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The Crystal Structure of Bis [aqua-μ-(2-chloropropionato-O,O')-di(2-chloropropionato)-μ_3-(2-diethylaminoethanolato-N,μ_3-O)-μ-(2-diethylaminoethanolato-N,μ-O)-μ_3-hydroxo-tricopper(II)]

KIMMO SMOLANDER

Department of Chemistry, University of Joensuu, PL 111, SF-80101 Joensuu 10, Finland

$[Cu_3(C_6H_{14}NO)_2(ClC_3H_4O_2)_3(OH)(H_2O)]_2$ is triclinic, space group $P\bar{1}$, with $a=10.712(7)$, $b=12.914(4)$, $c=13.295(7)$ Å, $\alpha=73.74(4)$, $\beta=67.57(4)$ $\gamma=85.35(4)°$ and $Z=1$. The structure was solved by direct and Fourier methods and refined to $R=0.075$ for 2834 reflections.

The crystal structure is composed of centrosymmetric hexanuclear complexes where the copper(II) ions are linked by triply bridging ethanolato oxygen atoms and OH^- ions, and by carboxylato and ethanolato oxygen bridges. The three independent copper(II) ions have a square-pyramidal coordination. Carboxylato, aqua and ethanolato oxygens are in apical positions at distances 2.349(9), 2.469(11) and 2.301(8) Å from Cu1, Cu2 and Cu3, respectively. In the basal planes the distances vary between 1.920 and 2.013 Å for Cu–O and between 2.054 and 2.062 Å for Cu–N.

Two of the three independent 2-chloropropionato groups are unidentate. The third carboxylato group bridges a basal coordination site of Cu2 with the apical site of Cu1 in an asymmetric *syn-syn* configuration.

Many carboxylato complexes of copper(II) with N,N-dialkylaminoethanol ($R_2NCH_2CH_2OH = R_2LOH$) as the second ligand have been reported.[1,2] The structures of $[Cu(Bu_2LO)(acetato)]_2$[3] and $[Cu(Et_2LO)(benzoato)]_2$[4] complexes are dimeric. The $[Cu_3(Bu_2LO)_2(benzoato)_4(ethanol)_2]$[5] forms a linear trinuclear structure. Haloacetato complexes[6,7] of the general formula $[Cu(R_2LO)-(R'COO)]_4$ have tetrameric cubane-type structures. The $[Cu_3(Et_2LO)_2(acetato)_3(OH)]_2 \cdot H_2O$[8] complex has a centrosymmetric, hexanuclear structure with a triply bridging hydroxo ion. A μ_3-bridging OH^- group is not very common. A Cu_3OH group in copper(II) complexes is found in $[Cu_3(3\text{-(phenylimino)-butanone 2-oximato})_3(OH)(ClO_4)] \cdot ClO_4$,[9] $[Cu_2(quinoline)_2(F_3CCOO)_3(OH)]_2$,[10] $[Cu_3(pyridine\text{-}2\text{-}carbaldehyde\ oximato)_3(OH)(SO_4)] \cdot 16.3H_2O$[11] and in $[Cu_3(2\text{-propylamino-2-methyl-3-butane oximato})_3(OH_3)(H_2O)_3] \cdot (ClO_4)_{3/2}(H_2O)_4$.[12] To obtain further information on aminoalcohol copper(II) complexes, we have prepared bis[aqua-μ-(2-chloropropionato-O,O')-di(2-chloropropionato)-μ_3-(2-diethylaminoethanolato-N,μ_3-O)-μ-(2-diethylaminoethanolato-N,μ-O)-μ_3-hydroxo-tricopper(II)] which is a new compound in the Et_2LOH series.

EXPERIMENTAL

Copper(II) 2-chloropropionate was synthesized from basic copper(II) carbonate (Merck) and 2-chloropropionic acid (Merck) by the method of Bateman and Conrad.[13] 1.5 g of the starting material was dissolved in 60 ml methanol and the solution was heated. To this boiling solution 1.35 ml of 2-diethylaminoethanol (Fluka AG) in 20 ml methanol was added with stirring. The solution was filtered and propanol was added so that the final methanol–propanol ratio was 3:1. After some weeks at about 5 °C dark blue crystals had formed. A single crystal, $0.81 \times 0.80 \times 0.78$ mm was used for the measurements of crystal and intensity data.

The unit cell parameters and the orientation matrix were determined by a least-square refinement based on 19 centered reflections measured at 24–25 °C on a Syntex $P2_1$ diffractometer. Intensity data were collected ($5 < 2\theta < 45°$) in the ω-scan mode, using graphite-monochromatized Mo$K\alpha$

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radiation. The scan range was $\pm 0.5°$ and the scan speed varied from 3.0 to 29.3° min^{-1}, depending on the number of counts accumulated in a preliminary scan. Background measurements were taken at both ends of the scan with a displacement of 1.0° from the Mo$K\alpha$-peak. Each background was measured for half the scan time. Two selected reflections were monitored as standard after every 100 measurements. Their intensities showed no significant change with time. The intensities were corrected for Lorentz and polarization effects and for absorption from empirical ψ-scan data from six reflections. Of the 3852 reflections collected, 2834 had $|F_o| > 5\sigma(F_o)$ and were used in subsequent calculations.

