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Crystal and Molecular Structures of Two Dimeric Copper(II) Fluoroacetates. $Cu_2(FH_2CCOO)_4(H_2O)_2$ and the Novel N-Disubstituted Aminoalcohol Compound $(Et_2NHCH_2CH_2OH)_2[Cu_2(FH_2CCOO)_4(FH_2CCOO)_2]$

KIMMO SMOLANDER

Department of Chemistry, University of Joensuu, P.O. Box 111, SF-80101 Joensuu 10, Finland

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Abstract

The crystal and molecular structures of $Cu_2(FH_2CCOO)_4(H_2O)_2$ (I) and $(C_6H_{16}NO)_2[Cu_2(FH_2CCOO)_4(FH_2CCOO)_2]$ (**II**) have been determined by three-dimensional X-ray crystallography. The compound **I** is monoclinic, space group *C*2/*c*, $a = 12.736(4)$, $b = 9.537(3)$, $c = 13.683(4)$ Å, $\beta = 118.09(2)°$, and compound **II** is triclinic, space group $P\bar{1}$, $a = 7.825(5)$, $b = 8.817(7)$, $c = 12.986(6)$ Å, $\alpha = 74.28(5)$. $\beta = 86.57(4)$ and $\gamma = 85.18(6)°$. The structures were solved by direct methods and refined by blocked-cascade full-matrix least-squares methods to *R* value 0.032 and 0.031 using 1188 and 3337 independent reflections.

Both compounds consist of centrosymmetric dinuclear units in which the two Cu(II) ions are bridged by four carboxyl groups in *syn–syn* configuration, with Cu–Cu distances of 2.674(1) and 2.685(1) Å, respectively. The carboxyl oxygen atoms are in the basal planes (Cu–O ≃ 1.969(2) and 1.976(2) Å), the water or unidentate fluoroacetato ligand in *anti* configuration ($Cu–O_{axial} = 2.131(4)$ and 2.135(1) Å) is in the fifth site, and the copper(II) ion is in the sixth site. The Cu(II) ion deviates 0.314 or 0.219 Å from the mean basal plane toward the apical oxygen atom.

Compound **II** is the first example of an uncoordinated 2–dialkylaminoethanol ligand. The hydroxyl group is not deprotoned and the amino group has taken a proton to form a hydrocation $(Et_2NHCH_2CH_2OH)^+$, which is then hydrogen-bonded to the anion $[Cu_2(FH_2CCOO)_4(FH_2CCOO)_2]^{2-}$.

The electronic spectra in Nujol show two bands having maxima at 13 900, 28 000 and 13 500, 28 000 cm^{-1}.

The known structures of copper(II) acetato and haloacetato adducts are tabulated.

Introduction

A large number of transition-metal carboxylato complexes, $M_2(RCCOO)_4L_2$, have been reported [1–3]. In these compounds the metal–metal interactions vary from very weak single bonds to exceptionally strong multiple bonds [1, 4]. Reviews of dimeric copper(II) carboxylates consisting of four triatomic bridges have concentrated on structural, spectral and magnetic data [5–7].

The effects of the carboxylate substituents R and of the axial donor ligands on the exchange coupling constant ($-2J$) [8], and also on the Cu–Cu distances [5–7] have been attracting great interest. The magnetic interaction [8] and the Cu–Cu distances [5–7, 9] are expected to increase as either the terminal or the bridging ligands become better electron donors. A stronger axial ligand coordination tends to weaken the Cu–Cu interaction.

All the reported copper(II) complexes with dialkylated aminoethanols are polynuclear (di-, tri-, tetra- and hexa-nuclear), where oxygen atoms of aminoethanolato ligands form bridges between the copper(II) ions [10]. Normally the hydroxyl group is deprotonated with unit negative charge and the ligand coordinates via nitrogen and oxygen atoms to copper(II) ions, forming puckered five-membered rings. Amirov *et al.* [11] have reported one mononuclear bis complex with 2–aminoethanol, where the hydroxyl group of the ligands is not deprotonated.

We report the details of the crystal and molecular structure and electronic spectral properties of $Cu_2(FH_2CCOO)_4(H_2O)_2$ and $(C_6H_{16}NO)_2[Cu_2(FH_2CCOO)_4(FH_2CCOO)_2]$. The latter compound differs from all other known dialkylaminoethanolato complexes in that the ligand is not chelated. The hydroxyl group is not deprotonated and the amino group of 2–diethylaminoethanol has taken a proton to form a hydrocation, which is then hydrogen-bonded to the anion.

