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**SYNTHESIS, X-RAY CRYSTAL STRUCTURE AND IR STUDY OF
NEW TRINUCLEAR, BASE CARBOXYLATE COMPLEX OF
[Cu₃O(OAc)₆(H₂O)₃]Cl.CH₃OH.6H₂O**

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ABSTRACT

The synthesis of [Cu₃O(OAc)₆(H₂O)₃]Cl.CH₃OH.6H₂O is described. The X-ray crystallographic study of the complex revealed an isosceles triangle of copper atoms with a triply bridging oxo atom nearly in the plane of the triangle. The coordination sphere around each metal center is close to distorted octahedral and the central {Cu₃(μ₃-O)} core is planar. Every two copper atoms were connected to each other, by two bridge of alkyl acetate. The water molecule as a monodentate ligand is connected to every copper. Counter ion of this complex is a group that contain one atom of chlorine, one molecule of methanol and six molecule of water. This compound crystallizes in the orthorhombic system, space group *P2₁2₁2*, with four molecules per unit cell. The unit cell dimension were $a = 1359.3(1)\text{Å}$, $b = 2317.3(1)\text{Å}$, $c = 908.4(1)\text{Å}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$ and $V = 2861.4(4)10^6(\text{pm}^3)$. The final *R* value is 0.0667 for 5321 measured reflections. The identification, IR investigation and elemental analysis data are consistent with a unit cell composed of [Cu₃O(AcO)₆(H₂O)₃]Cl.CH₃OH.6H₂O

Keyword: Copper, X-ray crystallography, synthesis, infrared, band assignment

INTRODUCTION

Oxo-bridged polyiron centers are widespread in mineralogy and biological worlds. Trinuclear, basic carboxylate, containing $\{M_3(\mu_3-O)\}$ core has been known for some time and studied extensively^[1-5]. General formula for these compounds is $[M_3O(OAc)_6L_3]A.nS$, where M is metal atom, L is terminal monodentate ligand, A is the counter ion and S is solvent molecule of crystallization. Three metal atoms are bridged by oxygen atom located at the center of the three angles of metals and also by the six carboxylate ligands in the circumference. The first compound of this class that has been characterized in detail, $[Fe_3O(O_2CCH_3)_6(H_2O)_3].2H_2O$, was synthesized in 1944^[6]. Mössbauer spectroscopy and magnetochemistry of these compounds have been examined extensively^[7-19]. Variable-temperature IR study has established that most compounds under investigation are, at least partially, valence-localized complexes^[20-22]. The electron transfer of this group of complexes has been researched^[23]. Although bridged Cu complexes such as $[Cu_2(\mu-DMP)_4(DMSO)_2]n$ ^[24] are prepared, but to the best of our knowledge there are a few papers on the complexation of this bridge acetates with transition metals such as Fe, Cr, Mn, Ru and Ir, but there are not any paper about copper. The title complex crystallizes in the orthorhombic system, space group $P2_12_12$, with four molecules per unit cell. The unit cell dimension are $a = 1359.3(1)\text{Å}$, $b = 2317.3(1)\text{Å}$, $c = 908.4(1)\text{Å}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$ and $V = 2861.4(4)10^6(\text{pm}^3)$. The final R value is 0.0667 for 5321 measured reflections.

Single-crystal X-ray structures have been reported for several trinuclear, base carboxylate complexes. In this report, the cluster compound of $[Cu_3O(OAc)_6(H_2O)_3]Cl.CH_3OH.6H_2O$ were synthesized, identified and investigated by X-ray crystallography determination, IR spectroscopy and elemental analysis.

Experimental Section

Materials: Chemical reagents were obtained from commercial suppliers and used after further purification. Copper chloride was recrystallized and solvents were used as received or were distilled prior to use.

Instrumentation: Infrared spectra recorded using KBr disks on a Perkin-Elmer 8343 Spectrophotometer. Microanalysis of the compounds was performed on GNBH-West Ger. elemental analyzer.

X-ray structure determination

The X-ray data were collected on a diffractometer (Mo K_{α} , 0.71073 Å radiation, graphite-monochromator) at 193 K. Data were collected to a maximum 2θ value of 52.41° and the structure was solved by automatic direct methods using SHELXS-97. The structure was refined by full-matrix least-square analysis on F^2 with SHELXL. The absorption correction was applied according to the multi-scan technique by SADABS. The non-hydrogen atoms were refined anisotropically and all the hydrogen atoms were located from subsequent difference Fourier maps and refined with riding model to a final R indices (all data) of $R_1(0.0667)$, and $WR_2(0.1890)$. Details of crystal parameters, data collection, and structure refinement are summarized in Table 1. The final atomic coordinates of non-hydrogen atoms and selected bond lengths and angles are listed in Table 2. ORTEP respective of the complex and stereoview of the unit-cell packing of this compound are presented in Figures (2) and (3), respectively.

