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## Exchange Interactions in a "Bicapped-Cubane" $\text{Cu}_6\text{O}_8$ Cluster. Crystal Structure and Magnetic Susceptibility of Tetrakis( $\mu_3$ -2-amino-2-methyl-1-propanolato)tetrakis( $\mu$ -2-amino-2-methyl-1-propanolato)hexacopper(II) Perchlorate<sup>1</sup>

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The structure of the title compound was solved from single-crystal X-ray data. The compound,  $[\text{Cu}_6(\text{C}_4\text{H}_{10}\text{NO})_8](\text{ClO}_4)_4$ , crystallizes in the tetragonal space group  $P4_2/c$  with  $a = b = 13.516$  (2) Å and  $c = 16.204$  (3) Å and with two hexanuclear molecules per unit cell. The least-squares refinement led to an  $R$  value of 0.042. The compound contains discrete  $[\text{Cu}_6(\text{C}_4\text{H}_{10}\text{NO})_8]^{4+}$  cations and  $\text{ClO}_4^-$  anions. The complex cation has a  $\text{Cu}_6\text{O}_8$  core formed by alternating copper(II) and alkoxo oxygen atoms. There is a cubane-like  $\text{Cu}_4\text{O}_4$  subcore. Two of six faces of the subcore (the top and bottom) are capped by copper atoms. The capping copper atoms lie on the  $\bar{4}$  axis. One capping copper atom is joined via oxygen bridges to the two copper atoms in the top face, and the other is likewise joined to the two copper atoms in the bottom face. In the  $\text{Cu}_4\text{O}_4$  cubane the Cu...Cu separations are 3.095 (1) (×4) and 3.122 Å (×4), and the Cu-O distances are 1.955 (3) (×4), 2.013 (4) (×4), and 2.269 (4) Å (×4). The Cu...Cu separation between the capping and the cubane copper atoms is 3.525 (1) Å (×4). The Cu-O distances within the Cu-O-Cu capping bridge are 1.916 (4) and 1.928 (5) Å, and the bridge angle is 133.1 (3)°. The cubane copper atoms have distorted square-pyramidal coordination while the capping copper atoms have planar coordination. The temperature dependence of the magnetic susceptibilities in the range 4.2-300 K yielded the following exchange couplings:  $J_1 = -152 \text{ cm}^{-1}$ , between the capping and the cubane copper atoms;  $J_2 = -52 \text{ cm}^{-1}$ , between the copper atoms within the side faces of the cubane;  $J_3 = 57 \text{ cm}^{-1}$ , between the copper atoms within the top or bottom faces of the cubane.

### Introduction

In a previous paper<sup>3</sup> we noted that one of the goals in the study of complexes formed by the N-unsubstituted aminoalcohols with copper(II) is to determine if they form mainly dimeric bis( $\mu$ -alkoxo oxygen)-bridged or tetrameric  $\text{Cu}_4\text{O}_4$  cubane-like complexes. On the basis of the copper(II) complexes of 2-amino-2-methyl-1-propanol, for which structures are known from X-ray diffraction measurements, it appears that N-unsubstituted aminoalcohols have a strong tendency to form bis complexes, and these may act as building blocks in the formation of polynuclear complexes. Six different types of planar bis complexes of aminoalcohols can be formed. These include cis and trans arrangements of protonated and deprotonated forms of the ligand. Examples of compounds having four of the six configurations are known.<sup>1,3,4</sup>

2-Amino-2-methyl-1-propanol can also function as a ligand in the customary way of N-substituted aminoalcohols and not form a bis complex. Examples of this kind of coordination are provided by the chloro and bromo complexes  $[\text{CuLX}]_4$  (X = Cl or Br), which have the tetrameric  $\text{Cu}_4\text{O}_4$  cubane core structures.<sup>5</sup> We have now succeeded in joining a bis(aminoalcohol)copper(II) complex with a  $\text{Cu}_4\text{O}_4$  cubane-like tetramer to form a new type of structure for aminoalcohol complexes. The new compound is a  $\text{Cu}_6\text{O}_8$  "bicapped-cubane"-like hexamer. The synthesis, results of the X-ray structural determination, and studies of exchange interactions by magnetic susceptibility measurements are reported in this paper.

### Experimental Section

**Synthesis of the Complex.** A 0.01-mol sample of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  was dissolved in 0.02 mol of  $\text{C}_4\text{H}_{11}\text{NO}$  in about 150 mL of methanol. The solution was left to stand at room temperature in a closed Erlenmeyer flask. After several weeks the large, blue crystals that had precipitated were collected by filtration. *Caution!* Compound may explode if heated until dry.

Table I. Crystal Data and Details of the Structure Determination

formula	$[\text{Cu}_6(\text{C}_4\text{H}_{10}\text{NO})_8](\text{ClO}_4)_4$
fw	1484.1
cryst syst	tetragonal
$a = b$	13.516 (2) Å
$c$	16.204 (3) Å
space group	$P4_2/c$
$V$	2960 (1) Å <sup>3</sup>
$Z$	2
$d_{\text{calcd}}$	1.67 g cm <sup>-3</sup>
$d_{\text{obsd}}$	1.68 g cm <sup>-3</sup>
diffractometer	Nicolet P3
cryst dimens	0.37 × 0.60 × 1.10 mm
radiation	$\lambda = 0.7107$ Å (graphite-monochromated Mo $K\alpha$ )
temp	20 (1) °C
abs coeff	24.6 cm <sup>-1</sup>
data colld	$4 < 2\theta < 53^\circ$ (+h, +k, +l)
scan type	$\omega$
scan speed	2.1-29.3°/min
scan range	$[2\theta(\text{Mo } K\alpha_1) - 1.0] - [2\theta(\text{Mo } K\alpha_2) + 1.0]^\circ$
bkgd time/scan time	0.5
no. of std reflns	2 (no significant variation)
abs cor	empirical with 9 reflns from $\psi$ -scan data; transmission factors 0.64-1.00
no. of reflns colld	3458
no. of obsd reflns	1435 ( $F > 6\sigma(F)$ )
function minimized	$\sum w( F_o  -  F_c )^2$
weighting scheme	$w = 1.00(\sigma^2(F_o) + 0.0002F_o^3)$
no. of params refined	169
$R = \sum( F_o  -  F_c ) / \sum F_o $	0.042
$R_w = [\sum w( F_o  -  F_c )^2 / \sum w F_o ^2]^{1/2}$	0.048

**X-ray Structure Determination.** Accurate unit cell parameters and the orientation matrix were obtained by a least-squares fit of 21 centered and indexed reflections in the range  $25 < 2\theta < 31^\circ$ . Details of the crystallographic data collection and the results are summarized in Table I. Intensities were corrected for Lorentz and polarization effects but not for extinction. The systematic absences revealed the space group to be  $P4_2/c$ , uniquely. The positions of Cu1, O1, and N1 were identified by MULTAN80,<sup>6</sup> and these were used in the first step of the Fourier synthesis.