CRYSTAL DATA

$[Cu_3(C_6H_{14}NO)_2(ClC_3H_4O_2)_3(OH)(H_2O)]_2$,
$FW = 1561.25$;
Crystal system: Triclinic;
Space group: $P\bar{1}$ (No. 2);
$a = 10.712(7)$, $b = 12.914(4)$, $c = 13.295(7)$ Å;
$\alpha = 73.74(4)$, $\beta = 67.57(4)$, $\gamma = 85.35(4)°$;
$V = 1631.2$ Å^3, $Z = 1$, $F(000) = 802$;
μ(Mo$K\alpha$) = 23.1 cm^{-1}, λ(Mo$K\alpha$) = 0.71069 Å;
$D_m = 1.58$ g cm^{-3} (by flotation);
$D_x = 1.59$ g cm^{-3}.

STRUCTURE DETERMINATION

Direct methods (MULTAN 78)[14] gave the positional parameters of the three copper atoms. The remaining non-hydrogen atoms of the structure were found from successive Fourier syntheses. The discrepancy factor R was 0.168 with isotropic temperature factors and 0.136 after the copper atoms were made anisotropic.

Some of the carbon and chlorine atoms (C4*a*, C3*c*, C2*d*, C3*d*, Cl*d* and Cl*e*) had unusually large thermal motions and a difference Fourier map indicated that the structure might be disordered. First they were all given a site occupation factors 0.5, which were subsequently refined. The two disordered positions of atoms C3*c* and Cl*e* refined well and the corresponding bond length pairs were fixed together and refined as such. The disordered positions of C4*a* gave site occupation factors about one and zero, and thus C4*a* was considered ordered in subsequent calculations.

Considerable residual electron density was observed near the C2*d*, C3*d* and Cl*d* atoms, indicating rotational disorder or librational motion of the chloroethyl group of the carboxylato ligand. Attemps to account for rotational disorder in the chloroethyl group failed.

Experiments for the refinement in the non-centrosymmetric space group $P1$ were also made, but the positional parameters were nearly the same as before. Since there was no improvement in the disorder resolution the subsequent calculations were performed in the space group $P\bar{1}$. Atoms C3*c* and C3*e* were refined isotropically because anisotropic refinements did not give positive definite temperature factors.

The hydrogen atoms bonded to carbon were included at calculated positions with fixed bond lengths (C–H = 0.96 Å) and constrained angles. The isotropic thermal parameters for the hydrogen atoms were set 1.2 times the equivalent isotropic thermal parameters for the corresponding carbon atom. The hydrogen atom positions of the aqua and hydroxo ligands could not be found from a regular difference Fourier map.

Consequently, a second difference Fourier map was calculated using approximately two-thirds of the data (1781 reflections; $(\sin\theta)/\lambda \leq 0.31$ Å^{-1}). This map showed peaks of density about 0.3 e/Å^3 near the aqua and hydroxo oxygen atoms. The same peaks appeared in a third map using 1436 reflections ($(\sin\theta)/\lambda \leq 0.40$ Å^{-1}) and the hydrogen atoms were fixed at these positions.

The refinement converged to an R value of 0.075 and a weighted discrepancy factor $R_w = \Sigma \| F_o | - | F_c \| \sqrt{w}$ of 0.074 with the weighting scheme $w^{-1} = \sigma^2(F_o) + 0.0005 |F_o|^2$. The largest peaks in a final difference Fourier map had a maximum density of 1.1 e/Å^3 and were in the region of the atoms C3*e* and Cl*d* belonging to the disordered chloroethyl groups.

The structure was refined by the blocked-cascade full-matrix least-squares method.[15] The neutral atom scattering factors have been taken from *International Tables for X-Ray Crystallography*.[16] The preliminary refinements were performed with a Univac 1108 computer using programs from XRAY 76.[17] The final calculations were performed on a Nicolet R3m diffractometer system with SHELXTL[15] software for minicomputer (Nova 3). The figures were drawn with SHELXTL[15] programs on a Zeta-plotter. The final atomic positional and thermal parameters with their e.s.d. for non-hydrogen atoms and including the hydrogen atoms H*h*, H1*w* and H2*w* are given in Table 1. Bond distances and angles are given in Table 2 and intermolecular contact less than 3.6 Å in Table 3.

Table 1. Fractional atomic coordinates ($\times 10^4$) and thermal parameters ($\times 10^3$) with e.s.d.'s in parentheses.