Experimental

Preparation of the Complexes

Compound **I**, $Cu_2(FH_2CCOO)_4(H_2O)_2$, was prepared from copper(II) hydroxide (Fluka AG) and

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TABLE I. Crystal and Refinement Data of $Cu_2(FH_2CCOO)_4(H_2O)_2$ (I) and $(C_6H_{16}NO)_2[Cu_2(FH_2CCOO)_4(FH_2CCOO)_2]$ (II)

Compound	I	II
Stoichiometry	$C_8H_{12}O_{10}F_4Cu_2$	$C_{24}H_{44}N_2O_{14}F_6Cu_2$
Formula weight	471.3	825.7
Crystal system	monoclinic	triclinic
Space group	*C*2/*c*	$P\bar{1}$
a (Å)	12.736(4)	7.825(5)
b (Å)	9.537(3)	8.817(7)
c (Å)	13.683(4)	12.986(6)
α (°)		74.28(5)
β (°)	118.09(2)	86.57(4)
γ (°)		85.18(6)
V (Å^3)	1466.1	857.7
Z	4	1
D_o (g cm^{-3})	2.12	1.60
D_c (g cm^{-3})	2.13	1.60
μ (mm^{-1})	3.12	1.39
F(000)	936	426
2θ range (°)	3–55	2–55
Scan speed (° min^{-1})	2.5–29.3	2.5–29.3
Scan range	1	1
Reflections measured	3243	3948
Observed reflections ($I > 2.5\sigma(I)$)	1188	3337
Number of variables	121	305
Residual electron density (e Å^{-3})	0.42	0.58
Crystal size (mm^3)	0.12 × 0.20 × 0.22	0.31 × 0.30 × 0.41
R (= $\Sigma\Delta/\Sigma\lvert F_o\rvert$)[a]	0.031	0.031
R_w (= $\Sigma\Delta w^{1/2}/\Sigma\lvert F_o\rvert w^{1/2}$)[b]	0.031	0.033

[a] $\Delta = \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert$. [b] $w^{-1} = \sigma^2(F_o) + 0.0005F^2$.

fluoroacetic acid (Merck) by the method of Bateman and Conrad [12]. For compound **II**, $(C_6H_{16}NO)_2$-$[Cu_2(FH_2CCOO)_4(FH_2CCOO)_2]$, 0.01 mol of compound **I** was dissolved in 50 ml methanol solution. To this boiling solution, 0.01 mol of 2–diethylaminoethanol (Fluka AG) in 20 ml methanol was added with stirring. The solution was filtered and hexane was added so that the final methanol/hexane ratio was 2:1. After one week at ambient temperature, light green crystals were formed.

Spectral Studies

Electronic spectra in the region 300–850 nm were measured with a Shimadzu UV-240 spectrophotometer using Nujol suspension technique.

Data Collection

The crystal and refinement data are given in Table I. The unit cell parameters and the orientation matrix were determined by a least-squares refinement based on well-centred reflections measured at 20 °C on a Nicolet R3m diffractometer. Intensity data were collected on the same diffractometer, by the ω-scan technique, using graphite-crystal monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). The intensity of one check reflection recorded after every 99 measurements remained essentially constant throughout the data collection. The intensities were corrected for Lorentz and polarization effects and for absorption from empirical ψ-scan data (compound **II**).

Structure Determination

The structures were solved by direct methods [13] and Fourier techniques and refined by blocked-cascade full-matrix least-squares with anisotropic temperature factors for all non-hydrogen atoms. The hydrogen atoms were located from difference Fourier syntheses. The positional parameters and also the isotropic thermal parameters of hydrogen atoms for compound **II** were refined. For compound **I** the isotropic thermal parameters were set 1.2 times the equivalent isotropic thermal parameters for the corresponding atom.

The calculations were performed on a Nicolet R3m diffractometer system with SHELXTL [13] software for minicomputer (Nova 3). The neutral atom scattering factors have been taken from ref. 14. The figures were drawn with SHELXTL programs on a Zeta-plotter. The final atomic positional and equivalent thermal parameters with their e.s.d.s for non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms are given in Tables II–V.