- (1) Preliminary report of the structure has been presented: Muhonen, H.; Hatfield, W. E. "Abstracts of Papers", 36th Southeastern Regional Meeting, American Chemical Society, Raleigh, NC, Oct 1984, American Chemical Society: Washington, DC, 1984; Abstract No. 305.
- (2) (a) University of Helsinki. (b) The University of North Carolina at Chapel Hill.
- (3) Muhonen, H.; Hatfield, W. E. *Acta Chem. Scand., Ser. A*, in press.
- (4) (a) Bertrand, J. A.; Fujita, E.; VanDerveer, D. G. *Inorg. Chem.* **1980**, *19*, 2022. (b) Muhonen, H.; Hämäläinen, R. *Acta Chem. Scand., Ser. A*, **1978**, *A32*, 121. (c) Muhonen, H. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1983**, *C39*, 536. (d) Muhonen, H. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *B38*, 2041. (e) Muhonen H. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1981**, *B37*, 953.
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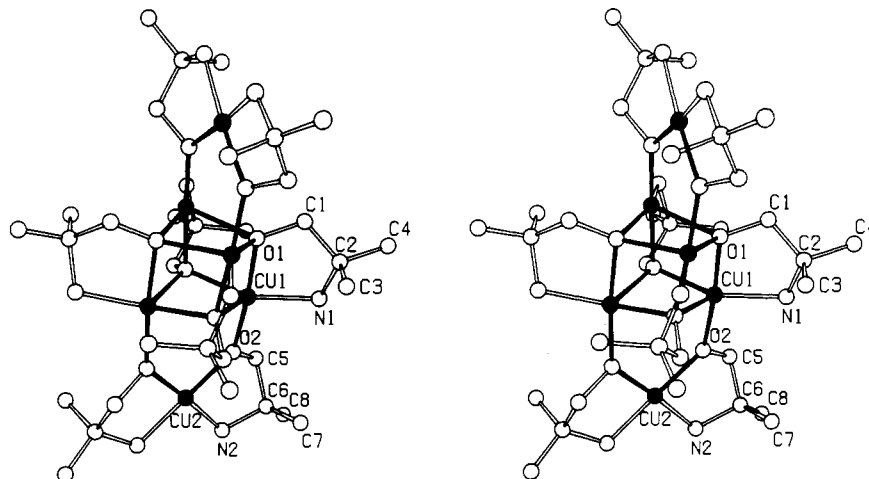


Figure 1. Stereoview of the hexanuclear copper(II) cluster cation.

Table II. Final Fractional Coordinates and  $U_{eq}$  ( $\times 10^3$ ) Values for Non-Hydrogen Atoms<sup>a</sup>

atom	x	y	z	$U_{eq}$ , Å <sup>2</sup>
Cu1	0.11261 (6)	-0.02067 (6)	0.06869 (5)	2.41 (3)
Cu2	0.00000	0.00000	0.26420 (6)	3.36 (6)
C1	-0.0307 (2)	-0.2744 (3)	0.3730 (2)	10.5 (2)
N1	0.2581 (4)	0.0160 (5)	0.0565 (3)	3.7 (3)
N2	0.1013 (5)	-0.0255 (7)	0.3487 (4)	6.0 (4)
O1	0.1077 (3)	-0.0065 (3)	-0.0513 (2)	2.3 (2)
O2	0.1026 (4)	-0.0327 (4)	0.1862 (3)	3.5 (3)
O3	0.0596 (8)	-0.3207 (13)	0.3672 (13)	23.4 (15)
O4	-0.1035 (7)	-0.3332 (8)	0.4025 (8)	14.1 (9)
O5	-0.0456 (9)	-0.2238 (10)	0.3018 (6)	15.4 (10)
O6	-0.0205 (20)	-0.1996 (12)	0.4357 (7)	24.5 (17)
C1	0.2050 (4)	-0.0055 (5)	-0.0850 (3)	2.9 (3)
C2	0.2744 (5)	0.0518 (5)	-0.0308 (5)	3.2 (4)
C3	0.2528 (6)	0.1635 (6)	-0.0319 (6)	4.5 (4)
C4	0.3825 (5)	0.0325 (6)	-0.0545 (6)	5.3 (5)
C5	0.1761 (6)	-0.0902 (6)	0.2283 (5)	4.5 (4)
C6	0.2005 (6)	-0.0427 (8)	0.3085 (5)	5.9 (6)
C7	0.2491 (9)	0.0557 (10)	0.2932 (8)	8.5 (8)
C8	0.2682 (9)	-0.1054 (13)	0.3606 (6)	11.1 (10)

$$^a U_{eq} = 1/3(U_{11} + U_{22} + U_{33}).$$

The structure was developed by iterating least-squares refinements and Fourier syntheses. After location of the Cu2 atom on the 4 axis, its x and y coordinates were fixed at (0, 0) and the multiplicity at 0.5. Refinement with non-hydrogen atoms using isotropic temperature factors led to the R value of 0.078. Difference syntheses calculated during the refinement provided the locations of all the hydrogen atoms, and their parameters were introduced into the refinement without allowing them to change. An isotropic thermal parameter,  $U_{iso} = 0.06$  Å<sup>2</sup>, was assigned to all hydrogen atoms. Final refinement by the full-matrix least-squares method using anisotropic temperature factors for all non-hydrogen atoms converged to the R value of 0.042. The highest peaks in the difference Fourier map calculated at the end of the refinements were 0.84 e Å<sup>-3</sup> in the copper atom environments near Cu2, and 0.40 e Å<sup>-3</sup> elsewhere. All calculations except the phase determination were carried out with the programs of the X-RAY 76 system.<sup>7</sup> The atomic scattering factors were those of the program system, and a dispersion correction was applied for copper and chlorine atoms.<sup>8</sup> A Univac 1108 computer was used for calculations.

