0.115 (7)	0.047 (4)	−0.022 (5)	0.006 (4)	−0.009 (5)
C(11B)	0.3267 (6)	0.6607 (6)	0.9315 (5)	0.049 (5)	0.160 (10)	0.039 (4)	−0.010 (6)	−0.004 (4)	−0.015 (6)
C(12B)	0.3918 (6)	0.7073 (5)	0.9128 (5)	0.040 (5)	0.112 (7)	0.054 (5)	−0.002 (5)	−0.014 (4)	−0.033 (5)
C(13B)	0.3922 (6)	0.7260 (5)	0.8373 (6)	0.040 (4)	0.064 (5)	0.097 (6)	−0.014 (4)	0.003 (5)	−0.019 (5)
C(14B)	0.3261 (6)	0.6998 (4)	0.7769 (5)	0.046 (4)	0.058 (5)	0.058 (5)	−0.005 (4)	−0.003 (4)	−0.006 (4)
C(MB)	0.0525 (6)	0.6897 (5)	0.7707 (5)	0.049 (5)	0.082 (6)	0.061 (5)	0.020 (4)	−0.001 (4)	−0.036 (4)
C(1C)	0.0187 (5)	0.5478 (4)	0.2931 (4)	0.039 (4)	0.045 (4)	0.042 (4)	0.002 (4)	0.008 (3)	−0.003 (4)
C(2C)	0.1222 (5)	0.5259 (4)	0.3061 (4)	0.037 (4)	0.049 (5)	0.045 (4)	−0.002 (4)	0.011 (3)	−0.001 (4)
C(3C)	−0.0390 (5)	0.5535 (4)	0.2137 (4)	0.044 (4)	0.057 (5)	0.035 (4)	−0.004 (4)	0.005 (3)	−0.002 (4)
C(4C)	−0.0343 (6)	0.5032 (5)	0.1573 (4)	0.055 (5)	0.069 (5)	0.047 (4)	−0.014 (4)	0.005 (4)	−0.004 (4)
C(5C)	−0.0895 (7)	0.5095 (5)	0.0842 (5)	0.085 (6)	0.101 (7)	0.046 (5)	−0.039 (5)	0.010 (4)	−0.014 (5)
C(6C)	−0.1478 (7)	0.5658 (6)	0.0691 (5)	0.073 (6)	0.127 (9)	0.051 (5)	−0.019 (6)	−0.014 (5)	0.021 (6)
C(7C)	−0.1534 (7)	0.6139 (6)	0.1238 (5)	0.085 (7)	0.123 (8)	0.055 (5)	0.031 (6)	−0.002 (5)	0.019 (6)
C(8C)	−0.0994 (7)	0.6079 (5)	0.1947 (5)	0.087 (6)	0.081 (6)	0.040 (4)	0.020 (5)	0.004 (4)	0.006 (5)
C(9C)	0.1740 (5)	0.5176 (4)	0.2371 (4)	0.037 (4)	0.063 (5)	0.038 (4)	0.002 (4)	0.005 (3)	0.001 (4)
C(10C)	0.2097 (6)	0.4545 (5)	0.2166 (5)	0.068 (5)	0.074 (6)	0.046 (4)	0.015 (5)	0.008 (4)	−0.007 (4)
C(11C)	0.2657 (7)	0.4500 (5)	0.1556 (5)	0.072 (6)	0.104 (7)	0.051 (5)	0.030 (5)	0.012 (4)	−0.012 (5)
C(12C)	0.2879 (7)	0.5059 (7)	0.1169 (5)	0.070 (6)	0.176 (11)	0.049 (5)	0.018 (7)	0.029 (4)	−0.012 (6)
C(13C)	0.2527 (8)	0.5679 (6)	0.1336 (6)	0.121 (7)	0.126 (9)	0.081 (6)	−0.025 (7)	0.059 (5)	0.021 (6)
C(14C)	0.1948 (7)	0.5744 (5)	0.1938 (5)	0.072 (6)	0.083 (7)	0.080 (6)	0.006 (5)	0.032 (4)	0.005 (5)
C(MC)	0.2657 (5)	0.5070 (5)	0.3987 (5)	0.022 (4)	0.091 (6)	0.060 (5)	0.009 (4)	0.003 (3)	−0.003 (5)

atom	x	y	z	U, Å^2	atom	x	y	z	U, Å^2
H(4A)	−0.414 (5)	0.642 (4)	0.614 (4)	5 (2)	H(10B)	0.218 (5)	0.600 (3)	0.886 (4)	5 (2)
H(5A)	−0.466 (5)	0.670 (3)	0.733 (4)	5 (2)	H(11B)	0.327 (5)	0.645 (3)	0.984 (4)	4 (2)
H(6A)	−0.374 (5)	0.736 (4)	0.832 (4)	5 (2)	H(12B)	0.436 (5)	0.725 (3)	0.953 (4)	5 (2)
H(7A)	−0.231 (5)	0.781 (3)	0.806 (4)	5 (2)	H(13B)	0.434 (5)	0.759 (4)	0.824 (4)	5 (2)
H(8A)	−0.185 (5)	0.765 (3)	0.675 (4)	4 (2)	H(14B)	0.323 (5)	0.714 (3)	0.722 (4)	5 (2)
H(10A)	−0.471 (5)	0.623 (3)	0.437 (4)	4 (2)	H(4C)	0.005 (5)	0.461 (3)	0.173 (4)	5 (2)
H(11A)	−0.616 (5)	0.675 (3)	0.426 (4)	5 (2)	H(5C)	−0.083 (5)	0.474 (3)	0.043 (4)	6 (2)
H(12A)	−0.631 (5)	0.789 (3)	0.460 (4)	5 (2)	H(6C)	−0.181 (5)	0.568 (3)	0.019 (4)	5 (2)
H(13A)	−0.499 (5)	0.856 (3)	0.506 (4)	5 (2)	H(7C)	−0.197 (5)	0.652 (3)	0.111 (4)	4 (2)
H(14A)	−0.351 (5)	0.801 (3)	0.519 (4)	4 (2)	H(8C)	−0.101 (5)	0.643 (3)	0.231 (4)	4 (2)
H(4B)	0.316 (5)	0.493 (4)	0.792 (4)	5 (2)	H(10C)	0.192 (5)	0.415 (3)	0.247 (4)	5 (2)
H(5B)	0.476 (5)	0.467 (3)	0.809 (4)	5 (2)	H(11C)	0.290 (5)	0.408 (3)	0.139 (4)	4 (2)
H(6B)	0.563 (5)	0.472 (4)	0.706 (4)	6 (2)	H(12C)	0.327 (5)	0.504 (4)	0.077 (4)	6 (2)
H(7B)	0.513 (5)	0.526 (3)	0.588 (4)	4 (2)	H(13C)	0.270 (5)	0.608 (3)	0.105 (4)	5 (2)
H(8B)	0.355 (5)	0.576 (3)	0.576 (4)	4 (2)	H(14C)	0.167 (5)	0.618 (3)	0.207 (4)	5 (2)