Atom	x	y	z	U[a]	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu1	1736(1)	1720(1)	-2316(1)	47(1)	44(1)	53(1)	-11(1)	-9(1)	-12(1)
Cu2	2936(1)	-246(1)	-891(1)	30(1)	44(1)	68(1)	-19(1)	-8(1)	-5(1)
Cu3	528(1)	415(1)	704(1)	34(1)	41(1)	53(1)	-15(1)	-10(1)	-9(1)
O*h*	1930(6)	1108(5)	-824(6)	28(4)	40(4)	56(5)	-13(4)	-1(4)	-10(3)
H*h*[b]	2525	1803	-738	54					
O*w*	3276(8)	-148(7)	815(7)	56(6)	70(6)	99(7)	-17(5)	-39(5)	-7(5)
H1*w*[b]	2881	410	1236	94					
H2*w*[b]	4287	-141	681	94					
O*a*	1136(6)	-825(5)	30(6)	33(4)	39(4)	60(5)	-17(4)	-15(4)	-9(3)
N*a*	3496(9)	-1802(8)	-908(9)	39(6)	60(7)	89(8)	-37(6)	-9(5)	-8(5)
C1*a*	1210(11)	-1954(9)	540(10)	39(7)	38(8)	69(9)	-7(6)	-16(6)	-16(6)
C2*a*	2196(11)	-2417(9)	-392(11)	50(8)	45(7)	103(11)	-30(7)	-27(8)	-3(6)
C3*a*	4366(14)	-2134(10)	-238(14)	65(10)	66(9)	162(15)	-41(10)	-70(10)	15(7)
C4*a*	4799(23)	-3336(13)	-70(25)	213(23)	80(13)	396(36)	-101(19)	-230(26)	65(14)
C5*a*	4301(15)	-1897(12)	-2078(12)	81(11)	84(11)	118(13)	-60(10)	3(10)	-7(9)
C6*a*	3657(18)	-1433(13)	-2911(13)	135(16)	104(13)	80(11)	-37(10)	-21(11)	-33(11)
O*b*	742(7)	443(6)	-2099(6)	46(5)	49(5)	54(5)	-9(4)	-2(4)	-23(4)
N*b*	1499(10)	2217(8)	-3847(8)	66(7)	69(7)	59(7)	-12(6)	-15(6)	-15(6)
C1*b*	636(14)	342(11)	-3106(10)	77(10)	81(10)	58(9)	-24(8)	-18(7)	-25(8)
C2*b*	1610(14)	1197(10)	-4121(11)	83(10)	68(10)	55(9)	-5(8)	-15(8)	-14(8)
C3*b*	2666(14)	2965(12)	-4750(11)	71(10)	79(11)	71(10)	-2(8)	-7(8)	-19(8)
C4*b*	2614(18)	3234(15)	-5922(11)	116(14)	152(17)	47(10)	25(10)	-15(10)	-56(12)
C5*b*	186(14)	2702(11)	-3759(12)	81(11)	76(10)	76(10)	11(8)	-29(9)	-5(8)
C6*b*	-7(18)	3793(12)	-3509(15)	110(14)	95(13)	106(14)	3(11)	-27(11)	32(11)
O1*c*	336(7)	1724(6)	1188(7)	39(5)	56(5)	62(5)	-30(4)	-8(4)	-7(4)
O2*c*	2130(10)	1516(8)	1648(9)	61(7)	93(8)	117(9)	-45(7)	-40(6)	1(6)
C1*c*	1150(12)	2014(10)	1529(10)	51(8)	66(8)	52(8)	-23(7)	-5(6)	-21(6)
C2*c*	866(13)	3122(13)	1799(12)	57(9)	109(12)	73(10)	-60(9)	3(7)	-18(8)
C3*c*[c]	469(21)	3992(15)	950(16)	69(7)					
C3*c**[c]	1999(25)	3914(22)	1511(26)	48(10)					
Cl*c*	-367(6)	2818(4)	3225(4)	143(5)	159(5)	109(4)	-78(4)	21(3)	-44(4)
O1*d*	2231(10)	3169(7)	-2458(8)	96(8)	37(5)	83(7)	-4(5)	-20(6)	-28(5)
O2*d*	3295(11)	2914(8)	-1261(9)	129(9)	66(6)	108(8)	-14(6)	-45(7)	-50(6)
C1*d*	2892(15)	3464(9)	-2006(12)	104(12)	36(7)	85(10)	4(7)	-19(9)	-34(7)
C2*d*	3302(35)	4713(17)	-2500(17)	476(46)	132(18)	120(16)	20(13)	-147(24)	-188(24)
C3*d*	3714(27)	5170(14)	-3616(16)	378(37)	98(15)	125(17)	78(13)	-100(21)	-172(20)
Cl*d*	3626(21)	5225(8)	-1713(10)	960(37)	164(8)	279(12)	9(8)	-258(17)	-228(14)
O1*e*	3995(9)	1309(7)	-3222(7)	68(6)	89(6)	69(6)	-26(5)	-4(5)	-7(5)
O2*e*	4703(7)	411(7)	-1835(8)	33(5)	62(6)	82(7)	-13(5)	-8(5)	-17(4)
C1*e*	4870(12)	1050(11)	-2775(12)	40(8)	66(9)	61(9)	-23(8)	-4(7)	-8(7)
C2*e*	6348(13)	1464(10)	-3496(13)	79(12)	83(12)	135(15)	2(11)	-15(11)	-45(9)
C3*e*	7286(18)	686(10)	-4040(15)	51(3)					
Cl*e*[c]	6476(11)	2688(8)	-4300(15)	136(9)	136(9)	212(18)	18(8)	33(9)	-31(6)
Cl*e**[c]	6683(20)	2461(23)	-3111(27)	127(15)	273(28)	169(28)	-76(22)	-18(14)	-56(16)