The final atomic positional parameters and  $U_{eq}$  values for non-hydrogen atoms are listed in Table II. Anisotropic temperature factor coefficients for non-hydrogen atoms and fractional coordinates for hydrogen atoms are listed in Tables SI and SII, respectively.<sup>9</sup> A listing of the observed and calculated structure factors is available.<sup>9</sup>

**Magnetic Measurements.** Magnetic susceptibility measurements in the range 77–300 K were performed on a powdered sample weighing about

Table III. Interatomic Distances (Å) and Angles (deg)<sup>a</sup>

Copper and Oxygen Atom Environments			
Cu1-O1	1.955 (4)	O2-Cu1-O1 <sup>ii</sup>	98.3 (2)
Cu1-O1 <sup>i</sup>	2.013 (5)	N1-Cu1-O1 <sup>ii</sup>	114.3 (2)
Cu1-O1 <sup>ii</sup>	2.269 (5)	Cu1-O1-Cu1 <sup>i</sup>	95.0 (2)
Cu1-O2	1.916 (4)	Cu1-O1-C1	110.5 (3)
Cu1-N1	2.038 (6)	Cu1-O1-Cu1 <sup>ii</sup>	103.7 (2)
Cu2-O2	1.928 (5)	Cu1 <sup>i</sup> -O1-C1	131.7 (4)
Cu2-N2	1.966 (7)	Cu1 <sup>i</sup> -O1-Cu1 <sup>ii</sup>	92.4 (2)
O1-Cu1-O1 <sup>i</sup>	83.8 (2)	Cu1 <sup>ii</sup> -O1-C1	118.6 (4)
O1-Cu1-O2	174.0 (2)	O2-Cu2-O2 <sup>iii</sup>	98.1 (2)
O1-Cu1-N1	85.0 (2)	O2-Cu2-N2	85.1 (2)
O1-Cu1-O1 <sup>ii</sup>	77.3 (2)	O2-Cu2-N2 <sup>iii</sup>	175.9 (3)
O1 <sup>i</sup> -Cu1-O2	91.9 (2)	N2-Cu2-N2 <sup>iii</sup>	91.8 (3)
O1 <sup>i</sup> -Cu1-N1	154.2 (2)	Cu1-O2-Cu2	133.1 (3)
O1 <sup>i</sup> -Cu1-O1 <sup>ii</sup>	85.6 (2)	Cu1-O2-C5	118.0 (4)
O2-Cu1-N1	100.7 (2)	Cu2-O2-C5	108.1 (4)
Cubane Amino Alcohol Skeleton			
C1-O1	1.424 (7)	C1-C2-C4	111.2 (6)
C1-C2	1.500 (10)	C1-C2-N1	107.0 (5)
C2-C3	1.538 (11)	C3-C2-C4	110.2 (6)
C2-C4	1.533 (10)	C3-C2-N1	107.3 (6)
C2-N1	1.511 (9)	C4-C2-N1	108.6 (6)
O1-C1-C2	111.0 (5)	Cu1-N1-C2	108.0 (4)
C1-C2-C3	112.4 (6)		
Capping Amino Alcohol Skeleton			
C5-O2	1.434 (9)	C5-C6-C8	112.4 (9)
C5-C6	1.487 (12)	C5-C6-N2	104.3 (7)
C6-C7	1.504 (17)	C7-C6-C8	109.0 (9)
C6-C8	1.506 (17)	C7-C6-N2	108.9 (9)
C6-N2	1.509 (11)	C8-C6-N2	112.7 (7)
O2-C5-C6	109.6 (7)	Cu2-N2-C6	110.2 (5)
C5-C6-C7	109.5 (8)		
Perchlorate Anion			
Cl-O3	1.374 (13)	O3-C1-O5	107.7 (10)
Cl-O4	1.352 (11)	O3-C1-O6	106.5 (13)
Cl-O5	1.356 (11)	O4-C1-O5	119.3 (7)
Cl-O6	1.439 (15)	O4-C1-O6	103.5 (10)
O3-C1-O4	113.7 (9)	O5-C1-O6	105.1 (8)

<sup>a</sup> The symmetry codes are as follows: (i) = y, -x, -z; (ii) = -y, x, -z; (iii) = -x, -y, z.

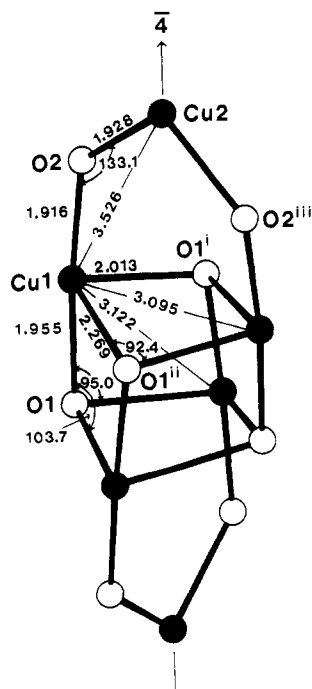
15 mg with use of a Faraday type balance consisting of a Cahn 2000 electrobalance equipped with an Anac 3472 HA electromagnet and 502 Lewis coils from George Associates, Berkeley, CA. Automatic data collection was controlled by Tektronix 4052A Graphic computing system as has been described elsewhere.<sup>10</sup> At low temperatures, from 4.2 to 100 K, magnetic susceptibility data were collected at 10 kOe on a powdered sample weighing 180 mg with a PAR Model 155 vibrating sample magnetometer (VSM) by using procedures that have been described

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(8) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV p 149.

(9) Supplementary material.

(10) Weller, R. R. Ph.D. Dissertation, The University of North Carolina at Chapel Hill, 1980.