[a] The form of the anisotropic thermal parameter is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

approximately at right angles to one another at the rim of the molecule.[10]

The analogous atomic and bonding data for [Cu$_3$OL'$_3$(ClO$_4$)]$_2$ are given in Tables Ib, IIb, and IIIB. Figure 3 shows a stereoview of the [Cu$_3$OL'$_3$(ClO$_4$)]$_2$ molecule; the six phenyl rings are omitted for clarity. Figure 4 shows a side view of the [Cu$_3$O]$_2$ unit alone. The complex consists of Cu$_3$OL'$_3$(ClO$_4$) units with weak links between pairs of these units to form neutral [Cu$_3$OL'$_3$(ClO$_4$)]$_2$ centrosymmetric molecules. In that regard, this complex resembles the series [Cu$_3$(OH)RSal$_3$(F$_3$CCOO)$_2$]$_2$.[1,13]

Both complexes contain a weakly coordinated perchlorate ligand. In [Cu$_3$OHL$_3$(ClO$_4$)]ClO$_4$, the bonded perchlorate is a bidentate bridged between two neighboring copper atoms, Cu(C)–O(2) = 2.43 (2) Å and Cu(A)–O(1) = 2.552 (9) Å, while the perchlorate in [Cu$_3$OL'$_3$(ClO$_4$)]$_2$ is monodentate between Cu(B) and O(1) (2.585 (3) Å).

The OH oxygen in [Cu$_3$OHL$_3$(ClO$_4$)]$^+$ is in a roughly tetrahedral coordination sphere of Cu, Cu, Cu, H ligands, and it is located 0.695 Å above the Cu$_3$ plane. By contrast, in [Cu$_3$OL'$_3$(ClO$_4$)]$_2$, the central oxygen is pushed closer to the Cu$_3$ plane and is only 0.352 Å above it. The displacement of

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(12) Sinn, E.; Harris, C. M. *Coord. Chem. Rev.* **1969**, *4*, 391. Sinn, E. *Ibid.* **1970**, *5*, 313.

(13) Butcher, R. J.; Sinn, E., paper presented at the 176th National American Chemical Society meeting, Miami, Florida September 1978.

Table II. Bond Lengths and Closest Intermolecular Contacts (Å)[a]

(a) $[Cu_3OHL_3(ClO_4)]ClO_4$

Cu(A)–O	1.978 (6)	N(2A)–C(2A)	1.274 (10)
Cu(A)–O(B)	1.930 (5)	N(2A)–C(3A)	1.492 (10)
Cu(A)–O(1)	2.552 (9)	N(2B)–C(2B)	1.268 (9)
Cu(A)–N(1A)	1.961 (6)	N(2B)–C(3B)	1.463 (10)
Cu(A)–N(2A)	1.999 (7)	N(2C)–C(2C)	1.265 (10)
Cu(B)–O	1.946 (6)	N(2C)–C(3C)	1.422 (10)
Cu(B)–O(C)	1.938 (5)	C(1A)–C(2A)	1.470 (11)
Cu(B)–N(1B)	1.954 (5)	C(1A)–C(9A)	1.533 (12)
Cu(B)–N(2B)	1.964 (8)	C(2A)–C(10A)	1.522 (14)
Cu(C)–O	1.969 (4)	C(3A)–C(4A)	1.289 (14)
Cu(C)–O(A)	1.911 (5)	C(3A)–C(8A)	1.439 (13)
Cu(C)–O(2)	2.428 (16)	C(4A)–C(5A)	1.407 (12)
Cu(C)–N(1C)	1.962 (6)	C(5A)–C(6A)	1.385 (14)
Cu(C)–N(2C)	1.981 (5)	C(6A)–C(7A)	1.328 (16)
O(1)–Cl	1.426 (5)	C(7A)–C(8A)	1.424 (12)
O(2)–Cl	1.460 (5)	C(1B)–C(2B)	1.501 (10)
O(3)–Cl	1.256 (14)	C(1B)–C(9B)	1.563 (10)
O(4)–Cl	1.252 (11)	C(2B)–C(10B)	1.520 (13)
O(A)–N(1A)	1.350 (8)	C(3B)–C(4B)	1.343 (16)
O(B)–N(1B)	1.365 (7)	C(3B)–C(8B)	1.348 (17)
O(C)–N(1C)	1.313 (8)	C(4B)–C(5B)	1.370 (12)
N(1A)–C(1A)	1.242 (11)	C(5B)–C(6B)	1.316 (18)
N(1B)–C(1B)	1.243 (10)	C(6B)–C(7B)	1.353 (22)
N(1C)–C(1C)	1.286 (8)	C(7B)–C(8B)	1.459 (13)
C(1C)–C(2C)	1.526 (11)	Cl(2)–O(5)	1.37 (3)
C(1C)–C(9C)	1.485 (11)	Cl(2)–O(6)	1.32 (3)
C(2C)–C(10C)	1.547 (9)	Cl(2)–O(7)	1.28 (3)
C(3C)–C(4C)	1.404 (17)	Cl(2)–O(8)	1.55 (3)
C(3C)–C(8C)	1.428 (17)	O–H(0)	1.03 (5)
C(4C)–C(5C)	1.384 (13)	⟨C–H⟩	0.98
C(5C)–C(6C)	1.482 (20)	Cu(B)–O(5)	2.701 (20)
C(6C)–C(7C)	1.385 (20)	Cu(A)–O(6)	2.974 (20)
C(7C)–C(8C)	1.382 (13)	O(1)–C(10A)	3.368 (8)
C(7A)–C(1C)	3.409 (9)^{ii}		