[a] U_{11} or U_{iso}. [b] Fixed atom. [c] The site occupation factors are 0.65 for atoms C3*c* and Cl*e* and 0.35 for atoms C3*c** and Cl*e**.

Table 2. Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses.[a]

The copper(II) environments

Cu1 – Oh	2.004(8)	Cu2 – Oh	1.984(7)	Cu3 – Oh	2.013(6)
Cu1 – Ob	1.929(8)	Cu2 – Oa	1.922(6)	Cu3 – Oa	1.995(8)
Cu1 – Nb	2.062(12)	Cu2 – Na	2.054(10)	Cu3 – O1c	1.941(9)
Cu1 – O1d	1.925(10)	Cu2 – O1e	1.931(7)	Cu3 – Ob^i	1.920(9)
Cu1 – O2e	2.349(9)	Cu2 – Ow	2.469(11)	Cu3 – Oa^i	2.301(8)
Oh – Cu1 – Ob	91.0(3)	Oh – Cu2 – Oa	79.7(3)	Oh – Cu3 – Oa	77.3(3)
Oh – Cu1 – Nb	175.1(4)	Oh – Cu2 – Na	164.9(4)	Oh – Cu3 – Ob^i	171.5(3)
Oh – Cu1 – O1d	94.1(4)	Oh – Cu2 – O1e	97.3(3)	Oh – Cu3 – O1c	92.7(3)
Nb – Cu1 – Ob	84.3(4)	Na – Cu2 – Oa	87.0(3)	Ob^i – Cu3 – Oa	94.2(3)
Nb – Cu1 – O1d	90.8(5)	Na – Cu2 – O1e	95.9(4)	Ob^i – Cu3 – O1c	95.7(3)
Ob – Cu1 – O1d	163.8(4)	Oa – Cu2 – O1e	176.9(3)	Oa – Cu3 – O1c	167.8(3)
O2e – Cu1 – Oh	89.0(3)	Ow – Cu2 – Oh	86.9(3)	Oa^i – Cu3 – Oh	90.1(3)
O2e – Cu1 – Ob	103.5(3)	Ow – Cu2 – Oa	89.9(3)	Oa^i – Cu3 – Oa	92.5(3)
O2e – Cu1 – Nb	90.5(4)	Ow – Cu2 – Na	100.2(4)	Oa^i – Cu3 – Ob^i	90.6(3)
O2e – Cu1 – O1d	92.0(4)	Ow – Cu2 – O1e	90.5(3)	Oa^i – Cu3 – O1c	94.5(3)
Cu1 – Oh – Cu2	107.4(4)	Cu1···Cu2	3.213	Oa···Oh	2.503
Cu1 – Oh – Cu3	129.8(4)	Cu1···Cu3	3.638	Oa···Ob	3.013
Cu2 – Oh – Cu3	92.7(3)	Cu1···$Cu1^i$	6.433	Oa···Oa^i	3.111
		Cu1···$Cu2^i$	5.250	Oa···Ob^i	2.869
Cu1···Oa	3.745	Cu1···$Cu3^i$	3.448	Oa···Oh^i	3.060
Cu1···Oa^i	3.392	Cu2···Cu3	2.891	Ob···Ob^i	4.994
Cu2···Ob	3.261	Cu2···$Cu2^i$	5.865	Ob···Oh	2.805
Cu2···Oa^i	4.283	Cu2···$Cu3^i$	3.643		
Cu3···Oh^i	3.342	Cu3···$Cu3^i$	2.978		
Cu3···Ob	3.635				
Cu3···Ow	3.024				