**Figure 2.** View of the "bicapped-cubane" core including selected interatomic distances and angles.

previously.<sup>11</sup> Both instruments were calibrated with  $\text{HgCo}(\text{NCS})_4$ . Susceptibilities were corrected for the diamagnetism of the constituent atoms, which was estimated to be  $-117 \times 10^{-6}$  cgsu/Cu atom, and for the temperature-independent paramagnetism,  $N\alpha$ , of copper(II), which was estimated to be  $60 \times 10^{-6}$  cgsu/Cu atom.

### Description of the Structure

The molecular structure consists of a discrete hexanuclear  $[\text{Cu}_6(\text{C}_4\text{H}_{10}\text{NO})]^{4+}$  cation and four  $\text{ClO}_4^-$  anions. The shortest of the Cu–O(perchlorate) distances is 3.146 (13) Å for Cu2–O5. There are no short contacts between neighboring molecules, and hydrogen bonding is not important in the structure. An ORTEP stereoview of the cation is shown in Figure 1. Bond lengths and angles are given in Table III. The complex cation has a  $\text{Cu}_6\text{O}_8$  core formed by alternating copper(II) and alkoxo oxygen atoms. The core is shown in Figure 2, where it may be seen that a cubane-like  $\text{Cu}_4\text{O}_4$  subcore has two of its six faces (the top and bottom) capped by a copper atom. The capping copper atoms lie on the  $\bar{4}$  axis. One capping copper atom is joined via oxygen bridges to the two copper atoms in the top face, and the other is likewise joined to the two copper atoms in the bottom face. The symmetry of the cation and the core is  $\bar{4}$  ( $S_4$ ). In the  $\text{Cu}_4\text{O}_4$  cubane portion of the structure, the Cu...Cu separations are 3.095 (1) (×2) and 3.122 (1) Å (×4), and the Cu–O distances are 1.955 (3) (×4), 2.013 (4) (×4), and 2.269 (4) Å (×4). The Cu–O–Cu angle in the top and bottom faces is 92.4 (2)°, and the two unequal Cu–O–Cu angles in the side faces are 95.0 (2) and 103.7 (2)°. Since there are eight short and four intermediate Cu–O bonds, the latter being within the pseudodimers of the capped faces, the  $\text{Cu}_4\text{O}_4$  subcore represents an intermediate type between the two extremes, types I and II, in the classification presented by Mergehenn and Haase<sup>12</sup> for the  $\text{Cu}_4\text{O}_4$  cores in (dialkylamino)-ethanol complexes. The  $\text{Cu}_4\text{O}_4$  core is unique in that the four shortest Cu–O bonds in the core do not exist within the pseudodimers of the capped faces, but they are between the faces. These four short Cu–O bonds are mutually parallel. The dihedral angle between the least-squares top and side faces in the  $\text{Cu}_4\text{O}_4$  subcore is 86.2 (1)°, and the angle between neighboring side faces is 89.7 (1)°. The top face is bent along the O...O line so that the dihedral

angle between the planes  $[\text{Cu}1, \text{O}1^i, \text{O}1^{ii}]$  and  $[\text{Cu}1^{iii}, \text{O}1^i, \text{O}1^{ii}]$  is 20.8 (2)°. In the side faces the respective bending is slight, the dihedral angle being 4.6 (2)°.

The cubane copper atoms have a square-pyramidal coordination geometry, which is distorted toward a trigonal-bipyramidal arrangement. The basal plane of the square-pyramid is made up by atoms O1, O2, N1, and O1<sup>i</sup>, and O1<sup>iii</sup> is at the apex. The Cu1–(basal atom) bond lengths vary in the range 1.916 (4)–2.038 (6) Å, and the apical Cu1–O1<sup>iii</sup> distance is 2.269 (5) Å. The basal plane is tetrahedrally distorted with the deviations of the O1, O2, N1, and O1<sup>i</sup> atoms from the plane being 0.249 (4), 0.204 (6), –0.215 (6), and –0.237 (4) Å, respectively. The deviation of the Cu1 atom from the plane toward the apical O1<sup>iii</sup> atom is only 0.172 (3) Å, being less than those of the plane determining atoms. The O1–Cu1–O2 and N1–Cu1–O1<sup>i</sup> angles in the basal plane are 174.0 (2) and 154.2 (2)°, respectively, the latter angle deviating markedly from 180°. The (basal atom 1)–Cu1–(basal atom 2) angles (where atoms 1 and 2 represent adjacent atoms) are in the range 83.8 (2)–100.7 (2)°, the mean value being 90.4°. The O1<sup>iii</sup>–Cu1–(basal atom) angles from the apical O1<sup>iii</sup> atom to the basal atoms vary in the range 77.3 (2)–114.3 (2)°, with the mean value being 93.9°.

The bond lengths and angles, which make the contracted trigonal-bipyramidal arrangement around Cu1 a less suitable description of coordination geometry, are described as follows: (1) In the triangular basal plane made up by atoms O1<sup>i</sup>, O1<sup>iii</sup>, and N1, the Cu1–N1 distance (the apical distance in the square-pyramidal coordination) is considerably longer than the other two basal distances Cu1–O1<sup>i</sup> and Cu1–O1<sup>iii</sup>. (2) The N1–Cu1–O1<sup>i</sup> and O1<sup>i</sup>–Cu1–O1<sup>iii</sup> angles in the basal plane are 154.2 (2) and 85.6 (2)°, respectively. These values deviate remarkably from 120° even though their mean value is 119.9°. The third basal angle, N1–Cu1–O1<sup>iii</sup>, of 114.3 (2)°, is close to 120°. In the trigonal-bipyramidal description of the structure, the Cu1 atom is displaced 0.244 (2) Å from the basal plane toward the axial O2 atom.

The Cu...Cu separation between the capping and the cubane copper atoms is 3.525 (1) Å (×4). The Cu–O distances within the Cu1–O2–Cu2 capping bridge are 1.916 (4) Å for Cu1–O2 and 1.928 (5) Å for Cu2–O2, and the bridge angle is 133.1 (3)°. The capping copper atoms have planar coordination with the bond lengths being 1.928 (5) Å for Cu2–O2 and 1.966 (7) Å for Cu2–N2. According to our earlier classification, the bis(aminoalcoholato)copper(II) moiety is type *cis-(a)*, in which type the aminoalcohols are arranged in *cis* configuration around the copper atom and both aminoalcohols are deprotonated.<sup>3</sup> The present compound is the first example in which the bis(aminoalcohol)-copper(II) fragment exhibits this configuration. The coordination plane,  $[\text{O}2, \text{O}2^{iii}, \text{N}2, \text{N}2^{iii}]$ , around the capping copper atom makes an angle of 90.0 (2)° with the top face of the cubane.

