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Metal Complexes with Mixed Ligands. 19. The Molecular and Crystal Structure of Di-μ-hydroxybis[di(2-methylimidazole)-copper(II)] Diperchlorate Dihydrate: $Cu_2(OH)_2(CH_3C_3H_3N_2)_4(ClO_4)_2.2H_2O$

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The crystal structure of $Cu_2(OH)_2(CH_3C_3H_3N_2)_4(ClO_4)_2.2H_2O$ has been determined from three-dimensional X-ray diffraction data, collected with a linear diffractometer, using Mo$K\alpha$-radiation. The crystals are monoclinic, space group $C2/m$ (No. 12) with $Z=2$ and cell dimensions $a=14.930(1)$ Å, $b=13.725(1)$ Å, $c=7.481(2)$ Å and $\beta=103.40(1)°$. Full-matrix least-squares refinements, based on 2649 independent reflexions, resulted in a final R value of 0.041.

The dimeric structure is built from isolated $Cu_2(OH)_2(CH_3C_3H_3N_2)_4(ClO_4)_2$ complexes and water molecules. The complexes are connected by hydrogen bonds in a three-dimensional framework. In the complex the two $Cu(CH_3C_3H_3N_2)_2$ units are connected by two double bridges, one is a diol bridge, Cu–OH–Cu, the other one is through the perchlorate group, Cu–O–Cl–O–Cu. The distorted octahedral (4+2) coordination around the copper atom is completed with two Cu–N bonds. The bond distances to copper are: Cu–O(H) = 1.959 Å, Cu–N = 1.977 Å, Cu–O(ClO_4) = 2.827 Å.

In aqueous solution the existence of hydroxo-bridged copper ions has been established in the system copper-imidazole perchlorate.[1] Attempts to crystallize these complexes failed and only two non-hydroxo crystalline phases could be obtained, namely the trinuclear complex $Cu_3(C_3H_3N_2)_2(C_3H_4N_2)_8(ClO_4)_4$ and the mono-nuclear complex $Cu(C_3H_4N_2)_4(ClO_4)_2$. The structures of these are previously reported.[2,3]

Reedijk *et al.*,[4] however, reported the existence of a crystalline phase with 2-methylimidazole as a ligand, where spectral data indicated the presence of hydroxo-bridged copper atoms. The structure of this phase is the aim of this work.

EXPERIMENTAL

Crystal preparation and analyses. The crystals were prepared according to Reedijk *et al.*[4] The copper content of the crystals was determined electrolytically. (Calc. wt % 17.54, found 17.41.) Thermogravimetric analysis was also performed and this confirmed the title formula.

Crystal data. $Cu_2(OH)_2(CH_3C_3H_3N_2)_4(ClO_4)_2.2H_2O$. Space group $C2/m$ (No. 12). $a=14.930(1)$ Å, $b=13.725(1)$ Å, $c=7.481(2)$ Å, $\beta=103.40(1)°$, $Z=2$, $D_m=1.56(1)$ g cm^{-3}, $D_x=1.55$ g cm^{-3}, μ(Mo$K\alpha$) = 17.2 cm^{-1}.

Rotation photographs around the c- and b-axes and corresponding Weissenberg photographs (zero, first and second levels) taken with Cu$K\alpha$-radiation, showed that the crystals are monoclinic. Systematic extinctions were found for hkl, $h+k=2n+1$, which is characteristic for the space groups $C2$, Cm and $C2/m$. The centrosymmetric space group $C2/m$ was assigned on the basis of the complete structure determination. The final unit cell parameters were determined from a powder photograph recorded with a Guinier-Hägg camera with Cu$K\alpha$-radiation ($\lambda=1.54051$ Å) and Si ($a=5.43059$ Å) as internal standard.

The density was determined by the flotation method using a bromoform-acetone solution.

Collection and reduction of intensity data. A crystal with dimensions 0.35 × 0.30 × 0.28 mm was mounted

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along the *a*-axis. Intensities for 3837 reflexions ($\sin\theta \leq 0.604$) were measured by omega-scan, using an automatic linear diffractometer (PATLRED). Mo$K\alpha$-radiation, monochromatized with a graphite crystal was used.