TABLE II. Atom Coordinates (×10^4) and Temperature Factors (×10^3) with e.s.d.s in Parentheses for $Cu_2(FH_2CCOO)_4(H_2O)$

Atom	x	y	z	U[a]
Cu	491(1)	858(1)	4556(1)	23(1)
O(11)	−1072(2)	654(3)	3220(2)	32(1)
O(12)	−1902(2)	−780(3)	3959(2)	32(1)
C(11)	−1905(3)	−109(4)	3172(3)	26(1)
C(12)	−2973(4)	−221(5)	2048(3)	37(2)
F(1)	−3919(2)	−803(3)	2121(2)	55(1)
O(21)	971(2)	−934(3)	4174(2)	31(1)
O(22)	120(2)	−2379(3)	4900(2)	35(1)
C(21)	694(3)	−2109(4)	4379(3)	26(1)
C(22)	1113(4)	−3382(4)	4003(3)	32(2)
F(2)	1641(3)	−3003(3)	3369(2)	52(1)
O(31)	1348(3)	1960(3)	3774(2)	43(1)
H1(C12)[b]	−277(4)	−65(4)	148(4)	44
H2(C12)	−326(4)	59(5)	153(4)	44
H1(C22)	54(4)	−394(5)	363(4)	38
H2(C22)	153(4)	−384(6)	451(4)	38
H1(O31)	125	164	313	52
H2(O31)	144	264	380	52

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor for non-hydrogen atoms. [b] (×10^3).

TABLE III. Atom Coordinates (×10^4) and Temperature Factors (×10^3) with e.s.d.s in Parentheses for $(C_6H_{16}NO)_2[Cu_2(FH_2CCOO)_4(FH_2COO)_2]$

Atom	x	y	z	U[a]
Cu	777(1)	3840(1)	5761(1)	27(1)
F(1)	1660(2)	3706(2)	1765(1)	67(1)
O(11)	1746(2)	3057(1)	4545(1)	38(1)
O(12)	477(2)	5019(2)	3280(1)	37(1)
C(11)	1382(3)	3754(1)	3595(2)	32(1)
C(12)	2181(3)	2944(3)	2778(2)	43(1)
F(2)	−3852(2)	910(2)	5856(1)	68(1)
O(21)	−2636(1)	4696(1)	4468(1)	38(1)
O(22)	−1321(1)	2755(2)	5730(1)	37(1)
C(21)	−2544(3)	3359(2)	5133(2)	31(1)
C(22)	−4103(3)	2428(3)	5218(2)	44(1)
F(3)	1738(3)	−1755(2)	6768(1)	62(1)
O(31)	2104(2)	2119(2)	6989(1)	36(1)
O(32)	3012(3)	−211(2)	8022(2)	55(1)
C(31)	2299(3)	613(2)	7224(2)	34(1)
C(32)	1583(4)	−119(3)	6437(2)	51(1)
O	5819(3)	3313(2)	1234(2)	54(1)
N	6477(3)	6754(2)	1481(1)	37(1)
C(1)	7280(4)	4182(3)	969(2)	50(1)
C(2)	7534(3)	5203(3)	1698(2)	43(1)
C(3)	6793(4)	7830(3)	390(2)	47(1)
C(4)	8645(5)	8140(5)	140(3)	66(2)
C(5)	4598(3)	6490(3)	1750(2)	48(1)
C(6)	3449(4)	7975(4)	1631(3)	70(2)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

TABLE IV. Atom Coordinates (×10^4) and Temperature Factors (×10^3) for Hydrogen Atoms for $(C_6H_{16}NO)_2[Cu_2(FH_2CCOO)_4(FH_2CCOO)_2]$ e.s.d.s in Parentheses

Atom	x	y	z	U
H1(C11)	3419(39)	2944(35)	2806(24)	59(8)
H1(C12)	1856(36)	1992(33)	2940(22)	47(7)
H1(C21)	−5083(38)	2955(35)	5470(24)	60(8)
H1(C22)	−4326(37)	2335(33)	4529(22)	51(8)
H1(C31)	465(44)	174(38)	6305(26)	71(9)
H1(C32)	2143(41)	189(38)	5799(26)	71(9)
H1(C1)	7180(34)	4735(31)	284(22)	54(7)
H2(C1)	8322(42)	3407(38)	990(26)	70(9)
H1(C2)	7258(36)	4661(34)	2468(23)	56(8)
H2(C2)	8737(35)	5426(32)	1688(22)	49(7)
H1(C3)	6079(39)	8849(37)	436(25)	60(8)
H2(C3)	6317(37)	7399(35)	−89(24)	54(8)
H1(C4)	9295(44)	7217(41)	206(28)	79(10)
H2(C4)	9206(47)	8417(41)	668(29)	72(10)
H3(C4)	8741(55)	8862(52)	−499(37)	93(13)
H1(C5)	4540(40)	5872(38)	2514(27)	60(9)
H2(C5)	4267(38)	5820(34)	1326(23)	56(8)
H1(C6)	3374(52)	8474(48)	828(33)	109(13)
H2(C6)	3790(43)	8685(38)	1935(26)	72(9)
H3(C6)	2265(51)	7708(48)	2028(32)	101(12)
H(O)	6149(45)	2411(44)	1504(27)	68(10)
H(N)	6827(32)	7235(30)	1926(20)	39(6)