The 2-diethylaminoethanolato ligands *a* and *b*

	a	*b*		*a*	*b*
O – C1	1.44(1)	1.43(2)	C1 – O – Cu3	131.4(7)	
C1 – C2	1.52(2)	1.55(2)	C1 – O – $Cu3^i$	114.2(7)	115.9(7)
N – C2	1.48(2)	1.45(2)	Cu – O – $Cu3^i$		127.2(5)
N – C3	1.49(2)	1.53(2)	Cu2 – O – Cu3	95.1(3)	
N – C5	1.50(2)	1.47(2)	Cu2 – O – $Cu3^i$	118.9(3)	
C3 – C4	1.56(2)	1.52(2)	Cu3 – O – $Cu3^i$	87.5(3)	
C5 – C6	1.49(3)	1.52(2)			
	n = 2	*n* = 1			
Cu*n* – N – C2	103.7(7)	100.2(8)			
Cu*n* – N – C3	107.7(9)	111.8(10)			
Cu*n* – N – C5	112.2(7)	112.9(8)			
C2 – N – C3	113.3(9)	108.3(9)			
C2 – N – C5	112.2(12)	111.7(12)			
C3 – N – C5	107.6(10)	111.4(9)			
N – C2 – C1	109.5(11)	109.8(10)			
N – C3 – C4	115.1(18)	113.0(14)			
N – C5 – C6	114.5(12)	115.4(15)			
O – C1 – C2	106.3(8)	108.0(12)			
C1 – O – Cu*n*	108.7(6)	113.9(6)			

Table 2. Continued.

The 2-chloropropionato ligands *c*, *d* and *e*

	c	*d*	*e*
O1 – C1	1.25(2)	1.23(2)	1.25(2)
O2 – C1	1.23(2)	1.25(2)	1.27(2)
C1 – C2	1.55(2)	1.59(3)	1.55(2)
C2 – C3	1.52(3)	1.34(3)	1.49(2)
C2 – C3*	1.52(3)		
C2 – C1	1.80(1)	1.54(4)	1.62(2)
C2 – C1*			1.62(2)
O1 – C1 – O2	126.1(13)	128.7(12)	126.8(11)
O1 – C1 – C2	114.8(11)	113.0(17)	114.8(13)
O2 – C1 – C2	119.0(14)	118.3(19)	118.2(11)
C1 – C2 – C3	114.9(15)	119.9(21)	116.1(8)
C1 – C2 – C3*	121.7(14)		
C1 – C2 – Cl	104.4(8)	115.2(16)	113.8(10)
C1 – C2 – Cl*			109.9(13)
Cl – C2 – C3	114.8(11)	122.0(22)	115.0(7)
Cl – C2 – C3*	116.6(17)		
C3 – C2 – C3*	84.1(16)		
C3 – C2 – Cl*			129.3(8)
Cl – C2 – Cl*			59.9(14)
Cu1 – O1 – C1		128.3(8)	126.4(8)
Cu2 – O1 – C1			119.2(9)
Cu3 – O1 – C1	123.1(9)		

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

[a] E.s.d.'s were not calculated for distances >2.5 Å.

DISCUSSION

The crystal structure of bis[aqua-μ-(2-chloropropionato-*O*,*O'*)-di(2-chloropropionato)-μ_3-(2-diethylaminoethanolato-*N*,μ_3-*O*)-μ-(2-diethylaminoethanolato-*N*,μ-*O*)-μ_3-hydroxo-tricopper(II)],$[Cu_3(Et_2LO)_2(ClC_3H_4O_2)_3(OH)(H_2O)]_2$, is composed of centrosymmetrical hexanuclear molecules located at the inversion center (0,0,0), Fig. 1. The closest intermolecular contact is 2.916 Å between the oxygen atoms of the 2-chloropropionato, (O2*e*), and aqua (1-*x*, -*y*, -*z*) ligands, which might be considered as weak hydrogen bonds. Other short contacts lie in the range 3.3 – 3.6 Å and correspond to van der Waals contact distances,[18] see Table 3.

The bridging oxygen and copper atoms form a centrosymmetric Cu_6O_6 core which is built up of two distorted and fused cubes with the common face Cu3-O*a*-Cu3^{i}-O*a*^{i}. These cubes have two long non-bonding Cu – O distances (Cu2-O*b* = 3.261 and Cu1-O*a*^{i} = 3.392 Å) perpendicular to each other and two parallel bonding Cu – O distances (Cu3-O*a*^{i} = 2.301 Å). The short Cu – O distances completing a cube vary between 1.922 and 2.013 Å, see Fig. 2.

Table 3. Intermolecular contacts <3.6 Å.