The half scan interval (ω) was 1.5° for $\theta \geq 20°$ and 2.2° for $\theta \leq 20°$. Reflexions for which the total number of counts (I_{tot}) from one scan did not exceed 2000, were scanned twice ($N = 2$). Background radiation was measured for 40 s (t) at each end of the scan interval (B_1, B_2). The scan speed used was 1° min^{-1} (v). The net intensity (I_{obs}) and the statistical error ($\sigma(I)$) for each reflexion were calculated using the expressions:

$$I_{obs} = I_{tot}/N - \frac{\omega(B_1 + B_2)}{(v/60)t}$$

$$\sigma(I) = \frac{I_{tot}}{N^2} + \left(\frac{\omega}{(v/60)t}\right)^2 (B_1 + B_2) + \left(\frac{I_{tot}}{N}\right)^2 p^2$$

p is the linear error of the diffractometer and was estimated to be 0.01 based on repeated measurements on different crystals. Reflexions with $I_{obs} < 2\sigma(I)$ were considered unobserved, which resulted in 2649 observed independent reflexions. When the refinements were completed the structure factors for all "unobserved reflexions" were calculated and found to be lower than or close to the threshold value. Corrections for Lorentz and polarization effects and absorption correction were made. The linear absorption coefficient is 17.2 cm^{-1}. The transmission factor varied between 0.635 and 0.697.

The computer programs used were those reported by Antti.[5]

Structure determination and refinement. The positions of the copper and chlorine atoms were found from a three dimensional Patterson synthesis. The other non-hydrogen atoms were located by standard Fourier methods. The refinement of the structure was performed by full-matrix least squares techniques assuming the centrosymmetric space group $C2/m$. The weighting function used was $w = 1/\sigma^2_{mod}$, where $\sigma^2_{mod} = (C_1\sigma(F_o))^2 + (C_2F_o)^2$ with $C_1 = 1.1$ and $C_2 = 0.03$ and the function minimized was $\sum w(|F_o| - |F_c|)^2$. With isotropic temperature factors the refinement, based on the nonhydrogen atoms, resulted in a conventional R-value of 0.110. ($R = \sum||F_o| - |F_c||/\sum|F_o|$). Further refinement using anisotropic temperature factors gave an R-value of 0.046. The probable positions of the hydrogen atoms were located from a difference Fourier synthesis. Final refinement, including positional coordinates and isotropic thermal parameters for the hydrogen atoms, resulted in an R-value of 0.041 and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.052$. All parameter shifts in the final iteration were less than 10 % of the estimated standard deviations. The atomic scattering factors used for Cu^{2+}, Cl, O, N, C and H were those given in International Tables for X-Ray Crystallography (1974).[6]

A final difference electron density map showed no abnormalities. Final fractional atomic coordinates and thermal parameters are listed in Tables 1 and 2.

The observed and calculated structure factors can be obtained from the author on request.

Table 1. Final fractional atomic coordinates and thermal parameters with their estimated standard deviations in parenthesis. All values multiplied by 10^4. Anisotropic temperature factors have been calculated according to the formula $\exp[-(h^2\beta_{11} + \ldots + 2kl\beta_{23})]$. For the labelling of the atoms, see Fig. 1.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	5000	3912(0)	0	25(0)	19(0)	129(1)	0	21(0)	0
Cl	6686(1)	5000	4003(1)	42(0)	36(0)	110(1)	0	13(1)	0
OH	4475(1)	5000	1110(3)	28(1)	23(1)	111(3)	0	20(1)	0
Aq	2621(1)	5000	680(3)	28(1)	36(1)	178(5)	0	23(2)	0
O1	6585(2)	4158(2)	2879(4)	99(2)	57(1)	306(6)	19(1)	3(3)	−54(2)
O2	7496(3)	5000	5407(7)	68(2)	137(4)	261(9)	0	−46(3)	0
O3	5908(3)	5000	4848(5)	75(1)	109(3)	239(8)	0	65(3)	0
N1	4223(1)	2930(1)	853(2)	31(1)	25(1)	141(3)	−03(1)	22(1)	−01(1)
N2	3363(1)	1659(1)	1013(3)	38(1)	35(1)	200(4)	−12(1)	25(1)	5(2)
C1	3803(1)	2160(1)	−0058(2)	29(1)	28(1)	163(4)	−04(1)	17(1)	−01(1)
C2	3493(2)	2123(2)	2674(4)	51(1)	51(1)	181(5)	−12(1)	45(2)	12(2)
C3	4025(2)	2903(2)	2571(3)	42(1)	38(1)	153(4)	−05(1)	33(2)	−03(2)
CM	3805(2)	1859(2)	−1957(4)	53(1)	49(1)	180(5)	14(1)	28(2)	26(2)

Table 2. Fractional atomic coordinates and isotropic thermal parameters for the hydrogen atoms. The fractional coordinates have been multiplied by 10^3. For the labelling of the atoms, see Fig. 2.