Synthesis

Preparation of

$[Cu_3O(OAc)_6(H_2O)_3]Cl.CH_3OH.6H_2O$:

$CuCl_2.4H_2O$ (9.5g, 0.05 mol) were dissolved in water (50 ml) and NaOH (50 ml, 2 mol) was added by stirring. Then the precipitate was filtered, dissolved in 7 ml (0.12 mol) glacial acetic acid and $KMnO_4$ (2 ml, 0.1 mol)

was added to primary solution. The resulted solution was heated for 8 hours in 45-50 °C under reflux and stirring. The solution was then placed at room temperature, after two weeks blue crystals were formed. Then crystals were dried and dissolved in HCl (30ml, 0.5mol). After two weeks suitable dark blue crystals were formed. Crystals were washed with a mixture of iso-octane and acetone and then dried in a vacuum desiccator for one week. Anal. Calcd: Cu, 29.48; C, 22.1; H, 3.68; Cl, 5.45. Found: Cu, 29.23; C, 22.35; H, 3.51; Cl, 5.41. The results confirm that $[\text{Cu}_3\text{O}(\text{OAc})_6(\text{H}_2\text{O})_3]\text{Cl}\cdot\text{CH}_3\text{OH}\cdot 6\text{H}_2\text{O}$ was obtained.

Result and discussion

The X-ray crystallography of the title complex were consisted of the well-known arrangement of three Cu atoms linked by a central μ_3 -O atom and further bridged by two pivalate groups between each pair of copper atom. The octahedral coordination of each Cu atom is completed by a water ligand that is nearly coplanar with the central Cu_3O core. All three copper sites have the same crystallographic data and the oxidation state for Cu is (3+)(figure1). X-ray crystallography of $[\text{Cu}_3\text{O}(\text{OAc})_6(\text{H}_2\text{O})_3]\text{Cl}\cdot\text{CH}_3\text{OH}\cdot 6\text{H}_2\text{O}$ was shown that the hydrogen bonds between water molecule coordinated in complex with non-bonded molecules of water, methanol and chloride ions. Selected bond distances and angles are listed in table 2.

The central O1 atom is placed on the plane defined by the three copper atoms within the estimated standard deviation (O1 indicates a central oxygen atom in this study). The central Cu_3O group forms nearly an isosceles triangle array (in which three Cu-O-Cu angles and Cu-O distance are nearly equivalent). e.g. Cu2-O1, Cu1-O1 and Cu3-O1 distance are 1.897(4), 1.896(4) and 1.896(4)pm respectively. The averaged distance between the Cu1 atom and six coordinated oxygen atoms, Cu1-Oav, Cu2-Oav and Cu3-Oav are 1.973, 1.969 and 1.974 respectively. The O1-Cu-Ocarbox angles (averaged angle of the four bonds constructed by O1, Cu and an oxygen atom from carboxylate ligands) also depend on the oxidation states. The O1-Cu1-Ocarbox

angle is smaller than those of the other two copper atom sites. From the distances of the Cu-O1 bond and the angles of O1-Cu-Ocarbox, it appears that copper species in this complex have the same oxidation state.

This compound was crystallized in blue layers. In figure (2) cause to locate Oxygen and Carbon up of together, arbitrary radius was selected. Water and methanol molecules have surrounded the molecule of complex in the crown shape and connected to complex with Hydrogen-bridging. In addition, rest of lattice connections occurs by hydrogen-bridging. So planar layer of (010) was formed that was connected with hydrogen-bridging. In this route Chloride ions also were participated. Therefore, layers of complex molecules, solvent molecules and chloride ions exchange along (010).

In order to confirm this synthesized complex, the infrared spectra of this compound were analyzed. Vibrational spectra of three centered oxo-carboxylates are discussed generally based on the vibrational behavior of particular unit in molecule. Clearly, all the three centered oxo-carboxylates show similar structure, but differ in the kind of non acetate ligands. It was realized that acetate and L ligand vibrations were approximately independent of the central skeleton ^[25]. This is, if monodentate ligands are similar or not similar, M_3O and MO_4 vibrations will not change ^[26].