O2*e*···O*w*^{ii}	2.916	O*w*···O*w*^{ii}	3.483
O2*d*···C4*a*^{ii}	3.327	Cl*e**···C5*b*^{v}	3.534
C3*a*···C4*a*^{ii}	3.371	O2*c*···C3*a*^{ii}	3.537
Cl*e*···C3*d*^{iii}	3.379	C3*b*···C4*b*^{vi}	3.576
C3*a*···C3*a*^{iv}	3.365		

Symmetry codes

ii: $1-x, -y, -z$	iv: $-x, 1-y, -z$
iii: $1-x, 1-y, -1-z$	v: $1+x, y, z$
	vi: $x, y, 1+z$

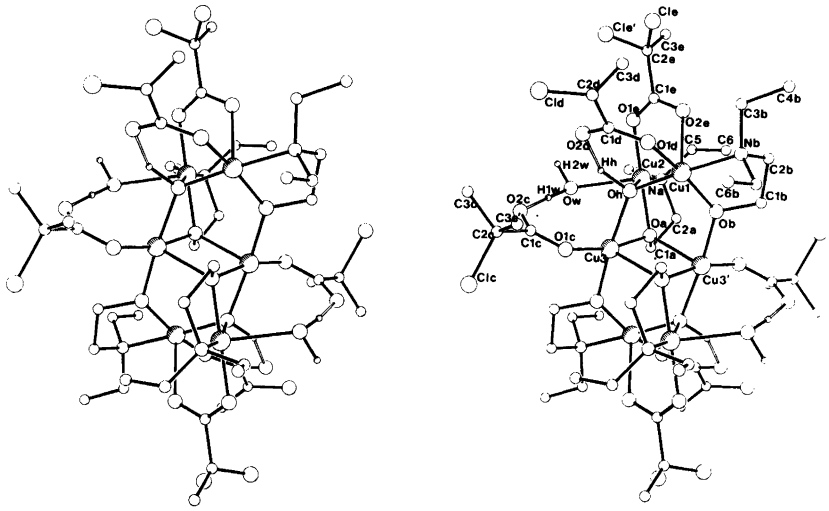

Fig. 1. Stereoview of $[Cu_3(C_6H_{14}NO)_2(ClC_3H_4O_2)_3(OH)\,(H_2O)]_2$.

The $[Cu_3(Et_2LO)_2(H_3CCOO)_3(OH)]_2 \cdot H_2O$ [8] complex has a similar Cu_6O_6 core, where the long perpendicular Cu–O distances of the cubane skeleton are 3.063 and 3.404 Å and the two parallel ones both are 2.369 Å. The short distances vary from 1.919 to 2.048 Å.

These cubes can be compared to those of the $[Cu(R_2LO)\,(R'COO)]_4$ tetramers with respect to the arrangement of the long and short Cu–O distances. In the tetramers there are two pairs of long Cu–O distances perpendicular to each other giving the cubane skeleton a boat-like conformation. The long Cu–O distances vary from 2.52 to 3.01 Å and the short Cu–O distances from 1.85 to 2.02 Å.[6,7]

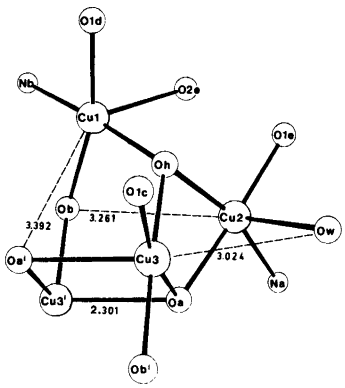

Fig. 2. The central cubane fragment.

In the present investigation all the three copper(II) ions have a square-pyramidal coordination in contrast to $[Cu_3(Et_2LO)_2(H_3CCOO)_3(OH)]_2 \cdot H_2O$,[8] where the coordination number varies from four to six depending on the site population parameter of water. The basal atoms of the Cu1 environment have the largest deviations from their least-squares plane. The *Ob* and *O1d* atoms lie 0.14 and 0.13 Å below and Nb and Oh atoms 0.14 and 0.13 Å above the plane. The dihedral angle between Cu1,-*Oh*,O1*d* and Cu1,*Ob*,Nb is 15.5° indicating some distortion. Cu2 and Cu3 are 0.69 and 0.68 Å above their least-squares basal planes towards the apical oxygen atoms as compared to 0.121 Å for Cu1. All these planes have the triply bridging oxygen atom of the hydroxo ion in common. In addition the Cu2 and Cu3 atoms are bridged by the oxygen atom O*a*. The angles between the least-squares basal planes of Cu1–Cu2 (*a-b*), Cu1–Cu3 (*a-c*) and Cu2–Cu3 (*b-c*) are 91.8, 53.1 and 38.7°, respectively, (Table 4).