(b) $[Cu_3OL'_3(ClO_4)]_2$

Cu(A)–O	1.854 (2)	O(A)–N(A1)	1.321 (4)
Cu(A)–O(C)	1.956 (3)	O(B)–N(B1)	1.312 (4)
Cu(A)–N(A1)	1.991 (3)	O(C)–N(C1)	1.334 (4)
Cu(A)–N(A2)	1.980 (3)	N(A1)–C(1A)	1.293 (5)
Cu(B)–O	1.860 (2)	N(A2)–C(2A)	1.303 (5)
Cu(B)–O(A)	1.958 (3)	N(A2)–C(MA)	1.491 (5)
Cu(B)–N(B1)	1.988 (3)	N(B1)–C(1B)	1.292 (4)
Cu(B)–N(B2)	1.971 (3)	N(B2)–C(2B)	1.311 (5)
Cu(C)–O	1.890 (2)	N(B2)–C(MB)	1.500 (5)
Cu(C)–O(B)	1.999 (2)	N(C1)–C(1C)	1.298 (5)
Cu(C)–N(C1)	1.999 (3)	N(C2)–C(2C)	1.269 (5)
Cu(C)–N(C2)	1.980 (3)	N(C2)–C(MC)	1.507 (5)
Cl–O(1)	1.438 (4)	C(1A)–C(2A)	1.507 (5)
Cl–O(2)	1.399 (4)	C(1A)–C(3A)	1.489 (6)
Cl–O(3)	1.436 (4)	C(2A)–C(9A)	1.501 (5)
Cl–O(4)	1.405 (5)	C(3A)–C(4A)	1.431 (6)
C(3A)–C(8A)	1.373 (6)	C(1C)–C(2C)	1.505 (6)
C(4A)–C(5A)	1.354 (7)	C(1C)–C(3C)	1.493 (5)
C(5A)–C(6A)	1.329 (9)	C(2C)–C(9C)	1.484 (5)
C(6A)–C(7A)	1.381 (9)	C(3C)–C(4C)	1.383 (6)
C(7A)–C(8A)	1.441 (8)	C(3C)–C(8C)	1.368 (6)
C(9A)–C(10A)	1.375 (6)	C(4C)–C(5C)	1.389 (7)
C(9A)–C(14A)	1.388 (6)	C(5C)–C(6C)	1.372 (8)
C(10A)–C(11A)	1.361 (7)	C(6C)–C(7C)	1.335 (8)
C(11A)–C(12A)	1.360 (8)	C(7C)–C(8C)	1.348 (7)
C(12A)–C(13A)	1.376 (8)	C(9C)–C(10C)	1.385 (6)
C(13A)–C(14A)	1.362 (6)	C(9C)–C(14C)	1.379 (7)
C(1B)–C(2B)	1.470 (5)	C(10C)–C(11C)	1.392 (7)
C(1B)–C(3B)	1.503 (5)	C(11C)–C(12C)	1.330 (9)
C(2B)–C(9B)	1.514 (5)	C(12C)–C(13C)	1.349 (9)
C(3B)–C(4B)	1.391 (6)	C(13C)–C(14C)	1.402 (8)
C(3B)–C(8B)	1.389 (6)	⟨C–H⟩	0.96
C(4B)–C(5B)	1.417 (7)	Cu(A)–Cu(B)	3.177 (1)^{iii}
C(5B)–C(6B)	1.340 (8)	Cu(A)–Cu(C)	3.183 (1)^{iii}
C(6B)–C(7B)	1.342 (8)	Cu(B)–Cu(C)	3.172 (1)^{iii}
C(7B)–C(8B)	1.401 (7)	Cu(A)–Cu(C)*	3.217 (1)^{iv}
C(9B)–C(10B)	1.385 (6)	Cu(A)–O(B)*	2.828 (1)^{iv}
C(9B)–C(14B)	1.381 (6)	Cu(B)–Cu(C)*	3.415 (1)^{iv}
C(10B)–C(11B)	1.367 (6)	Cu(C)–Cu(C)*	3.107 (1)^{iv}
C(11B)–C(12B)	1.357 (7)	Cu(C)–O*	2.334 (3)^{iv}
C(12B)–C(13B)	1.344 (7)	Cu(B)–O(1)	2.585 (3)^{v}
C(13B)–C(14B)	1.392 (6)		

[a] Symmetry operations: (i) $-x, 1-y, -z$; (ii) $x-{}^1/_2, {}^1/_2-y, z-{}^1/_2$; (iii) x, y, z; (iv) $-x, 1-y, 1-z$; (v) ${}^1/_2-x, {}^1/_2+y, {}^3/_2-z$. Asterisks indicate distances across the inversion center, as shown in Figure 4.

the Cu_3O oxygen atom from the Cu_3 plane is in the direction of the weaker Cu(C)–O bond (2.334 (3) Å), which links the two Cu_3O subunits together. But for this Cu_3O–Cu_3O bonding, the central oxygen would undoubtedly have been pushed even further into the Cu_3 plane. The angles between the different oxime-to-ligand planes, attached to the Cu_3OH and Cu_3O fragment, and the angles between the ligand planes and the Cu_3 planes are generally smaller in the $[Cu_3OL'_3(ClO_3)]_2$ complex, in keeping with a $Cu_3OL'_3(ClO_4)$ subunit that is significantly flatter than the $[Cu_3OHL_3(ClO_4)]^+$ ion.[10]

The bond distances between the copper atoms and the central oxygens in the Cu_3OH and Cu_3O subunits (1.964 and 1.868 Å in Cu_3OH and Cu_3O, respectively) reflect the difference in the OH^- and O^{2-} electronic charges. The other three principal ligand atoms on each copper atom are moved appropriately so as to produce similar average Cu–ligand distances in the two complexes (1.958 and 1.952 Å in $[Cu_3OHL_3(ClO_4)]ClO_4$ and $[Cu_3OL'_3(ClO_4)]_2$, respectively; Table IV).