The M_3O unit with a lone pair of electrons at oxygen, stands at the center of the triangle with C_{3v} local symmetry. Although this situation is probable for compounds with full d-orbitals, the formation of $d\pi$ - $p\pi$ bonds for complexes of the type $[\text{Cu}_3\text{O}(\text{AcO})_6(\text{L})_3]^+$ results in a planar Cu_3O with D_{3h} symmetry. Thus, it is expected that M_3O vibrations shift to higher energies for these compounds. It should be noted that contribution of π -bonds in the central M_3O depends on the hardness of the outer ligands bonded to the triangle. polarizability of M-L bonds and shifts of the spectral bands are dependent to the hardness of the metal center and contribution of $\pi(\text{MO})$ bonds. Thus we think that Cu -O vibrations in $500\text{-}700\text{ cm}^{-1}$ are affected by changes in D_{3h} symmetry of the central triangle, M_3O , and C_{2v}

symmetry of $\text{Cu O}_4\text{O}'\text{O}''$ units around the triangle. Correlations of vibrational modes of these two units are summarized in Tables 5.

Planer unit of M_3O with D_{3h} symmetry has four main vibration modes of A_1' , A_2'' , and $2\text{E}'$. According to selection rules, A_1' is active in Raman spectroscopy, A_2'' is active in infrared spectroscopy and $2\text{E}'$ is active in both infrared and Raman spectroscopies. About Cu_3O , in many trinuclear complexes, an absorption band appears in the region of $\sim 500\text{ cm}^{-1}$ to $\sim 700\text{ cm}^{-1}$ that is related to $\nu_{\text{asy}}(\text{Cu}_3\text{O})$. This band is related to E' vibration mode and vibration mode of A_2'' is related to $\delta_{\text{sy}}(\text{Cu}_3\text{O})$ appearing in area of 290 cm^{-1} , also there is an absorption band for E' related to $\delta_{\text{asy}}(\text{Cu}_3\text{O})$ that appears in the area of 100 cm^{-1} . Existence of absorption bands (δ_{sy} , δ_{asy} and ν_{asy}) of central unit (M_3O) in infrared spectrum of prepared complexes is a reason for confirmation of the trinuclear structure of these complexes. For IR spectra analyzes of this complex, we divide it to three part of M-OH_2 , M_3O (in center of the molecule body) and MO_4 (from bridging acetate bonds). These parts, with regard to angle and bond length are different together. According to the general structure of molecule in figure (1), CuO_4 side units and Cu_3O triangle are perpendicular to each other. We believe that final vibration of the general structure of this compound is the result of combination of vibration of $\text{MO}_4\text{O}'\text{O}''$ unit with C_{2v} local symmetry with vibration of central Cu_3O skeleton with D_{3h} local symmetry. Considering figure (1) the atoms O3, O5, O10 and O13 are homoplanar oxygens of four neighboring acetates (one oxygen atom from each acetate), O' oxygen of the central triangle, and O'' oxygen of water molecules. Thus Cu-O' and Cu-O'' bonds are distinct and the general skeleton of this ion is similar to hexagon. Bond length for central square is consist of; Cu1- O5: $1.961(4)\text{Å}$, Cu1- O3: $1.973(4)\text{Å}$, Cu1- O10: $1.987(4)\text{Å}$, Cu1- O13: $1.983(4)\text{Å}$ and angles for central square is consist of; O3-Cu1-O5: $93.7(2)(\text{deg})$, O5-Cu1-O10: $85.9(2)(\text{deg})$, O10-Cu1-O13: $89.3(2)(\text{deg})$, O13-Cu1-O3: $89.8(2)(\text{deg})$.

According to the above discussions, $\text{CuO}'\text{O}''\text{O}_4$ unit is more likely to be C_{2v} than D_{4h} symmetry. Spectral information of Cu_3O complex is shown in table 4. Correlation between vibrational modes of $\text{MO}_4\text{O}'\text{O}''$ (C_{2v}) and M_3O (D_{3h}) has been shown in table 5.