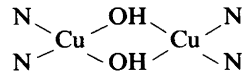
Atom	*x*	*y*	*z*	*B*
H1	306(3)	113(3)	58(5)	3.3(7)
H2	332(2)	190(2)	365(4)	1.9(5)
H3	422(2)	338(2)	347(4)	1.7(4)
H4	432(3)	141(3)	−186(6)	4.6(7)
H5	403(3)	230(3)	−252(6)	4.7(7)
H6	319(3)	161(3)	−252(5)	4.1(6)
H7	261(4)	500	164(7)	2.9(9)
H8	333(3)	500	71(7)	2.9(8)
H9	463(3)	500	208(6)	1.6(7)

DESCRIPTION AND DISCUSSION

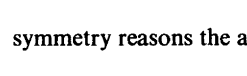
The structure consists of dimeric $Cu_2(OH)_2(CH_3C_3H_3N_2)_4(ClO_4)_2$-complexes of 2/*m* symmetry and water molecules. The copper atoms are positioned on the twofold axis and the hydroxo groups, the Cl-atoms and half of the perchlorate oxygens are located in the mirror plane. The two hydroxo groups as well as the two perchlorate groups, are bridging the $Cu(CH_3C_3H_3N_2)_2$-units (Fig. 1). The dimers are linked together by hydrogen bonds, mainly via the water molecules, giving a three-dimensional framework (Fig. 2).

The coordination round the copper atom. The coordination of the copper atoms is *trans* distorted octahedral (4 + 2). Two of the four shorter bonds are directed to the two bridging hydroxo groups (Cu − OH = 1.959(3) Å) and the other two towards the nitrogen atoms (Cu − N = 1.977(4) Å) from the methylimidazole ligands. The two longer bonds, to the axially positioned ligands of the octahedron, are to oxygen atoms from two bidentate perchlorate groups (Cu − O = 2.827(3) Å).

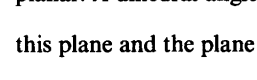
The two octahedra are edge-sharing and an



arrangement is formed. For symmetry reasons the atoms



are coplanar. A dihedral angle of 14.22° is found between this plane and the plane through



. Comparing the distances with similar hydroxo-bridged complexes,[7-15] the Cu − N distance is somewhat shorter in this structure than the average (2.02 Å, range 1.981 − 2.053 Å). The Cu − OH distance on the other hand is longer in this structure than the average (1.92 Å, range 1.895 − 1.948 Å). No significant differences for the distances Cu − N and Cu − OH, respectively, in four, five or six coordinated copper atoms could be noticed in the structures compared.[7-15] The shorter Cu − N distances in the title compound may be due to the fact that methylimidazole is a monodentate ligand, whereas the ligands in the other complexes are bidentate.

The interaction between the axially positioned oxygen atoms and the copper atom is weak, and can be described as semicoordinated (Hathaway and

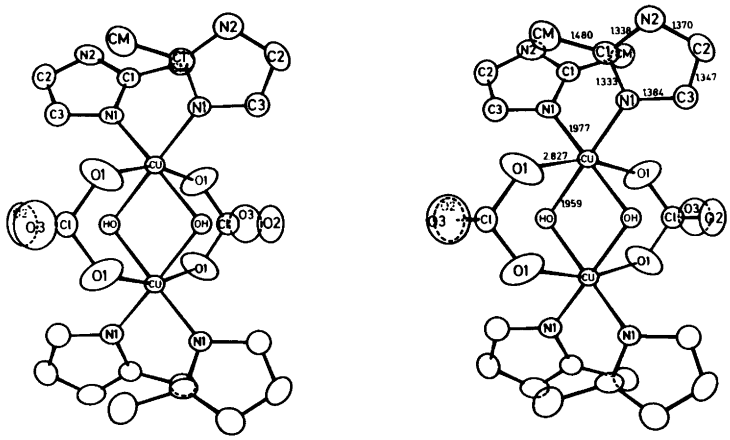


Fig. 1. A stereoscopic representation of the binuclear complex. All hydrogen atoms are excluded for clarity. Thermal ellipsoids are scaled to enclose 50 % probability.