The short Cu-ligand distances 1.920–2.013 Å for Cu–O, 2.054 and 2.062 Å for Cu–N are in the range normally observed for Cu(II) complexes.[1,2,4–12] In the apical site of Cu1 there is the second oxygen atom O2*e* of the 2-chloropropionato group coordinated to Cu2, the Cu1–O2*e* distance being 2.349(9) Å. Similar distances in other carboxylato complexes have been reported.[8,19]

The water molecule occupies the apical position of the tetragonal pyramid in the Cu2 coordination

Table 4. Least-squares planes (unit weights) and deviations from the planes (Å).

a. Plane defined by O*h*, O*b*, N*b*, O1*d*:
$8.263x-4.860y-2.985z=1.168$

O*h*	0.134	O1*d*	−0.132
O*b*	−0.144	Cu1	0.121
N*b*	0.142	O2*e*	2.459

b. Plane defined by O*h*, O*a*, N*a*, O1*e*:
$5.831x+2.743y+13.045z=0.413$

O*h*	−0.058	O1*e*	0.049
O*a*	0.063	Cu2	0.069
N*a*	−0.053	O*w*	2.520

c. Plane defined by O*h*, O*a*, O1*c*, O*b*^{i}:
$9.839x-0.838y+8.573z=1.156$

O*h*	−0.057	O*b*^{i}	−0.049
O*a*	0.056	Cu3	−0.068
O1*c*	0.049	O*a*^{i}	−2.368

d. Plane defined by O1*c*, O2*c*, C1*c*, C2*c*:
$2.700x+2.987y-9.191z=-0.488$

O1*c*	0.002	Cu3	0.108
O2*c*	0.002	O*w*	0.580
C1*c*	−0.005		
C2*c*	0.001		

e. Plane defined by O1*d*, O2*d*, C1*d*, C2*d*:
$6.331x-4.580y-6.605z=1.580$

O1*d*	0.004	Cu1	0.260
O2*d*	0.004	O*h*	−0.322
C1*d*	−0.011		
C2*d*	0.003		

f. Plane defined by O1*e*, O2*e*, Cl*e*, C2*e*:
$0.123x+11.905y+7.650z=-0.845$

O1*e*	−0.012	Cu1	1.143
O2*e*	−0.012	Cu2	−0.093
C1*e*	0.032		
C2*e*	−0.009		

sphere. The Cu−O*w* distances of 2.469(11) Å to Cu2 and 3.024 Å to Cu3 differ considerably from the corresponding distances, 2.60(2) and 2.75(3) Å, found in the $[Cu_3(Et_2LO)_2(H_3CCOO)_3(OH)]_2 \cdot H_2O$[8] complex. Thus in the acetato complex the O*w* oxygen forms two weak bonds with the copper(II) ions, while in the 2-chloropropionato complex it forms a somewhat elongated bond and a weak interaction. One reason for the difference coordination of water is the difference in packing between the acetato and 2-chloropropionato complexes. In the acetato complex the water only occupies half of the available positions, whereas in the 2-chloropropionato complex all the positions are occupied. The triply bridging 2-diethylaminoethanolato oxygen completes the coordination sphere of Cu3 (Cu3-O*a*^{i} = 2.301(8) Å). In the sixth site the water oxygen is situated, at a distance of 3.024 Å and with a 19.7° deviation from the *z*-axis, which allows the coordination of Cu3 to be described as 4+1 or 4+1+1*.[20-22]

With the triply bridging oxygen atom of the hydroxo group the three copper(II) ions form a trigonal pyramid, where the oxygen is on the top. The final evidence of this structure was provided by the location of a hydrogen atom at the expected position to complete a distorted tetrahedral environment around the oxygen atom. The Cu-Oh-Cu angles and the location of Oh 0.62 Å above the Cu1-Cu2-Cu3 plane agree well with the data of other Cu_3OH fragments,[8-12,25,26] Table 5. The hydrogen atom of the OH^- group forms a hydrogen bond to the unbonded carboxylato oxygen atom O2*d* (O-H = 1.12, H···O = 1.55, O···O = 2.66 Å and O-H···O = 149.7°).

Two of the three independent 2-chloropropionato ligands are unidentate. The carboxylato group, *c*, bonded to Cu3 is planar and forms a hydrogen bond with the axial water molecule (O−H = 1.00,

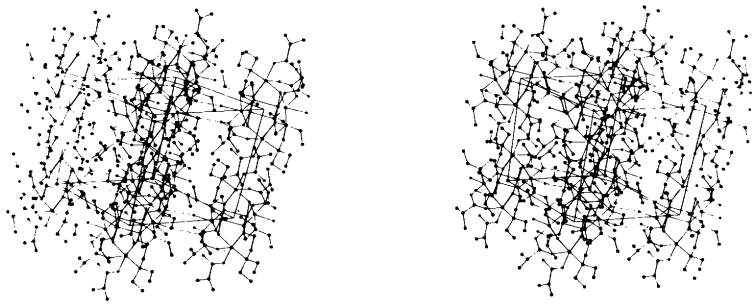

Fig. 3. Stereoview of the packing.

Table 5. The space groups, the interatomic distances (Å) and angles (°) and the deviation from the Cu–Cu–Cu planes in Cu_3OH fragments.