The magnetic data for the two complexes are given in Table V. The results have been corrected for temperature-independent paramagnetism (2×10^{-4} cgs emu/mol). For $[Cu_3OHL_3(ClO_4)]ClO_4$, the effective magnetic moment decreases as the sample is cooled from room temperature. If the trimeric unit has each metal equivalent and forms an equilateral triangle, the spin Hamiltonian in eq 1[12] will describe the interactions of the spins. A closed-form solution of the magnetic susceptibility may be derived from this Hamiltonian

$$\mathcal{H} = -2J(S_1 \cdot S_2 + S_2 \cdot S_3 + S_1 \cdot S_3) \qquad (1)$$

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

The magnetic susceptibility of $[Cu_3OHL_3(ClO_4)]ClO_4$ was analyzed with this equation, and in addition a molecular field correction[14] was added to compensate for intertrimer interactions which cause a further drop in the effective moment at very low temperatures. The data are plotted in Figure 5 along with the best fitted curve.

Since the three copper atoms have different environments, an equation for the magnetic moment derived for three different J values[12,15] is appropriated here. For the case of three different exchange constants, the exchange Hamiltonian takes the form

$$\mathcal{H} = -2[J_{12}S_1 \cdot S_2 + J_{13}S_1 \cdot S_3 + J_{23}S_2 \cdot S_3] \qquad (3)$$

However because of the rather small temperature dependence

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(14) Carlin, R. L.; O'Connor, C. J.; Bhatia, S. N. *J. Am. Chem. Soc.* **1976**, *98*, 3523. McElearney, J. N.; Shauble, G. E.; Schwartz, R. W.; Carlin, R. L. *J. Chem. Phys.* **1972**, *56*, 3755. Watanabe, T. *J. Phys. Soc. Jpn.* **1962**, *17*, 1856.

(15) Sinn, E. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 193.

Table III. Bond Angles (Deg)