All of the aminoalcohol chelate rings in the hexanuclear cation are oriented parallel to the  $\bar{4}$  axis. In the cubane  $\text{Cu}_4\text{O}_4$  complexes of N-substituted aminoalcohols, the chelate rings lie in the top and bottom faces of the cube. There are no known examples in which the chelate rings span the top and bottom faces as they do in the present complex. The chelate rings of 2-amino-2-methyl-1-propanol also lie in the top and bottom faces of the  $\text{Cu}_4\text{O}_4$  cubane in the  $[\text{CuLCl}]_4$  complex. In the hexamer, the aminoalcohol chelate rings have torsion angles O1–C1–C2–N1 and O2–C5–C6–N2 of 47.7 (7) and 50.8 (9)°, respectively, which indicate only a slight difference in the folding of the ligands around the capping and the cubane copper atoms.

### Magnetic Data

The temperature dependences of the magnetic susceptibility and of the effective magnetic moment of  $[\text{Cu}_6(\text{C}_4\text{H}_{10}\text{NO})_8](\text{ClO}_4)_4$  are shown in Figures 3 and 4, respectively, where it may be seen that both quantities decrease with decreasing temperature down to 20 K. The decrease in the magnetic susceptibility values is rapid in the temperature range 120–35 K. There is a minimum in magnetic susceptibility near 20 K, and below that temperature the magnetic susceptibility increases with a further decrease in temperature. In the vicinity of the susceptibility minimum the

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(12) Mergehenn, R.; Haase, W. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 1877.

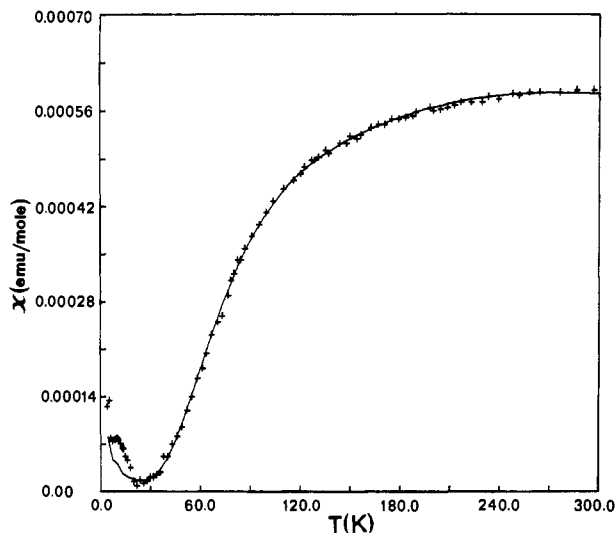


Figure 3. Temperature dependence of the magnetic susceptibility. The solid curve represents theoretical values.

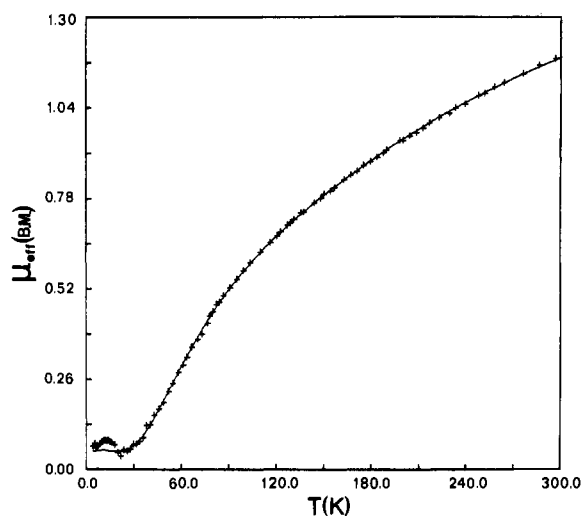


Figure 4. Temperature dependence of the effective magnetic moment. The solid curve represents theoretical values.

numerical values of susceptibilities are very small. For the purposes of modeling the exchange interactions between copper pairs the copper atoms within the hexanuclear cluster are renumbered in the following way: Cu1 and Cu2 are the copper atoms in the top face of the cubane; Cu3 and Cu4 are the copper atoms in the bottom face of the cubane; Cu5 and Cu6 are the capping copper atoms for the top and the bottom faces, respectively. The spin Hamiltonian appropriate for the exchange coupling problem in the "bicapped-cubane" cluster is

$$\mathbf{H} = -2(J_{15}\hat{S}_1\cdot\hat{S}_5 + J_{25}\hat{S}_2\cdot\hat{S}_5 + J_{36}\hat{S}_3\cdot\hat{S}_6 + J_{46}\hat{S}_4\cdot\hat{S}_6) - \\ 2(J_{13}\hat{S}_1\cdot\hat{S}_3 + J_{14}\hat{S}_1\cdot\hat{S}_4 + J_{23}\hat{S}_2\cdot\hat{S}_3 + J_{24}\hat{S}_2\cdot\hat{S}_4) - \\ 2(J_{12}\hat{S}_1\cdot\hat{S}_2 + J_{34}\hat{S}_3\cdot\hat{S}_4)$$

where exchange expected to be unimportant has been neglected. From the  $S_4$  symmetry it follows that  $J_1 = J_{15} = J_{25} = J_{36} = J_{46}$ ,  $J_2 = J_{13} = J_{14} = J_{23} = J_{24}$ , and  $J_3 = J_{12} = J_{34}$ . The interaction Hamiltonian and starting values for the magnetic variables were input into the CAMS program,<sup>10,13</sup> which uses a numerical method to determine eigenvalues. The program generates the spin-pair interaction matrix, block diagonalizes the matrix, and produces eigenvalues and eigenvectors from which the susceptibilities are calculated. The calculated susceptibilities were refined by the CAMSFIT program,<sup>10,13</sup> which uses a numerical nonlinear least-squares technique. The parameters  $g$ ,  $J_1$ ,  $J_2$ ,  $J_3$ , and PMI (percent