Each metal atom is surrounded by four acetate ions (Figure 2). Metal atom coordinated by four oxygen atoms create planar unit of MO_4 with C_{2v} symmetry. Two bands appear for CuO_4 in 410 cm^{-1} and 439 cm^{-1} along with a wedge in 360 cm^{-1} . Monodentate acetates produce three bending CO_2 in $270\text{-}290\text{ cm}^{-1}$ and one out of plane $\pi(\text{CO}_2)$ about 540 cm^{-1} . These bands are absent in bridged complexes. While a decrease in number of these bands are observed for bidentate complexes. Acetate group that bridged with two oxygen atoms has C_{2v} symmetry. $\nu_{\text{sy}}(\text{CO}_2)$ and $\nu_{\text{asy}}(\text{CO}_2)$ appear in position of 1460 cm^{-1} and 1610 cm^{-1} respectively which indicates the acetate is bridged between the two metal atoms [27-28]. Value of $\Delta\nu \sim 150\text{ cm}^{-1}$ and the related bands in prepared complexes confirm that acetate ions have bridged forms [27, 29]. Symmetric and asymmetric vibrations of bridged acetate appear in 1451 cm^{-1} and 1611 cm^{-1} . Vibration band of $\pi\text{ CO}_2$ appears in 622 cm^{-1} and $\delta\text{ CO}_2$ observed in 662 cm^{-1} . A distinct band at about $2500\text{-}2700\text{ cm}^{-1}$ due to $\nu(\text{OH})$ vibration is recognized for monodentate complexes.

The IR data are relevant to X-ray crystallography data and confirm that this product is a trinuclear, base carboxylate complex. Spectral data has been presented in table 4.

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Table 1. Crystallographic data of $[\text{Cu}_3\text{O}(\text{OAc})_6(\text{H}_2\text{O})_3]\text{Cl}\cdot\text{CH}_3\text{OH}\cdot 6\text{H}_2\text{O}$

instrument	IPDS II (Stoe)
radiation	Mo-K α
formula	$\text{C}_{13}\text{H}_{40}\text{ClCu}_3\text{O}_{23}$
formular Weight(g/mol)	793.53
crystal size	0.42x0.32x0.07
<i>a</i> (pm)	1359.3(1)
<i>b</i> (pm)	2317.3(1)
<i>c</i> (pm)	908.4(1)
α (°)	90
β (°)	90
γ (°)	90
unit cell volume (pm ³)	$2861.4(4)\cdot 10^6$
<i>Z</i>	4
<i>d</i> _{calc}	1.835
crystal system	orthorhombic
space group (No.)	$P2_12_12$
absorption correction	numerical
μ (cm ⁻¹)	24.0
temperature (K)	193
$2\theta_{\text{max}}$ (°)	52.41
hkl values	$-16 \leq h \leq 16, -28 \leq k \leq 26, -11 \leq l \leq 11$
measured reflection	36468
unique reflection	5744
<i>R</i> _{int}	0.1527
Reflection with $F_o > 4\sigma(F_o)$	5321
Parameter	379
Structure solution	direct methods (SIR-92 [])
Refinement against <i>F</i> ₂	SHELAL-97 []
H atoms	Fixed positions With common displacement parameter
Flack-Parameter	0.21(2) (refinement as racemic twin)
<i>R</i> ₁	0.0667
w <i>R</i> ₂ (all data)	0.1890
Max. residual electron	0.95
density (10 ⁻⁶ e/pm ³)	

$$\text{a) } w = 1/[\sigma^2(F_o^2) + (0.1527 \cdot P)^2]; P = [\max(F_o^2, 0) + 2 \cdot F_c^2]/3$$

Table2. Selected Angles (deg)

O1-Cu1-O14	179.0	O1-Cu2-O15	176.2	O1-Cu3-O16	177.9
O3-Cu1-O10	173.3	O2-Cu2-O7	171.1	O8-Cu3-O11	166.6
O5-Cu1-O13	168.1	O4-Cu2-O9	169.0	O6-Cu3-O12	172.1
O3-Cu1-O5	93.7	O2-Cu2-O4	90.5	O6-Cu3-O8	91.6
O3-Cu1-O13	89.8	O2-Cu2-O9	88.1	O6-Cu3-O11	86.2

Table3. Selected bond distances (Å) and angles(deg) for [Cu₃O(AcO)₆(H₂O)₃]Cl

Distances (Å)					
Cu1-O1	1.896	Cu2-O1	1.897	Cu3-O1	1.895
Cu1-O14	2.035	Cu2-O15	2.014	Cu3-O16	2.043
Cu1-O _{carbox} ^a	1.976	Cu2-O _{carbox} ^a	1.977	Cu3-O _{carbox} ^a	1.976
Cu1-O _{av} ^b	1.973	Cu2-O _{av} ^b	1.969	Cu3-O _{av} ^b	1.974
Angles (deg)					
Cu1-O1-Cu2	119.5	O1-Cu1-O _{carbox} ^c		94.45	
Cu1-O1-Cu3	120.2	O1-Cu2-O _{carbox} ^c		94.92	
Cu2-O1-Cu3	120.3	O1-Cu3-O _{carbox} ^c		95.22	

^aAveraged distances between copper and four oxygen atoms of carboxylate ligands.