		(a) $[Cu_3OHL_3(ClO_4)]ClO_4$					
O-Cu(A)-O(B)	92.1 (2)	N(1C)-Cu(C)-N(2C)	80.5 (2)	Cu(A)-N(2A)-C(3A)	120.5 (5)	N(2B)-C(2B)-C(1B)	113.7 (8)
O-Cu(A)-O(1)	97.1 (3)	Cu(A)-O(1)-Cl	125.4 (5)	C(2A)-N(2A)-C(3A)	126.6 (7)	N(2B)-C(2B)-C(10B)	128.4 (7)
O-Cu(A)-N(1A)	89.6 (3)	Cu(C)-O(2)-Cl	136.3 (9)	Cu(B)-N(2B)-C(2B)	115.1 (5)	C(1B)-C(2B)-C(10B)	117.8 (7)
O-Cu(A)-N(2A)	167.9 (3)	O(1)-Cl-O(2)	106.0 (8)	Cu(B)-N(2B)-C(3B)	122.2 (6)	N(2B)-C(3B)-C(4B)	117.0 (10)
O(B)-Cu(A)-O(1)	86.3 (3)	O(1)-Cl-O(3)	115.5 (5)	C(2B)-N(2B)-C(3B)	122.5 (8)	N(2B)-C(3B)-C(8B)	120.6 (10)
O(B)-Cu(A)-N(1A)	176.6 (4)	O(1)-Cl-O(4)	115.0 (6)	Cu(C)-N(2C)-C(2C)	114.6 (5)	C(4B)-C(3B)-C(8B)	122.1 (9)
O(B)-Cu(A)-N(2A)	98.7 (3)	O(2)-Cl-O(3)	115 (1)	Cu(C)-N(2C)-C(3C)	123.5 (5)	C(3B)-C(4B)-C(5B)	122.8 (12)
O(1)-Cu(A)-N(1A)	90.5 (3)	O(2)-Cl-O(4)	95.5 (1)	C(2C)-N(2C)-C(3C)	121.5 (6)	C(4B)-C(5B)-C(6B)	114.5 (11)
O(1)-Cu(A)-N(2A)	89.1 (3)	O(3)-Cl-O(4)	108 (1)	N(1A)-C(1A)-C(2A)	114.3 (7)	C(5B)-C(6B)-C(7B)	128.4 (12)
N(1A)-Cu(A)-N(2A)	79.9 (3)	Cu(A)-O-Cu(B)	109.3 (3)	N(1A)-C(1A)-C(9A)	123.0 (7)	C(6B)-C(7B)-C(8B)	114.9 (15)
O-Cu(B)-O(C)	92.7 (2)	Cu(A)-O-Cu(C)	110.0 (3)	C(2A)-C(1A)-C(9A)	122.6 (8)	C(3B)-C(8B)-C(7B)	117.2 (11)
O-Cu(B)-N(1B)	89.7 (2)	Cu(B)-O-Cu(C)	107.1 (3)	N(2A)-C(2A)-C(1A)	116.2 (7)	N(1C)-C(1C)-C(2C)	111.1 (6)
O-Cu(B)-N(2B)	169.1 (3)	Cu(C)-O(A)-N(1A)	113.8 (4)	N(2A)-C(2A)-C(10A)	124.5 (7)	N(1C)-C(1C)-C(9C)	123.2 (6)
O(C)-Cu(B)-N(1B)	176.0 (3)	Cu(A)-O(B)-N(1B)	110.1 (3)	C(1A)-C(2A)-C(10A)	119.3 (7)	C(2C)-C(1C)-C(9C)	125.6 (6)
O(C)-Cu(B)-N(2B)	97.9 (2)	Cu(B)-O(C)-N(1C)	111.5 (4)	N(2A)-C(3A)-C(4A)	120.4 (7)	N(2C)-C(2C)-C(1C)	116.2 (6)
N(1B)-Cu(B)-N(2C)	79.9 (3)	Cu(A)-N(1A)-O(A)	123.4 (5)	N(2A)-C(3A)-C(8A)	113.9 (9)	N(2C)-C(2C)-C(10C)	126.5 (7)
O-Cu(C)-O(A)	93.5 (2)	Cu(A)-N(1A)-C(1A)	116.5 (5)	C(4A)-C(3A)-C(8A)	124.7 (8)	C(1C)-C(2C)-C(10C)	116.6 (6)
O-Cu(C)-O(2)	81.2 (4)	O(A)-N(1A)-C(1A)	119.9 (6)	C(3A)-C(4A)-C(5A)	118.7 (7)	N(2C)-C(3C)-C(4C)	120.3 (10)
O-Cu(C)-N(1C)	88.8 (2)	Cu(B)-N(1B)-O(B)	123.5 (5)	C(4A)-C(5A)-C(6A)	118.5 (11)	N(2C)-C(3C)-C(8C)	118.7 (12)
O-Cu(C)-N(2C)	164.5 (4)	Cu(B)-N(1B)-C(1B)	116.2 (5)	C(5A)-C(6A)-C(7A)	122.3 (9)	C(4C)-C(3C)-C(8C)	120.8 (9)
O(A)-Cu(C)-O(2)	103.4 (4)	O(B)-N(1B)-C(1B)	120.1 (5)	C(6A)-C(7A)-C(8A)	120.7 (9)	C(3C)-C(4C)-C(5C)	122.6 (12)
O(A)-Cu(C)-N(1C)	177.7 (2)	Cu(C)-N(1C)-O(C)	123.8 (4)	C(3A)-C(8A)-C(7A)	114.2 (11)	C(4C)-C(5C)-C(6C)	113.4 (14)
O(A)-Cu(C)-N(2C)	97.2 (2)	Cu(C)-N(1C)-C(1C)	117.4 (5)	N(1B)-C(1B)-C(2B)	114.0 (6)	C(5C)-C(6C)-C(7C)	125.5 (10)
O(2)-Cu(C)-N(1C)	77.3 (5)	O(C)-N(1C)-C(1C)	118.7 (6)	N(1B)-C(1B)-C(9B)	124.2 (6)	C(6C)-C(7C)-C(8C)	117.5 (13)
O(2)-Cu(C)-N(2C)	107.2 (4)	Cu(A)-N(2A)-C(2A)	112.9 (5)	C(2B)-C(1B)-C(9B)	121.8 (7)	C(3C)-C(8C)-C(7C)	120.0 (14)
		(b) $[Cu_3OL'_3]ClO_4$					
O-Cu(A)-O(C)	96.4 (1)	Cu(B)-O-Cu(C)	115.5 (1)	C(1A)-C(3A)-C(8A)	120.2 (4)	C(6B)-C(7B)-C(8B)	118.8 (5)
O-Cu(A)-N(A1)	88.3 (1)	Cu(B)-O(A)-N(A1)	112.2 (2)	C(4A)-C(3A)-C(8A)	119.3 (4)	C(3B)-C(8B)-C(7B)	121.0 (5)
O-Cu(A)-N(A2)	166.9 (1)	Cu(C)-O(B)-N(B1)	112.0 (2)	C(3A)-C(4A)-C(5A)	120.5 (5)	C(2B)-C(9B)-C(10B)	122.7 (4)
O(C)-Cu(A)-N(A1)	168.7 (1)	Cu(A)-O(C)-N(C1)	113.3 (2)	C(4A)-C(5A)-C(6A)	121.4 (6)	C(2B)-C(9B)-C(14B)	118.8 (4)
O(C)-Cu(A)-N(A2)	95.5 (1)	Cu(A)-N(A1)-O(A)	123.4 (2)	C(5A)-C(6A)-C(7A)	120.8 (5)	C(10B)-C(9B)-C(14B)	118.5 (4)
N(A1)-Cu(A)-N(A2)	81.1 (1)	Cu(A)-N(A1)-C(1A)	116.0 (3)	C(6A)-C(7A)-C(8A)	120.4 (6)	C(9B)-C(10B)-C(11B)	121.3 (5)
O-Cu(B)-O(A)	92.9 (1)	O(A)-N(A1)-C(1A)	120.1 (3)	C(3A)-C(8A)-C(7A)	117.6 (5)	C(10B)-C(11B)-C(12B)	119.9 (5)
O-Cu(B)-N(B1)	91.0 (1)	Cu(A)-N(A2)-C(2A)	113.8 (3)	C(2A)-C(9A)-C(10A)	121.8 (4)	C(11B)-C(12B)-C(13B)	119.8 (4)
O-Cu(B)-N(B2)	171.7 (1)	Cu(A)-N(A2)-C(MA)	122.6 (3)	C(2A)-C(9A)-C(14A)	119.3 (4)	C(12B)-C(13B)-C(14B)	121.9 (5)
O(A)-Cu(B)-N(B1)	174.5 (1)	C(2A)-N(A2)-C(MA)	123.5 (3)	C(10A)-C(9A)-C(14A)	118.8 (4)	C(9B)-C(14B)-C(13B)	118.6 (4)
O(A)-Cu(B)-N(B2)	94.6 (1)	Cu(B)-N(B1)-O(B)	122.9 (2)	C(9A)-C(10A)-C(11A)	119.8 (5)	N(C1)-C(1C)-C(2C)	111.2 (3)
N(B1)-Cu(B)-N(B2)	81.3 (1)	Cu(B)-N(B1)-C(1B)	115.0 (3)	C(10A)-C(11A)-C(12A)	121.3 (5)	N(C1)-C(1C)-C(3C)	125.1 (4)
O-Cu(C)-O(B)	93.7 (1)	O(B)-N(B1)-C(1B)	122.0 (3)	C(11A)-C(12A)-C(13A)	120.0 (5)	C(2C)-C(1C)-C(3C)	123.6 (3)
O-Cu(C)-N(C1)	90.9 (1)	Cu(B)-N(B2)-C(2B)	113.0 (3)	C(12A)-C(13A)-C(14A)	119.1 (5)	N(C2)-C(2C)-C(1C)	116.1 (3)
O-Cu(C)-N(C2)	168.8 (1)	Cu(B)-N(B2)-C(MB)	122.5 (3)	C(9A)-C(14A)-C(13A)	121.1 (5)	N(C2)-C(2C)-C(9C)	124.6 (4)
O(B)-Cu(C)-N(C1)	168.1 (1)	C(2B)-N(B2)-C(MB)	122.9 (3)	N(B1)-C(1B)-C(2B)	113.4 (3)	C(1C)-C(2C)-C(9C)	119.2 (4)
O(B)-Cu(C)-N(C2)	95.2 (1)	Cu(C)-N(C1)-O(C)	122.1 (2)	N(B1)-C(1B)-C(3B)	124.6 (4)	C(1C)-C(3C)-C(4C)	120.9 (4)
N(C1)-Cu(C)-N(C2)	79.2 (1)	Cu(C)-N(C1)-C(1C)	116.8 (3)	C(2B)-C(1B)-C(3B)	121.9 (3)	C(1C)-C(3C)-C(8C)	121.3 (4)
O(1)-Cl-O(2)	106.4 (3)	O(C)-N(C1)-C(1C)	120.8 (3)	N(B2)-C(2B)-C(1B)	116.5 (3)	C(4C)-C(3C)-C(8C)	117.8 (4)
O(1)-Cl-O(3)	110.5 (3)	Cu(C)-N(C2)-C(2C)	116.0 (3)	N(B2)-C(2B)-C(9B)	123.8 (3)	C(3C)-C(4C)-C(5C)	119.6 (5)
O(1)-Cl-O(4)	108.1 (3)	Cu(C)-N(C2)-C(MC)	122.2 (3)	C(1B)-C(2B)-C(9B)	119.6 (3)	C(4C)-C(5C)-C(6C)	119.3 (5)
O(2)-Cl-O(3)	110.5 (3)	C(2C)-N(C2)-C(MC)	121.4 (3)	C(1B)-C(3B)-C(4B)	120.2 (4)	C(5C)-C(6C)-C(7C)	121.1 (5)
O(2)-Cl-O(4)	111.6 (4)	N(A1)-C(1A)-C(2A)	112.5 (3)	C(1B)-C(3B)-C(8B)	121.1 (4)	C(6C)-C(7C)-C(8C)	119.5 (6)
O(3)-Cl-O(4)	109.8 (3)	N(A1)-C(1A)-C(3A)	124.3 (4)	C(4B)-C(3B)-C(8B)	118.8 (4)	C(3C)-C(8C)-C(7C)	122.7 (5)
Cu(A)-O-Cu(B)	117.6 (1)	C(2A)-C(1A)-C(3A)	123.0 (3)	C(2C)-C(9C)-C(10C)	122.0 (4)	C(10C)-C(11C)-C(12C)	121.1 (5)
Cu(A)-O-Cu(C)	116.5 (1)	N(A2)-C(2A)-C(1A)	116.4 (4)	C(2C)-C(9C)-C(14C)	120.0 (4)	C(11C)-C(12C)-C(13C)	120.5 (5)
N(A2)-C(2A)-C(9A)	123.9 (4)	C(3B)-C(4B)-C(5B)	118.5 (5)	C(10C)-C(9C)-C(14C)	118.0 (4)	C(12C)-C(13C)-C(14C)	120.1 (6)
C(1A)-C(2A)-C(9A)	119.7 (3)	C(4B)-C(5B)-C(6B)	120.6 (5)	C(9C)-C(10C)-C(11C)	120.0 (5)	C(9C)-C(14C)-C(13C)	120.2 (6)
C(1A)-C(3A)-C(4A)	120.3 (4)	C(5B)-C(6B)-C(7B)	122.3 (5)				