monomeric impurity) were used as variables in the fitting processes, and the function minimized was  $F = \sum(\chi_i^{\text{obsd}} - \chi_i^{\text{calcd}})^2$ . The data below 37 K were not used in the refinement, for the experimental error due to very small numerical values of the susceptibilities below that temperature is high. Inspection of Figures 3 and 4, where experimental and calculated values for these points are also shown, reveals that no exceptional changes occur at very low temperatures. All five of the variables were not allowed to vary freely in the calculations. The parameters  $g$  and  $J_3$  are correlated, and if these were allowed to vary freely, unreasonable values of the parameters would result. Therefore, refinements were carried out by grouping the variables in different ways in separate refinements. Refinements revealed that the minima for variables other than  $J_3$  are sharp. The best minimum was reached with values for the variables of  $g = 2.03$ ,  $J_1 = -152 \text{ cm}^{-1}$ ,  $J_2 = -52 \text{ cm}^{-1}$ ,  $J_3 = 57 \text{ cm}^{-1}$  and PMI = 0.022%, with  $R$ , defined as  $[\sum(\chi_i^{\text{obsd}} - \chi_i^{\text{calcd}})^2 / (\chi_i^{\text{obsd}})^2]^{1/2}$ , equalling 0.0129. The minimum for  $J_3$  is flat, and refinements revealed that changes in the value of  $J_3$  up to approximately 15% have little effect on the shape of the calculated susceptibility curve.

### Exchange Interactions

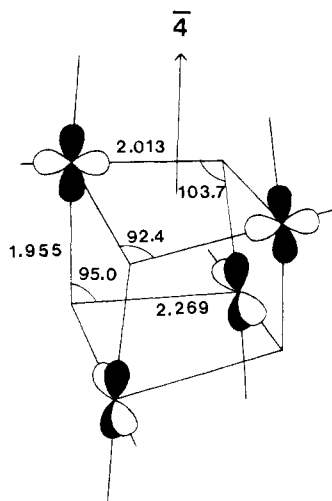
The calculated  $J$  values show that the interaction between the capping copper ion and the copper ions in the capped face is rather strongly antiferromagnetic with  $J_1 = -152 \text{ cm}^{-1}$ . The interaction between the copper ions in the side faces of the cubane is also antiferromagnetic with  $J_2 = -52 \text{ cm}^{-1}$ , whereas the interaction between the copper ions in the capped faces is fairly strongly ferromagnetic with  $J_3 = 57 \text{ cm}^{-1}$ . The exchange coupling constants can be understood in terms of the structural details of the hexametallallic molecule and the orbitals that are involved in the exchange processes. We present two models for the orbital mechanism. One is based on a square-pyramidal description of the geometry around the cubane copper atoms and on local coordinates, whereas the other is based on a trigonal-bipyramidal description of the arrangement around the cubane copper atoms and on the total symmetry of the hexametallallic molecule.

**Orbital Model Based on Local Coordinates.** First consider the exchange interaction between a capping copper ion and a copper ion in the capped face. According to the numbering scheme, these interactions are Cu1:Cu5, Cu2:Cu5, Cu3:Cu6, and Cu4:Cu6. Both units of the hexametallallic molecule, the Cu<sub>4</sub>O<sub>4</sub> and the two capping groups, have separately and together  $S_4$  point symmetry, but there is no symmetry operator that will transfer a capping copper (aminoalcohol) to a cubane copper (aminoalcohol). Since the capping copper ions, Cu5 and Cu6, have planar coordination, the magnetic orbital is clearly the  $\sigma^*$  orbital, and its lobes are directed toward O2, N2, and their  $C_2$  symmetry-related atoms.

It is not possible to state the nature of the magnetic orbital on Cu1 with such precision, and it is this ambiguity that requires the presentation of two exchange mechanisms. We have argued in the description of the structure that the cubane copper ions have square-pyramidal coordination with donor atoms N1, O2, O1, and O1<sup>i</sup> forming the basal plane and the axial position being occupied by O1<sup>ii</sup> at 2.269 (5) Å. Typically, the magnetic orbital in square-pyramidal coordination for copper(II) is a linear combination of (in local site terms)  $d_{x^2-y^2}$  and  $d_{z^2}$  with the contribution from  $d_{x^2-y^2}$  predominating. A pictorial representation of the four  $d_{x^2-y^2}$  orbitals is given in Figure 5. The fairly large antiferromagnetic coupling between the cubane copper ions and the capping copper ions is now easy to understand. The short copper-oxygen bond lengths [1.916 (4) and 1.928 (5) Å] and large Cu1-O2-Cu2 bridge angle of 133.1 (3)° offer a good pathway for an exchange interaction between the  $\sigma^*$  orbital in the cubane and the  $\sigma^*$  orbital of the copper in the cap transmitted through the orbitals of the bridging O2 atom.

Next consider the exchange interaction in the top and bottom faces, that is, in the pseudodimers which have coalesced to form the cubane core. Here the Cu1-O1-Cu1<sup>iii</sup> angle is rather close to 90°, the value being 92.4 (2)°, and ferromagnetic coupling is expected. This angle is smaller than the ground-state inversion Cu-O-Cu angle of 97.5° in the bis( $\mu$ -hydroxo)-bridged copper(II)

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**Figure 5.** Schematic representation of interacting orbitals in the square-pyramidal coordination for copper(II) ions of the  $\text{Cu}_4\text{O}_4$  subcore.

dimers<sup>14</sup> and  $95.7^\circ$  in the bis( $\mu$ -alkoxo)-bridged copper(II) dimers.<sup>15</sup> One of the Cu–O bonds within the pseudodimer is short [2.013 (5) Å] while the other Cu–O bond is of intermediate length [2.269 (5) Å]. These structural results suggest that there should be fairly strong ferromagnetic interactions within the top and bottom faces of the cubane in agreement with the experimental result. The tetrameric chloro and bromo complexes of the present aminoalcohol exhibit very strong pseudodimeric antiferromagnetic interactions with  $2J$  values of  $-507$  and  $-516$   $\text{cm}^{-1}$ , respectively.<sup>16</sup> However, there is an important structural difference. For example, in the chloro complex, the Cu–O–Cu angle and the Cu–O bond lengths in the pseudodimer have values of  $101.2$  (3) $^\circ$ ,  $1.959$  (7) Å, and  $1.970$  (7) Å.<sup>5</sup> In the case of the chloro and bromo complexes, the  $\sigma^*$  orbitals are directed toward the bridging oxygen atom. This directional property, along with the large Cu–O–Cu angle, accounts for the dramatic difference in properties.