^bAveraged distances between copper and coordinated six oxygen atoms. ^cAveraged of four angles constructed by O1, Cu, and four oxygen atoms of carboxylate ligands. This is a reason for deformation from regular hexagonal to orthorhombic system.

Table 4. Spectral vibrations of $[\text{CuO}_3(\text{OAc})_6(\text{H}_2\text{O})_3]\text{Cl}.\text{CH}_3\text{OH}.6\text{H}_2\text{O}$

Vibrational representation	Vibrating spices	$[\text{CuO}_3(\text{OAc})_6(\text{H}_2\text{O})_3]\text{Cl}.\text{CH}_3\text{OH}.6\text{H}_2\text{O}$
$\nu\text{-CO}_2$	sym. str	1460
$\nu\text{-CO}_2$	asym. str	1613
$\nu\text{-OH}$	bending	2700-2900
$\pi\text{-CO}_2$	out of plane	626
$\delta\text{-CO}_2$	sym. def	679
$\nu\text{-CO}$	sym. str	1628
$\nu\text{-MO}$	sym. str	542

Table 5. Correlation between $\text{MO}_4\text{O}'\text{O}''$ (C_{2v}) and M_3O (D_{3h}) vibrational modes

D_{3h}	$\nu_s(\text{A}_1')$ (R)	$\Pi(\text{A}_2'')$ (I.R)	$\nu_d(\text{E}')$ (I.R)	$\delta_d(\text{E}')$ (I.R)
C_{2v}	$\nu(\text{A}_1)$ (I.R)	$\Pi(\text{B}_1)$ (I.R)	$\nu_s(\text{A}_1) \nu_a(\text{B}_2)$ (I.R) (I.R)	$\delta_s(\text{A}_1) \delta_a(\text{B}_2)$ (I.R) (I.R)

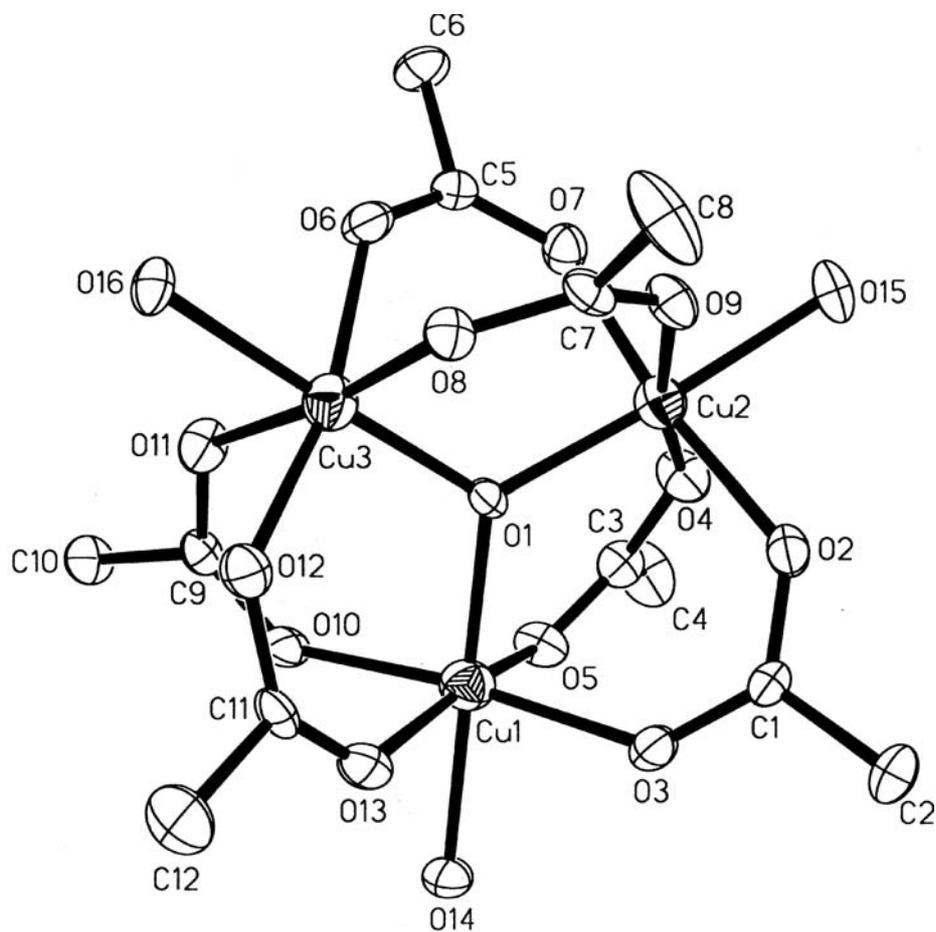


Figure 1.Ortep plot of molecular structure of $[\text{Cu}_3(\text{OAc})_6(\text{H}_2\text{O})_3]^-$ -ion.

