Orthorhombic
$Pna2_1$
a = 8.012 (3) Å
b = 7.638 (3) Å
c = 10.842 (5) Å
V = 663.6 (8) Å^3
Z = 4
D_x = 1.543 Mg m^{-3}
D_m not measured

Cell parameters from 25
  reflections
θ = 10.5–12.5°
μ = 0.146 mm^{-1}
T = 295 K
Prismatic
0.40 × 0.37 × 0.14 mm
Colourless

Data collection

Rigaku AFC-5R diffractom-
  eter
$\omega/2\theta$ scans
Absorption correction: none
1808 measured reflections
1418 independent reflections
1186 reflections with
  $I > 2\sigma(I)$

R_{int} = 0.038
θ_{max} = 34°
h = 0 → 12
k = 0 → 12
l = −1 → 16
3 standard reflections
  every 97 reflections
  intensity decay: none

Refinement

Refinement on F
R = 0.039
wR = 0.038
S = 1.26
1186 reflections
131 parameters
All H atoms refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max}$ = 0.07

$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}
Extinction correction:
  $I_{corr} = I_o(1 + gI_c)$
Extinction coefficient:
  g = 1.42 × 10^{-5}
Scattering factors from *Inter-
national Tables for X-ray
Crystallography* (Vol. IV)

Table 2. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1N1$\cdots$O2^i	0.87 (3)	2.02 (3)	2.847 (2)	158 (3)
N1—H2N1$\cdots$O3^{ii}	0.97 (3)	1.86 (3)	2.786 (2)	160 (2)
N1—H3N1$\cdots$O4^{iii}	1.14 (4)	1.72 (4)	2.796 (3)	154 (3)
N1—H4N1$\cdots$O5^{iv}	0.80 (4)	2.30 (4)	3.082 (3)	167 (3)
N2—H1N2$\cdots$O2^v	0.91 (3)	1.93 (3)	2.843 (2)	173 (3)
N2—H2N2$\cdots$O3	0.86 (3)	1.94 (3)	2.795 (3)	172 (2)
N2—H3N2$\cdots$O4^{vi}	0.93 (3)	1.99 (3)	2.869 (3)	158 (2)
N2—H4N2$\cdots$O2^{vii}	0.98 (3)	1.97 (3)	2.888 (2)	155 (2)

Symmetry codes: (i) $x - \frac{1}{2}, \frac{3}{2} - y, z$; (ii) $\frac{1}{2} - x, y - \frac{1}{2}, z - \frac{1}{2}$; (iii) $-\frac{1}{2} - x, y - \frac{1}{2}, z - \frac{1}{2}$; (iv) $-x, 2 - y, z - \frac{1}{2}$; (v) $1 - x, 2 - y, \frac{1}{2} + z$; (vi) $-x, 2 - y, \frac{1}{2} + z$; (vii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} + z$.

Data collection and cell refinement were carried out with *RASA*II (Rigaku Corporation, 1990). The structures of (I) and (II) were solved by direct methods using *MITHRIL* (Gilmore, 1984) and refined by full-matrix least squares using *TEXSAN* (Molecular Structure Corporation, 1985). H atoms were located from difference Fourier maps and refined isotropically. The displacement ellipsoid plots were made with the aid of *ORTEP*II (Johnson, 1976). The calculations were performed on a VAX 3100 computer using *TEXSAN* at the X-ray Laboratory of Okayama University.

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μ-Acetato-μ-aqua-μ-hydroxo-bis[(1,4-dimethyl-1,4,7-triazacyclononane-κ³N)-copper(II)] Diperchlorate

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Abstract

The structural characterization of the title complex, [Cu$_2$(OH)(C$_2$H$_3$O$_2$)(C$_8$H$_{19}$N$_3$)$_2$(H$_2$O)](ClO$_4$)$_2$, provides only the third example of a binuclear copper complex containing a bridging water molecule. The three bridging groups (aqua, acetato and hydroxo) are all different, a rare feature for spontaneous self-assembly reactions. The resulting geometry about the two Cu atoms is distorted octahedral, with the Cu—O(H) distance of 1.963 (2) Å distinguished from the Cu—O(H$_2$) distance of 2.737 (5) Å. The cation has crystallographically imposed mirror symmetry.

Comment

A triangular trinuclear arrangement of Cu atoms is necessary for the four-electron reduction of dioxygen to water for the blue copper oxidases (BCOs). This biologically unique arrangement has been structurally characterized for one member of the BCOs, ascorbate oxidase (Messerschmidt *et al.*, 1992). However, structural evidence in the form of intermediates supporting the proposed mechanism during enzymic activity remains elusive. The title complex, (I), addresses this deficit, providing a structural model complex for the Type 3 binuclear site [the Cu atoms are classified according to their spectroscopic properties as Type 1,

2 or 3 (T1, T2 or T3), after Fee (1975)]. The proposed catalytic cycle (Soloman *et al.*, 1993) suggests that dioxygen is first reduced to a hydroperoxide group prior to complete reduction to water. Identification of a bridging water molecule in a binuclear metal complex is rare, and often they are difficult to characterize structurally (Chaudhuri *et al.*, 1985; Christou *et al.*, 1990). Nevertheless, although a rare feature, a water molecule can clearly be stabilized through bridge formation between two Cu atoms. Furthermore, the presence of the three different bridging groups raises questions as to the interplay of subtle energetics for spontaneous self-assembly reactions.