Complex[a]	Space group	Cu1–O	Cu2–O	Cu3–O	Cu1–O–Cu2	Cu2–O–Cu3	Cu1–O–Cu3	Dev.	O···O	Ref.
$[Cu_3(Et_2LO)_2(H_3CCOO)_3(OH)]_2 \cdot H_2O$	$P\bar{1}$	1.934	1.999	2.048	104.1	130.4	94.5	0.63	2.64	8
$[Cu_3(Et_2LO)_2(ClC_3H_4O_2)_3(OH)(H_2O)]_2$	$P\bar{1}$	1.984	2.004	2.013	107.4	129.8	92.7	0.62	2.657	*b*
$[Cu_2(C_9H_7N)_2(F_3CCOO)_3(OH)]_2$	$P\bar{1}$	1.964	1.963	1.990	116.9	124.8	98.6	0.51	2.550	10
$Ag[Cu_2(C_8H_4O_4)_2(OH)] \cdot 5H_2O$	$P\bar{1}$	1.955	1.911	1.949	109.9	117.3	96.8		2.535	25
$[Cu_4(C_6H_5NO_3)_4(OH)_2(SO_4)(H_2O)_4]$	$C2$	1.99	1.97	1.95		117.9	92.1	0.53	2.51	26
$[Cu_3(C_{10}H_{11}N_2O)_3(ClO_4)(OH)] \cdot ClO_4$	$P2_1/n$	1.946	1.969	1.978	107.1	110.0	109.3	0.70		9
$[Cu_3(C_6H_5N_2O)_3(SO_4)(OH)] \cdot 16.3H_2O$	$P\bar{3}$	1.98	1.98	1.98	108.2	108.2	108.2	0.70	2.36	11
$[Cu_3(C_8H_{17}N_2O)_3(H_2O)_3(OH_{\frac{1}{2}})]$-$\cdot 1.5ClO_4 \cdot 4H_2O$	$R\bar{3}$	1.97	1.97	1.97	110.9	110.9	110.9	0.7	2.75	12

[a] Abbreviations: Et_2LO = 2-diethylaminoethanolato, $ClC_3H_4O_2$ = 2-chloropropionato, C_9H_7N = quinoline, $C_8H_4O_4$ = *o*-phthalato, $C_{10}H_{11}N_2O$ = 3-(phenylimino)-butane 2-oximato, $C_6H_5N_2O$ = pyridine-2-carbaldehyde oximato, $C_6H_5NO_3$ = isonicotinato *N*-oxide, $C_8H_{17}N_2O$ = 2-propylamino-2-methyl-3-butane oximato. [b] This work.

H···O = 1.70, O···O = 2.69 Å and O–H···O = 165.3°). The carboxylato group, *d*, is coordinated to the Cu1 and forms a hydrogen bond with the triply bridging hydroxo ion as mentioned before. The third carboxylato group, *e*, is bidentate bridging from the basal coordination site of Cu2 to the apical position of Cu1 in a *syn-syn* configuration. This coordination type is quite common in carboxylato complexes.[6–8,10,19]

The bond distances and angles of the 2-chloropropionato ligands are normal except for the C–Cl bond lengths. In the *c* ligand the C2-Cl 1.80(1) Å is in the range normally reported[23,24] but the other two C–Cl bonds are much shorter, 1.54(4) and 1.62(2) Å for the ligands *d* and *e*, respectively. One reason for this is the structural disorder. Since the 2-chloropropionato ligand is optically active and the complex has an inversion centre, the symmetry related molecules must have different enantiomorphs in the crystal structure. In this structure the enantiomorphs are probably mixed. This is also supported by the peaks observed close to the carboxylato groups in the difference Fourier maps.

The bond distances and angles of the two 2-diethylaminoethanolato ligands are as expected.[1–8] In the five-membered ethanolato-copper rings the dihedral angles O,Cl,C2,N are 55.1 and −43.8° for the ligands *a* and *b*. In the chelate ring of ligand *a*, C1 lies 0.48 Å above and C2 0.23 Å below the plane defined by O*a*-Cu2-N*a*. In the other chelate ring C1 and C2 lie on the same side and 0.32 and 0.84 Å from the plane defined by O*b*-Cu1-N*b*. The ethanolato O*a* is tetracoordinated, while O*b* is tricoordinated. The angles around O*a* are approximately tetrahedral (mean value 109.3°) as in the $[Cu_3(Et_2LO)_2(H_3CCOO)_3(OH)]_2 \cdot H_2O$[8] complex and in $[Cu(R_2LO)(R'COO)]_4$ tetramers.[6,7]

The bond angles around O*b* vary from 113.9 to 127.2° (mean 119.0°). The atom O*b* deviates 0.18 Å from the plane defined by Cu1–Cu3^i–C1*b*. The oxygen environment can be considered as a deformed tetrahedron.

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