In the present case, the magnetic orbitals do not mutually point in the direction of the bridging oxygen atom, the pseudodimer is related to the parallel-planar bimetallic case, which typically has an unsymmetrical (from the point of view of Cu–O bond lengths)  $\text{Cu}_2\text{O}_2$  exchange-coupled unit. Thus, the sign and magnitude of the exchange-coupling constant in the pseudodimers may be understood in terms of the  $92.4$  (2) $^\circ$  Cu–O–Cu angles and the relative orientation of the magnetic orbitals with respect to each other and the orbitals of the bridging oxygen atom.

The side faces of the cubane display all three different Cu–O–O bond lengths. The two unequal Cu–O–Cu angles in these faces are  $95.0$  (2) and  $103.7$  (2) $^\circ$  with the mean value being  $99.4^\circ$ . There has been considerable effort expended toward finding a correlation between the structural and magnetic parameters within the side faces of the cubane formed with N-substituted aminoalcohol complexes of copper(II). The most successful relationship takes the form of a logarithmic dependence of  $2J_{\text{ferro}}$  on the distance between the pseudodimeric planes.<sup>17</sup> Although the relationship may be valid only for complexes formed by specific aminoalcohols, it applies to ferromagnetic coupling within the side faces. Likewise, Nieminen has listed only ferromagnetic  $J$  values for the side faces of cubane-like copper(II) aminoalcohol complexes that correspond to the intermediate type.<sup>18</sup> The exchange interaction within the side faces of the cubane subcore of the present complex,  $[\text{Cu}_6(\text{C}_4\text{H}_{10}\text{NO})_8](\text{ClO}_4)_4$ , is clearly antiferromagnetic in nature. The overlaps of the magnetic orbitals on the copper

atoms with the orbitals on the bridging oxygen atom, which makes an angle of  $103.7$  (2) $^\circ$  with the copper atoms, form the interaction pathway, which leads to the observed moderate antiferromagnetic interaction. For the other pathway only a small positive value of  $J$  would be expected because of the Cu–O–Cu angle of  $95.0$  (2) $^\circ$ , which value is very close to the ground-state inversion angle of  $95.7^\circ$  found for bis( $\mu$ -alkoxo)-bridged copper(II) complexes and because of the roughly orthogonal orientation of the magnetic orbitals to each other.

**Orbital Model Based on the Total Symmetry.** The copper(II) complex of the Schiff base of 2-aminoethanol and acetylacetonate, Cu(EIA), crystallizes in the same space group as the present hexanuclear complex.<sup>19</sup> Cu(EIA) has a  $\text{Cu}_4\text{O}_4$  cubane structure with the coordination bond lengths and angles possessing values very similar to those that the cubane copper ion has in the hexanuclear complex. For Cu(EIA) a trigonal-bipyramidal geometry around copper ions was preferred to the square-pyramidal one. In Cu(EIA) the angles that the adjacent atoms in the triangular basal plane form with the copper ion have values of  $81$ ,  $120$ , and  $153^\circ$ . In the discussion, above, of the structure of  $[\text{Cu}_6(\text{C}_4\text{H}_{10}\text{NO})_8](\text{ClO}_4)_4$  the trigonal-bipyramidal geometry was regarded as a less suitable description of the structure of a cubane copper ion due to the values for basal angles of  $85.6$  (2),  $114.3$  (2), and  $154.2$  (2) $^\circ$ . In an interpretation of the magnetic properties of Cu(EIA), Ginsberg used an orbital model in which the unpaired electrons were assigned to  $d_{z^2}$  orbitals.<sup>20</sup> If we assume that the  $d_{z^2}$  orbitals make the greatest contribution to the magnetic orbitals of the cubane copper atoms of the hexametallate molecule, then an orbital model that is based on the total symmetry of the molecule may be generated.

First consider the interaction between a capping copper ion and a copper ion in the capped face. The  $S_4$  point symmetry of the molecule fixes the common  $z$  axis direction for the cubane and capping moieties. The  $x$  and  $y$  directions of the orthogonal coordinate systems in the two moieties can be chosen independently from each other. Since the capping copper ions Cu5 and Cu6 have planar coordination with the coordination planes being perpendicular to the top and bottom faces of the cubane, the magnetic orbital for Cu5 and Cu6 can be either the  $d_{xz}$  or the  $d_{yz}$  orbital. The short Cu–O bond lengths [1.916 (4) and 1.928 (5) Å] and the large Cu1–O2–Cu2 angle of  $133.1$  (3) $^\circ$  offer a good pathway for an exchange interaction between the  $d_{z^2}$  orbital of the cubane copper and the  $d_{xz}$  or  $d_{yz}$  orbital of the capping copper through the orbitals of the bridging O2 atom. The experimentally observed, fairly strong antiferromagnetic coupling is in agreement with this orbital model.

Next consider the exchange interaction in the top and bottom faces of the cubane. For the  $d_{z^2}$ – $d_{z^2}$  interaction, the tori of the  $d_{z^2}$  orbitals and the oxygen atom orbitals form the interaction pathway. Since the metal atom orbitals that participate in the interaction have the same symmetry and the orbitals are oriented parallel, the magnitude and sign of  $J$  for  $d_{z^2}$ – $d_{z^2}$  interaction depends on the Cu–O–Cu angle in the top and bottom faces. This angle of  $92.4$  (2) $^\circ$ , which value is much smaller than the ground-state inversion Cu–O–Cu angle of  $97.5^\circ$  in the bis( $\mu$ -hydroxo)-bridged copper(II) dimers<sup>14</sup> and of  $95.7^\circ$  in the bis( $\mu$ -alkoxo)-bridged copper(II) dimers,<sup>15</sup> together with the short [2.013 (5) Å] and intermediate [2.269 (5) Å] Cu–O bond lengths suggest that a ferromagnetic interaction should arise in agreement with the experimental result.