(I)
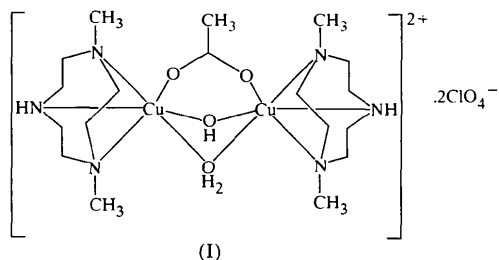
The complex cation has mirror symmetry, with the O atoms of OH and H$_2$O, and the C atoms of the acetate bridging groups lying on the crystallographic mirror plane, and with a consequent *syn* relationship of the secondary N atoms (N1) of the macrocyclic ligand (Fig. 1). The acetate group is in the familiar $\eta^1:\eta^1:\mu_2$ bridging mode. The coordination geometry of copper is distorted octahedral with the octahedron elongated along the O1(H$_2$O)—Cu—N7 axis. This results in the two Cu—*tert*-N bond lengths (Cu—N4 and Cu—N7) being very different (Table 2). This combination of bridging groups also occurs in bis(2,2'-bipyridine)-μ-aqua-μ-acetato-μ-hydroxo-dicopper(II) perchlorate (Christou *et*
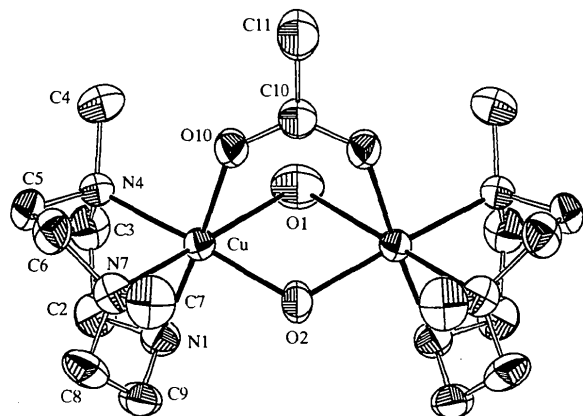

Fig. 1. A view of the title cation with displacement ellipsoids drawn at the 50% probability level. Atoms O1 and O2 are the water and hydroxy O atoms, respectively. H atoms and perchlorate groups have been omitted.

al., 1990). Here, the Cu atom is five-coordinate square pyramidal, with the water molecule at the apex and a Cu· · ·Cu separation of 3.035 Å.

Geometrical considerations indicate that the coordinated water molecule may be hydrogen bonded to perchlorate O atoms in the mirror plane [O12· · ·(H)O1(H)· · · O21$'^i$: O12· · ·O1 2.89 (1), O1· · ·O21$'^i$ 2.89 (4) Å and O12· · ·O1· · ·O21$'^i$ 122.2 (8)°; symmetry code: (i) 1 − *x*, 1 − *y*, $\frac{1}{2}$ + *z*], and there is a weak N1—H1· · ·O22^i interaction of 3.124 (6) Å. A hydrogen-bonding interaction could not be unequivocally assigned for the hydroxy group.

The three bridging motifs are formed by spontaneous self-assembly of the molecule in solution rather than employing directed synthesis. Thus, it is intriguing that the unsubstituted N atoms (N1) of the macrocycles are aligned *syn* with respect to each other. Although there is no indication of hydrogen bonding with μ-OH, this feature could be viewed as a 'pocket' suitable for molecular recognition.

Experimental

Crystal data

[Cu$_2$(OH)(C$_2$H$_3$O$_2$)- (C$_8$H$_{19}$N$_3$)$_2$(H$_2$O)](ClO$_4$)$_2$	Mo $K\alpha$ radiation λ = 0.71073 Å
M_r = 734.58	Cell parameters from 25
Orthorhombic	reflections
$Cmc2_1$	θ = 21.5–24.1°
a = 13.074 (2) Å	μ = 1.59 mm^{-1}
b = 17.354 (2) Å	T = 293 K
c = 13.794 (4) Å	Needle
V = 3129.7 (11) Å^3	0.61 × 0.24 × 0.16 mm
Z = 4	Blue
D_x = 1.559 Mg m^{-3}	
D_m not measured	

Data collection

Enraf–Nonius CAD-4 diffractometer	1884 reflections with $F^2 > 0$
$\omega/2\theta$ scans	R_{int} = 0.030
Absorption correction:	θ_{max} = 27.5°
Gaussian (Davenport *et al.*, 1995)	h = 0 → 16 k = 0 → 22
T_{min} = 0.687, T_{max} = 0.782	l = −17 → 17
3737 measured reflections	3 standard reflections
1947 independent reflections	frequency: 120 min intensity decay: 2%