Table IV. Bonding at the $Cu_3O(H)$ Cores of the Complexes

$[Cu_3OHL_3(ClO_4)]ClO_4$		$[Cu_3OL'_3(ClO_4)]_2$	
⟨Cu-OH⟩	1.964 Å	⟨Cu-O⟩	1.868 Å
⟨Cu-ON⟩	1.926 Å	⟨Cu-ON⟩	1.971 Å
⟨Cu-N(1)⟩	1.959 Å	⟨Cu-N(1)⟩	1.993 Å
⟨Cu-N(2)⟩	1.981 Å	⟨Cu-N(2)⟩	1.977 Å
⟨Cu-lig⟩[a]	1.958 Å av	⟨Cu-lig⟩[a, b]	1.952 Å av
⟨Cu-OH-Cu⟩	108.8°	⟨Cu-O-Cu⟩	116.5°

[a] Not including the weaker copper-perchlorate bonds. [b] Not including the weaker Cu-O bonds between the two trinuclear subunits.

of the moment, this equation provides too many parameters for accurate evaluation. An equation which uses two different J values[2,14] ($J = J_{12} = J_{23}$; $\alpha = J_{13}/J$) was tried. For this case the exchange Hamiltonian takes on the form

$$\mathcal{H} = -2J(S_1 \cdot S_2 + S_2 \cdot S_3) - \alpha J(S_1 \cdot S_3) \qquad (4)$$

Attempts to fit the data with this equation can be termed marginally successful. The residual error dropped by only 1%, and the value of α would not deviate more than 2% from 1.00. Since there was no improvement in the quality of the fit and the ratio of J_A/J_B remained very near 1.0, the fit to the J, J_{13} trimer equation was discarded. This is reasonable since the type of bridging between the different pairs of copper atoms is fairly similar. The best fit values from eq 2 plus the molecular field correction are listed in Table VI.

The magnetic data for the $Cu_3OL'_3$ complex is plotted in Figure 6 as χ^{-1} vs. T. The solid line is a best fit to the Curie–Weiss law

$$\chi = Ng^2\mu_B{}^2S(S + 1)/3k(T - \Theta)$$

where all of the parameters have their usual meanings and $S = {}^1/_2$ for the trinuclear species. The best fitted values of the parameters are listed in Table VI. The linear inverse sus-

Table V. Magnetic Measurements

(a) $[Cu_3OL'_3(ClO_4)]_2$

T, K	4.30	5.02	5.97	6.99	8.15	9.70	11.5	14.5	19.9	24.7
$10^6\chi_M$, emu/mol	66440	57040	47470	40210	34600	29050	24710	20080	15170	12680
μ_{eff}, μ_B	1.512	1.514	1.506	1.500	1.502	1.501	1.508	1.526	1.554	1.583
T, K	28.7	32.7	39.4	52.5	64.5	75.3	86.5	97.6	109	124
$10^6\chi_M$, emu/mol	11030	9780	8490	6840	5870	5180	4660	4200	3840	3390
μ_{eff}, μ_B	1.591	1.600	1.636	1.695	1.740	1.766	1.796	1.811	1.830	1.834
T, K	140	157	174	191	208	225	241	258	276	295
$10^6\chi_M$, emu/mol	3000	2680	2400	2220	2040	1890	1760	1640	1530	1460
μ_{eff}, μ_B	1.833	1.835	1.828	1.842	1.842	1.844	1.842	1.840	1.838	1.856