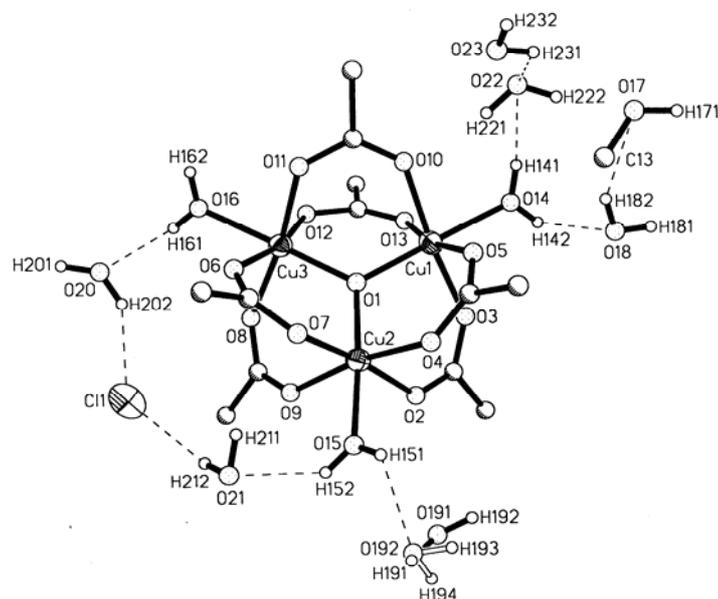


Figure 2. The molecular structure of the μ_3 -oxo-bridged trinuclear complex and formation of hydrogen bonds between water molecules coordinated in complex with molecules of water and methanol.

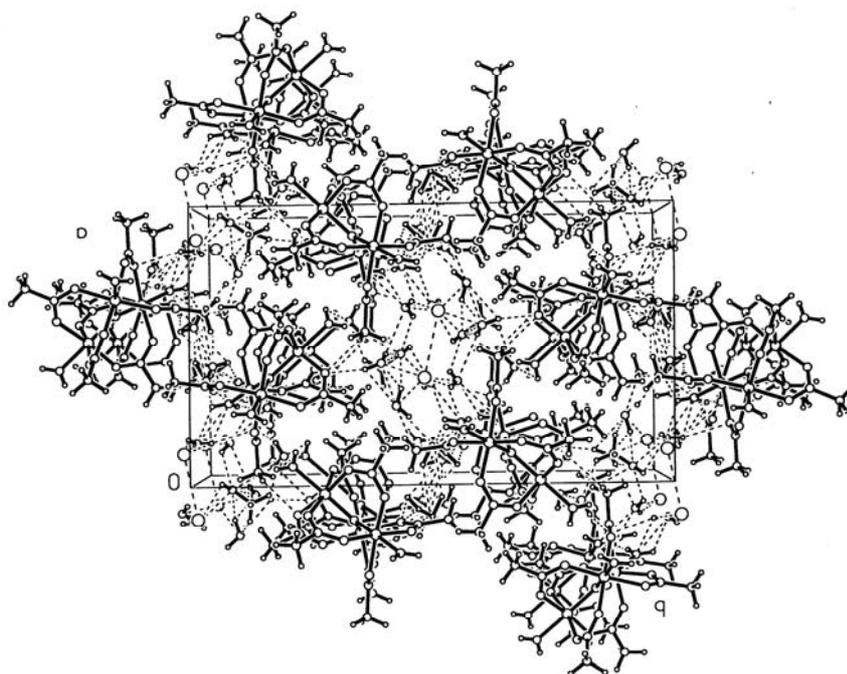


Figure 3. Stereoscopic view of the packing arrangement in $[\text{Cu}_3\text{O}(\text{AcO})_6(\text{H}_2\text{O})_3]\text{Cl}\cdot\text{CH}_3\text{OH}\cdot 6\text{H}_2\text{O}$

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