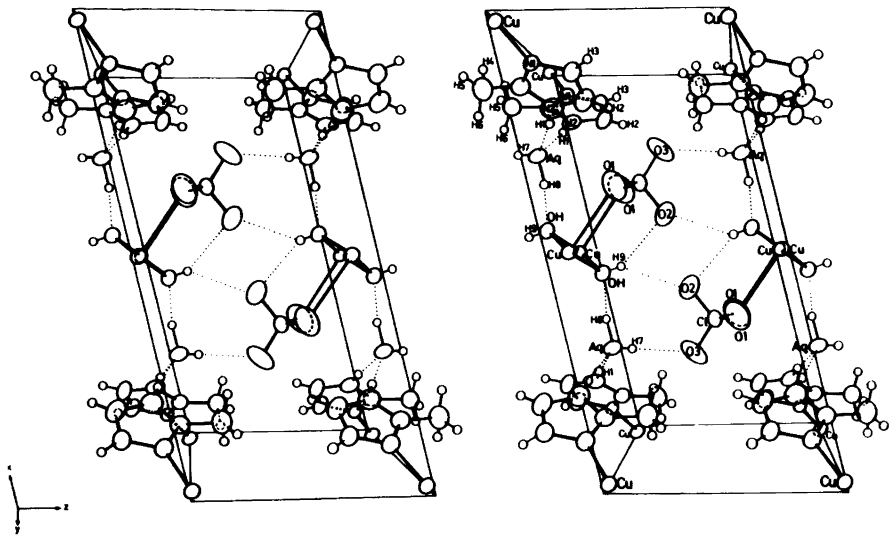


Fig. 2. A stereoscopic representation of the unit cell, with parts of its contents, illustrating the packing arrangement and the hydrogen bonds. Thermal ellipsoids are scaled to enclose 50 % probability.

Billing).[16] A similar situation is found in α-[Cu(CMAEP)OH]$_2$(ClO$_4$)$_2$[9], where there is a bidentate intramolecular perchlorate group with distances Cu–O = 2.782 and 2.716 Å. The variation of the axial Cu–O distances in five and six coordinated copper(II) complexes[7–12] is large, range 2.21 – 2.83 Å, due partly to the steric hindrance of the ligands in the equatorial plane and partly to the ligand field and shape of the axial ligands.[16]

The methylimidazole ligand. Distances and angles within the methyl imidazole are in agreement with previously reported values.[17] The bond distance C2 – C3 = 1.347 Å is, however, significantly shorter than the corresponding distance in imidazole (mean 1.39 Å, range 1.36 – 1.49 Å)[2].

A least squares plane, defined by the ring atoms,

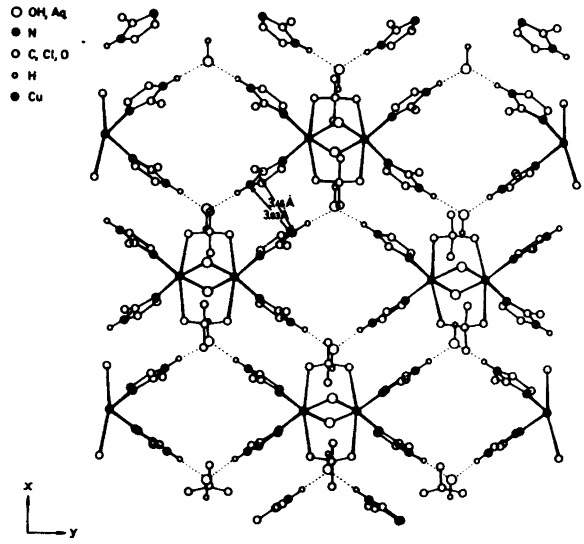


Fig. 3. A representation of the methylimidazole packing.

was calculated and all the ligand atoms except the hydrogens of the methyl group are situated in this plane (maximum deviation from the plane is 0.004(3) Å). The distance from the copper atom to the plane is 0.042 Å. A dihedral angle of 41.37° is found between the ligand plane and the plane defined by the three atoms Cu$\begin{smallmatrix}\diagup\mathrm{OH}\\ \diagdown\mathrm{OH}\end{smallmatrix}$. The packing of the methylimidazole groups from different complexes in the crystal can be seen in Fig. 3. The "imidazole planes" are in parallel orientation with an interplane distance of 3.46 Å, and N2–N2' = 3.83 Å, which means that there are van der Waals interactions between the methylimidazoles.

The perchlorate group. The geometry of the perchlorate group is that of a slightly distorted tetrahedron, with C_2 symmetry. Distances and angles are given in Table 3. The perchlorate oxygens take part in three kinds of interactions, as shown in Fig. 2. Two oxygens, O1 and O1', symmetry related by the mirror plane, are interacting with the two copper atoms in the dimer, at the distance 2.827 Å. O2 is an acceptor of two bifurcated hydrogen bonds from bridging hydroxo groups, intramolecular (O···O = 3.102 Å) as well as intermolecular (O···O = 3.205 Å). O3 is acceptor of a hydrogen bond from the water molecule (O···O = 2.972 Å). The perchlorate group acting as a bridge seems to be very uncommon, but has been reported before.[9] The O2 atom (Table 3) has a significantly longer distance to the chlorine atom than the other oxygens, which cannot be explained by the above mentioned interactions, but rather from the crystal packing forces.