(b) $[Cu_3OHL_3(ClO_4)]ClO_4$

T, K	4.30	5.50	8.17	14.4	19.8	24.5	29.0	36.8	48.5	56.0
$10^6\chi_M$, emu/mol	85830	67500	47700	26780	19880	16300	13890	11220	8720	7160
μ_{eff}, μ_B	1.718	1.723	1.766	1.756	1.775	1.787	1.795	1.817	1.839	1.791
T, K	72.0	83.0	94.0	109	124	140	157	174	191	208
$10^6\chi_M$, emu/mol	6170	5480	4930	4370	3850	3420	3140	2890	2690	2500
μ_{eff}, μ_B	1.885	1.908	1.925	1.952	1.954	1.957	1.986	2.006	2.027	2.040
T, K	225	241	258	276	295					
$10^6\chi_M$, emu/mol	2340	2210	2100	2040	1940					
μ_{eff}, μ_B	2.052	2.064	2.082	2.122	2.140					

Table VI. Magnetic Parameters for the Trimeric Units

	$[Cu_3OHL_3(ClO_4)]ClO_4$		
g	2.12	zJ', cm^{-1}	−0.6
J, cm^{-1}	−122	TIP, emu/mol	0.0002
	$[Cu_3OL'_3(ClO_4)]_2$		
g	2.27	TIP, emu/mol	0.0002
Θ, K	−3.00		

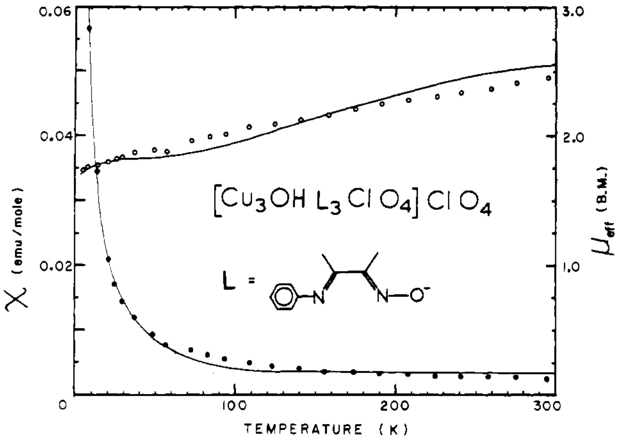

Figure 5. Plot of the magnetic susceptibility and effective magnetic moment as a function of temperature for $[Cu_3OHL_3(ClO_4)]ClO_4$. The curve is the best fit to the copper trimer equation as described in the text.

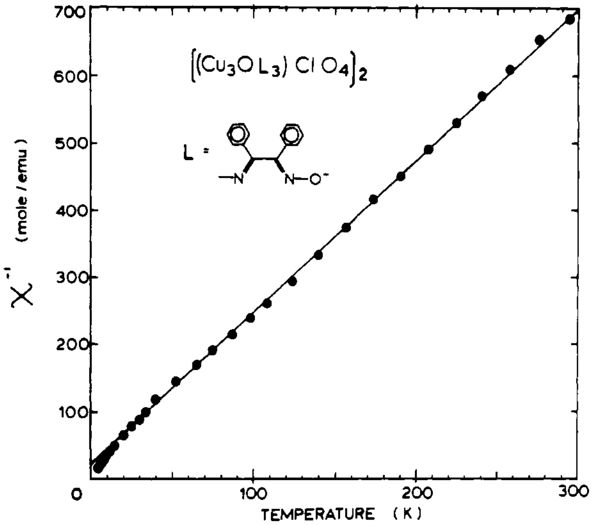

Figure 6. Plot of the inverse magnetic susceptibility as a function of temperature for $[Cu_3OL'_3(ClO_4)]_2$. The line is the best fit to the Curie–Weiss equation as described in the text.

ceptibility plot over the entire temperature range gives a good fit with but one unpaired electron for every three coppers. The negative value of Θ indicates that at very low temperatures the hexanuclear adduct exhibits antiferromagnetic coupling with the two trinuclear centers having spin $S = {}^1/_2$ each: a case directly analogous to an $S = {}^1/_2$ dimer.

$[Cu_3OHL_3(ClO_4)]^+$ resembles $[Cu_3(OH)Sal_3(F_3CCOO)_2]_2$[13] in its magnetic properties: the ground state has one unpaired electron per Cu_3 unit, but as temperature rises, there is partial occupancy of an excited $S = {}^3/_2$ state ($J \approx 120\ cm^{-1}$). At very low temperature (~5 K), a weak lattice (interionic) interaction is evident in $[Cu_3OHL_3(ClO_4)]^+$ while an intramolecular (interdimer interaction is manifested in $[Cu_3(OH)Sal_3(F_3CCOO)_2]_2$.

$[Cu_3OL'_3(ClO_4)]_2$ has a stronger antiferromagnetic (~−1000 cm^{-1}) interaction within the Cu_3O subunit, so that only a single unpaired electron is present in the entire subunit even at high temperatures. At low temperatures, a further (weaker) interaction is observed, again presumably intramolecular (intradimer) between the two Cu_3O units, to promote a further decrease in μ.