The top and bottom faces of the cubane are bent along the O–O line with the dihedral angle between the [Cu,O,O] planes being  $20.8$  (2) $^\circ$ . Because the ferromagnetic interaction within the pseudodimer is not a consequence of the different symmetry of the magnetic orbitals, it should be sensitive to structural changes in the surroundings of the cubane copper ion. Kahn and Charlot<sup>21</sup> have studied the effect of bending of the  $\text{Cu}_2\text{O}_2$  plane along the O–O line on the  $J$  values in bis( $\mu$ -oxo)-bridged copper(II) dimers

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by extended Hückel calculations. However, the magnetic orbitals in the top and bottom faces of the cubane are delocalized toward the bridging oxygen atom to a much lesser degree than the  $d_{xy}$  orbitals in the dimers<sup>22,23</sup> treated by Kahn and co-workers. This being the case, the bending of the pseudodimer in the present complex should have a smaller effect on the ferromagnetic interaction than the bending in the bis( $\mu$ -oxo)-bridged dimers.

The side faces of the cubane display all three different Cu–O–Cu bond lengths. The two unequal Cu–O–Cu angles in these faces are 95.0 (2) and 103.7 (2)° with the mean value being 99.4°. The exchange interaction within the side faces of the cubane subcore is clearly antiferromagnetic. The overlaps, in the side faces of the cubane, of the  $d_{z^2}$  magnetic orbitals on the copper atoms with the orbitals on the bridging oxygen atoms form interaction pathways that lead to the observed moderate antiferromagnetic interaction. There are contributions to the observed  $J$  value from both Cu–O–Cu pathways, and it is clear that the contribution involving the large Cu–O–Cu angle of 103.7 (2)°, which is ex-

pected to be antiferromagnetic, dominates the contribution from the 95.0 (2)° Cu–O–Cu pathway. This latter angle is very close the ground-state inversion angle of 95.7° in bis( $\mu$ -alkoxo)-bridged copper(II) dimers, and only a small positive value of  $J$  would have been expected for it.

This work has opened up two important new avenues of research. First, it is important that additional members of this new structural class of aminoalcohol complexes be prepared and characterized so that the nature of the superexchange interactions and pathways may be understood more clearly. Secondly, and perhaps more importantly, the question of capping additional faces now arises. These two problems will guide our research in this area.

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**Registry No.**  $[\text{Cu}_6(\text{C}_4\text{H}_{10}\text{NO})_8](\text{ClO}_4)_4$ , 100113-85-7.

**Supplementary Material Available:** Listings of observed and calculated structure factor amplitudes, anisotropic temperature factor coefficients for non-hydrogen atoms (Table SI), and fractional coordinates for hydrogen atoms (Table SII) (13 pages). Ordering information is given on any current masthead page.

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## A Structural Analysis of the Semibridging Carbonyl

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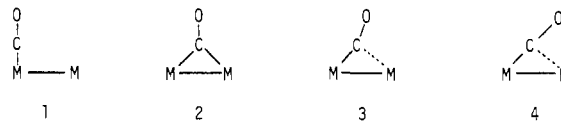
The structural data for terminal, linear and bent semibridging, and symmetrically bridging CO groups in 47 compounds are subjected to a detailed quantitative analysis. As first suggested by Cotton, the terminal, bent semibridging, and symmetrical bridging systems form a smooth structural continuum that can be identified with the terminal–bridge–terminal CO-exchange reaction trajectory. The linear semibridging carbonyls can be divided into three major types on structural and chemical grounds. Type I contains strongly interacting systems, with one linear semibridging CO per dimetal unit. Type II, with more than one such CO bridge and multiple M–M bonding, shows less interaction. Type III systems, containing a transition metal and either Au or a main-group metal have, it is proposed, no significant interaction between the second metal and the ostensibly bridging CO. Type IV is as yet only tentatively formulated as it contains but a single example:  $\text{Mn}_2(\text{CO})_5(\text{dppm})_2$ . The current bonding models are discussed with reference to these data, and their validity for the different structural types is considered.

A fascinating aspect of structural organometallic and coordination chemistry is the high structural variability that can be observed in such groups as  $\text{M}(\mu\text{-CO})\text{M}$ ,  $\text{M}(\mu\text{-H})\text{M}$ , and  $\text{C}(\mu\text{-H})\text{M}$ . The closest analogy outside organometallic chemistry is probably the hydrogen bond. In each case the interactions involved must be much weaker than the full covalent bonds normally encountered in structural chemistry. This variability allows us to learn something about the types of potential energy surfaces associated with these interactions.

This paper attempts to show how a detailed structural analysis of an inorganic functional group can provide useful information in two respects. First, it can help identify and characterize different structural types and test rival theoretical pictures of bonding. Second, it can, as emphasized by Bürgi and Dunitz<sup>1</sup> for organic systems, give information about reaction trajectories. Our earlier work in this area<sup>2</sup> involved the C–H...M bridge,<sup>3</sup> from which we were able to suggest a detailed reaction trajectory for  $\text{M} + \text{C-H} \rightarrow \text{C-M-H}$ . From these results we were able not only to confirm the main features of the C–H...M bonding but also to gain a deeper understanding of the factors that determine whether a metal complex will react with an alkane C–H bond (alkane activation) or with a ligand C–H bond (cyclometalation). We concluded that sterically uncongested systems would favor the alkane reaction.

We were also able to understand the observed selectivity for attack at unhindered alkane C–H bonds. The success of this work led us to ask whether the same method might also throw light on other organometallic problems.

This paper reports our results on CO, a ligand that occupies a place of central importance in organometallic chemistry. We were attracted to this group because it adopts a number of distinct structural forms in its complexes: terminal (1), symmetrically bridging (2), and semibridging (both bent (3) and linear (4) forms



have been identified). In the case of 4, the unusual linear semibridging form, rival views of the bonding description have been proposed and we hope to throw some light on this problem.

The bent semibridging carbonyl is closely associated with the important work of Cotton.<sup>4a</sup> He proposed that semibridging CO groups could be thought of as constituting a structural continuum that leads from the terminal to symmetrical bridging arrangements and that they represent “stopped-action views” (i.e. a kinetic

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