Refinement

Refinement on F^2
$R(F) = 0.039$
$wR(F^2) = 0.090$
$S = 1.706$
1883 reflections
203 parameters
H atoms not refined
$w = 1/\sigma^2(F^2)$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.52$ e Å^{-3}
$\Delta\rho_{min} = -0.33$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)
Absolute structure: Flack (1983)
Flack parameter = 1.01 (2)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cu	0.62611 (3)	0.17195 (2)	0.72711	0.0334 (2)
O1	1/2	0.2471 (4)	0.6000 (5)	0.070 (4)
O2	1/2	0.1123 (3)	0.7453 (3)	0.044 (2)
N1	0.6759 (3)	0.0924 (2)	0.6293 (3)	0.042 (2)
C2	0.7598 (4)	0.1224 (3)	0.5688 (4)	0.049 (3)
C3	0.7673 (4)	0.2084 (3)	0.5808 (4)	0.052 (3)
N4	0.7582 (3)	0.2310 (2)	0.6846 (3)	0.040 (2)
C4	0.7524 (5)	0.3153 (3)	0.6939 (5)	0.065 (3)
C5	0.8473 (3)	0.2024 (3)	0.7432 (4)	0.048 (3)
C6	0.8152 (4)	0.1680 (3)	0.8379 (4)	0.053 (3)
N7	0.7361 (3)	0.1083 (2)	0.8260 (3)	0.044 (2)
C7	0.6894 (5)	0.0877 (4)	0.9179 (4)	0.068 (4)
C8	0.7715 (4)	0.0406 (3)	0.7698 (5)	0.056 (3)
C9	0.7015 (4)	0.0226 (3)	0.6856 (4)	0.051 (3)
C10	1/2	0.2820 (4)	0.8365 (5)	0.045 (4)
O10	0.5856 (2)	0.2550 (2)	0.8155 (3)	0.051 (2)
C11	1/2	0.3552 (6)	0.8939 (8)	0.076 (6)
CI1	1/2	0.46626 (10)	0.5763 (2)	0.0544 (10)
O11	1/2	0.5402 (3)	0.6208 (5)	0.072 (4)
O12	1/2	0.4097 (6)	0.6448 (11)	0.204 (14)
O13	0.4119 (7)	0.4555 (5)	0.5300 (9)	0.197 (9)
CI2	1/2	0.8869 (1)	−0.1040 (1)	0.055 (1)
O21	1/2	0.9230 (8)	−0.1888 (8)	0.158 (11)
O22†	1/2	0.9365 (4)	−0.0196 (5)	0.080 (4)
O23†	0.4196 (11)	0.8390 (9)	−0.0955 (8)	0.252 (13)
O22'‡	0.599 (3)	0.895 (2)	−0.151 (3)	0.047 (8)
O21'‡	1/2	0.809 (2)	−0.096 (3)	0.022 (7)

† Site occupancy = 0.9.   ‡ Site occupancy = 0.1.

Table 2. *Selected geometric parameters (Å, °)*

Cu—O1	2.737 (5)	Cu—N7	2.269 (4)
Cu—O2	1.963 (2)	Cu—O10	1.960 (4)
Cu—N1	2.037 (4)	Cu···Cu^i	3.2975 (8)
Cu—N4	2.092 (4)		
Cu—O1—Cu^i	74.07 (16)	Cu—O2—Cu^i	114.3 (2)

Symmetry code: (i) $1 - x, y, z$.

H atoms on N and methylene C atoms were placed in calculated positions with a C(N)—H distance of 0.95 Å. H atoms on methyl C atoms were placed on peaks in the difference map. The hydroxy H atom was placed on a likely peak in the difference map, but the water H atoms could not be located and were not included in the refinement; $U_{iso}(H)$ was fixed at 0.07 Å^2 and coordinates were refined in intermediate cycles but not in the final cycle of refinement. The perchlorate ion (Cl2) is disordered. The disorder was modelled by including two orientations of the tetrahedra having Cl2 and O22 in common. Atoms Cl2, O21, O22 and O23 were refined with anisotropic displacement parameters and fixed occupancies for O21 and O23 of 0.9; atoms O21' and O22' were refined with isotropic displacement parameters and fixed occupancies of 0.1. The displacement ellipsoid of

O23 is elongated and is an indication of the limitations of the modelling of the disorder. The reported coordinates are for a crystal with the opposite hand to that used in the experiment. *Xtal*3.4 software (Hall *et al.*, 1995) was used throughout the analysis (structure solution and refinement, molecular graphics and preparation of material for publication).

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *Xtal*3.4.

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[Ti₂(O-2,4,6-Me₃C₆H₂)₂(OiPr)₄(μ-OiPr)₂]

$[\text{Ti}_2(\text{O-2,4,6-Me}_3\text{C}_6\text{H}_2)_2(\text{O}^i\text{Pr})_4(\mu\text{-O}^i\text{Pr})_2]$

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Abstract

The title titanium(IV) alkoxide dimer, bis(μ-isopropoxido-O:O)bis[triisopropoxido(2,4,6-trimethylphenoxido)titanium(IV)], [Ti₂(C₃H₇O)₆(C₉H₁₁O)₂], has been prepared and characterized by X-ray crystallography.