These results can be used to distinguish between related trinuclear copper(II) complexes with oxime and other ligands: very strong interactions are characteristic of a flattened Cu_3O bridge while a pyramidal bridge, as in Cu_3OH, produces much weaker interactions. Some earlier literature work on such systems seems to have involved mixtures.[16]

It is of interest to compare the structural and magnetic properties in these complexes. Previous work has established relationships between the magnetic coupling and certain structural features. These features include the Cu–O–Cu bridging angles in certain binuclear complexes,[17-19] planar-tetrahedral distortion,[12,20-25] coplanarity of principal ligand

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planes,[26] and strength of bridging bonds.[19] High planarity in oxime-bridged (Cu–O–N–Cu) dimers has been shown to provide strong coupling.[27] Features remote from the metal bridging framework such as ring substituents on ligand phenyl rings were found to be relatively unimportant, in general.[22–25] The most prominent structural difference in the bridging geometries of $[Cu_3OH(ClO_4)]ClO_4$ and $[Cu_3OL'_3(ClO_4)]_2$ is the tetrahedral oxygen coordination (sp^3) in the Cu_3OH complex and the nearly planar configuration (sp^2) in Cu_3O. Another important structural difference is the higher degree of coplalarity of the three principal ligand planes in the Cu_3O complex than in the Cu_3OH complex: in Cu_3OH, these three planes [O, O(A), N(1A), N(2A); O, O(B), N(1B), N(2B); O, O(C), N(1C), N(2C)] make angles of 40.3, 28.5, and 31.1° with each other, while in Cu_3O the angles are only 14.6, 20.4, and 26.6°. Thus, $[Cu_3OL'_3(ClO_4)]_2$ approaches more closely to the strongly antiferromagnetic planar oxime-bridged binuclear copper(II) complexes. A minor structural difference is the higher degree of coplanarity of the metal atoms with the ONCCN ligand planes in the Cu_3O complex (Cu atoms out of plane by 0.09 Å on the average; only Cu(C), which provides the intertrimer bridge, is markedly out of plane at 0.18 Å) than in the Cu_3OH complex (average 0.16 Å). This change in skeletal geometry can readily explain the difference in magnetic behavior between the two complexes.

The Cu_3OH complex has weaker magnetic exchange ($J = -122\ cm^{-1}$). The tetrahedral sp^3 hybridization forces the oxygen above the plane of the copper atoms and furthermore disrupts the coplanar oxime-bridging network due to the hindered $d_{x^2-y^2}$ overlap. The nonplanar bonding configuration is achieved at the expense of magnetic-exchange stabilization.

The Cu_3O complex on the other hand has nearly coplanar geometry; the Cu_3O oxygen is only slightly raised above the plane to form a weak intertrimer bond. As a result of the nearly coplanar configuration plus additional electrostatic effects, the Cu–O bonds are shorter for the Cu_3O complex. Since the oxygen exhibits the more flat sp^2 character, overlap with the copper $d_{x^2-y^2}$ orbitals still permits the oxime ligands to retain their coplanar geometry. This overall coplanar $Cu_3OL'_3$ structure permits larger magnetic exchange ($J \geq 300\ cm^{-1}$).

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Registry No. 1, 75701-18-7; 2, 75701-19-8; butane-2,3-dione oxime, 57-71-6; benzil oxime, 14090-77-8; aniline, 62-53-3; methylamine, 74-89-5.

Supplementary Material Available: Tables of least-squares planes and observed and calculated structure factors (30 pages). Ordering information is given on any current masthead page.

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Crystal Structures and Magnetic Properties of Cobalt(II) Pyrazinecarboxylate and Pyrazinedicarboxylate Complexes

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The synthesis and the structural and magnetic characterization of three cobalt(II) complexes of 2-pyrazinecarboxylic acid and 2,3-pyrazinedicarboxylic acid are reported. In each case the cobalt is in a distorted octahedral environment, coordinated to two nitrogen atoms and two carboxylate oxygens from different ligands and two water molecules. Pairs of like ligands are always trans to each other. The pyrazine ligands do not link adjacent cobalt atoms directly. The complexes all consist of three-dimensionally hydrogen-bonded polymers with potential magnetic-exchange pathways. In $[Co(pz(COO)COOH)_2(H_2O)_2]$, the carboxylate group at the 2-position is deprotonated, while the other carboxylate forms intramolecular hydrogen bonds with it and intermolecular hydrogen bonds with the coordinated water. In $[Co(pzCOO)_2(H_2O)_2]$, the coordinated carboxylate oxygen is hydrogen bonded to the coordinated water of adjacent molecules. This causes lengthening of the Co–O bond to the carboxylate and forms infinite chains along the *a* axis. It is the most direct linkage observed in the three complexes. The remainder of the three-dimensional network is formed by hydrogen bonding between the uncoordinated carboxylate oxygen and the coordinated water molecule. In $[Co(pzCOO)_2(H_2O)_2]\cdot 2H_2O$, the uncoordinated carboxylate groups form infinite chains along the *a* axis by hydrogen bonding to the coordinated water ligands of adjacent molecules. The remainder of the three-dimensional network is less direct, being completed by uncoordinated water molecules hydrogen bonding to both the uncoordinated carboxylate oxygens and coordinated water molecules of adjacent molecules. Powder magnetic susceptibilities were measured on each of the cobalt pyrazinecarboxylate complexes in the region 4–100 K. The low-temperature behavior of the Kramers doublet of cobalt(II) may be analyzed by the Curie–Weiss law. This procedure gives a Weiss constant of about $\Theta \approx -1.0$ K for each of the complexes. The small negative value of J is indicative of weak antiferromagnetic interactions, with critical regions below the temperature range of measurement. Crystal data for $[Co(pz(COO)COOH)_2(H_2O)_2]$: space group $P2_1/n$, $Z = 4$, $a = 9.396$ (3) Å, $b = 7.692$ (2) Å, $c = 10.136$ (2) Å, $\beta = 93.32$ (4)°, $V = 731$ Å^3, $R = 3.2\%$ for 1225 reflections. Crystal data for $[Co(pzCOO)_2(H_2O)_2]\cdot 2H_2O$: space group $P2_1/n$, $Z = 4$, $a = 7.259$ (3) Å, $b = 13.028$ (3) Å, $c = 8.271$ (5) Å, $\beta = 103.09$ (3)°, $V = 765$ Å^3, $R = 3.1\%$ for 1195 reflections. Crystal data for $[Co(pzCOO)(H_2O)_2]$: space group $P2_1/n$, $Z = 4$, $a = 5.2496$ (7) Å, $b = 11.140$ (1) Å, $c = 10.299$ (2) Å, $\beta = 99.55$ (1)°, $V = 594$ Å^3, $R = 2.2\%$ for 997 reflections.

Introduction

Pyrazine, when coordinated to transition metals, is an excellent bridging ligand.[2–12] It allows electron coupling between the metals via orbital overlap with the ligand orbitals[2–7] and is therefore a potential transmitter of magnetic-exchange in-

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