Table 3. Interatomic distances (Å) and angles (degrees) with standard deviations in parenthesis.

1. Around the copper atom

Cu–OH	1.959(1)	N1–Cu–N1$_a$	94.1(1)
Cu–N1	1.977(2)	N1–Cu–OH	93.5(1)
Cu–O1	2.827(3)	OH–Cu–OH$_a$	80.6(1)
Cu···Cu$_b$	2.988(1)	O1–Cu–OH	86.1(1)
		O1–Cu–OH$_a$	83.4(1)
		O1–Cu–N1	106.6(1)
		O1–Cu–N1$_a$	83.0(1)

2. Within the ligand 2-methylimidazole

N1–C1	1.333(3)	CM–H5	0.85(3)
C1–N2	1.338(3)	CM–H6	0.97(3)
N2–C2	1.370(4)	N1–C1–N2	109.8(2)
C2–C3	1.347(4)	C1–N2–C2	108.6(2)
C3–N1	1.384(3)	N2–C2–C3	106.2(2)
C1–CM	1.480(4)	C2–C3–N1	109.3(2)
N2–H1	0.87(4)	C3–N1–C1	106.1(2)
C2–H2	0.88(3)	N1–C1–CM	127.4(2)
C3–H3	0.93(3)	N2–C1–CM	122.7(2)
CM–H4	0.97(3)		

3. Within the perchlorate group

Cl–O1	1.416(3)	O1–Cl–O1$_b$	109.3(2)
Cl–O2	1.445(4)	O1–Cl–O3	113.5(1)
Cl–O3	1.407(4)	O1–Cl–O2	105.9(2)
		O3–Cl–O2	108.2(2)

Symmetry operations implied by the subscripts

a $\bar{x},y,\bar{z}$
b $x,\bar{y},z$

The water molecule. Fig. 2 shows that the water molecule links the binuclear complexes through hydrogen bonds. As a hydrogen-bond donor it is connected to the bridging hydroxo group of one complex unit (Aq–O = 2.71 Å; Table 4) and to one perchlorate oxygen of another complex unit (Aq–O = 2.97 Å). As an acceptor it is connected to two pyrrole hydrogens of a third and fourth complex unit (Aq–N2 = 2.84 Å). A tetrahedral arrangement of hydrogen atoms around the water oxygen is thus found. The angle H–Aq–H within the water molecule is 104(4)°.

Magnetic properties of hydroxo-bridged copper(II) complexes. Hydroxobridged binuclear copper complexes have recently received much attention because of their magnetic properties. A linear relationship has been established between the structural Cu–OH–Cu bridge angle (ϕ) and the magnetic singlet-triplet splitting parameter 2J.[10,18–20] Fig. 4

Table 4. Distances (Å) and angles (degrees) for the hydrogen bond contacts in the structure. Standard deviations are given in parenthesis.

Atoms	d_{O-H}	$d_{O\cdots O}$	$d_{O\cdots N}$	Angle
OH–H9$\begin{smallmatrix}\cdots\mathrm{O2}\\ \cdots\mathrm{O2_b}\end{smallmatrix}$	0.71(5)	3.102(4) 3.205(4)		143(4) 150(4)
Aq–H7···O3	0.72(6)	2.972(5)		178(5)
Aq–H8···OH	1.05(5)	2.712(3)		171(4)
N2–H1···Aq			2.843(3)	173(4)

b: Symmetry operation; $x,\bar{y},z$

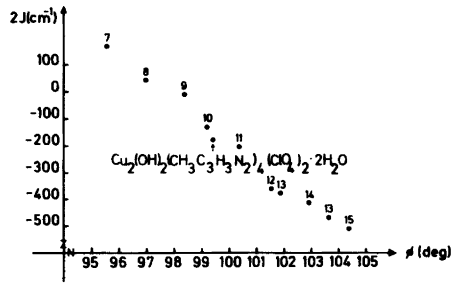


Fig. 4. Plot of the Cu – OH – Cu bridging angle ϕ *vs.* the singlet-triplet splitting parameter, $2J$, for hydroxo-bridged Cu(II) complexes. The figures (7 – 15) in the plot refer to the structures given in Refs. 7 – 15.

depicts this linearity, using values given for the structures in Refs. 7 – 15, which all are of the type $[CuL(OH)]_2^{2+}$. The title compound, with the value of $2J = -175 \pm 1$ [4] and $\phi = 99.4(1)°$, fits well into the linearity in spite of being of the type $[CuL_2(OH)]_2^{2+}$.

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