Results and Discussion

Figures 1 and 2 show stereoviews of the compounds, and Fig. 3 displays the packing for compound **II**. As mentioned above, the molecular structure of $(C_6H_{16}NO)_2[Cu_2(FH_2CCOO)_4(FH_2CCOO)_2]$ differs from that of other copper(II) complexes with dialkylated aminoethanols: it is the first compound with uncoordinated 2–dialkylaminoethanol. In all other compounds the ligand is chelated via nitrogen and oxygen atoms to copper(II) ion, forming puckered five-membered rings and polynuclear alkoxo-bridged complexes [10]. In the present compound the unit cell consists of one centrosymmetric dimeric $[Cu_2(FH_2CCOO)_4(FH_2CCOO)_2]^{2-}$ anion and two $(Et_2NHCH_2CH_2OH)^+$ cations (Fig. 4), joined together by hydrogen bonds between the oxygen atoms of the unidentate carboxyl groups and H(O) and H(N) atoms.

In both compounds the copper(II) ions are bridged by four carboxyl groups in *syn–syn* configuration. This is a molecular structure typical of carboxylato complexes, where the Cu–Cu distances are in the range 2.65–2.88 Å [5–7, 9, 15]. The Cu–Cu distance is 2.674(1) in compound **I** and 2.685(1) in compound **II**. The distorted octahedral coordination around the copper(II) ion is completed by a second copper(II) ion and the donor atom of the water (compound **I**) or unidentate fluoroacetato ligand in *anti* configuration (compound **II**).

TABLE V. Interatomic Distances (Å) and Angles (°) with e.s.d.s in Parentheses

The copper(II) environments

Compound	I	II		I	II
Cu–O(11)	1.978(2)	1.970(2)	O(11)–Cu–O(21)	88.4(1)	89.0(1)
Cu–O(21)	1.966(2)	1.975(2)	O(11)–Cu–O(22)^{i}	91.0(1)	89.7(1)
Cu–O(12)^{i}	1.981(2)	1.977(2)	O(11)–Cu–O(12)^{i}	167.4(1)	167.2(1)
Cu–O(22)^{i}	1.952(3)	1.982(2)	O(21)–Cu–O(12)^{i}	89.7(1)	88.6(1)
Cu–O(31)	2.131(4)	2.135(1)	O(21)–Cu–O(22)^{i}	167.6(1)	167.3(1)
Cu–Cu^{i}	2.674(1)	2.685(0)	O(12)^{i}–Cu–O(22)^{i}	88.2(1)	89.9(1)
Cu^{i}–Cu–O(11)	83.0(1)	84.8(0)	O(31)–Cu–O(11)	96.6(1)	97.1(1)
Cu^{i}–Cu–O(21)	81.9(1)	83.4(0)	O(31)–Cu–O(21)	89.9(1)	100.1(1)
Cu^{i}–Cu–O(12)^{i}	84.4(1)	82.4(0)	O(31)–Cu–O(12)^{i}	95.8(1)	95.7(1)
Cu^{i}–Cu–O(22)^{i}	85.7(1)	83.9(0)	O(31)–Cu–O(22)^{i}	102.4(1)	92.5(1)
Cu^{i}–Cu–O(31)	171.9(1)	176.0(0)			

The fluoroacetated ligands

	I		II		
	n = 1	*n* = 2	*n* = 1	*n* = 2	*n* = 3
C(*n*1)–O(*n*1)	1.263(5)	1.246(4)	1.258(2)	1.257(2)	1.278(3)
C(*n*1)–O(*n*2)	1.251(5)	1.265(6)	1.252(2)	1.257(3)	1.228(3)
C(*n*1)–C(*n*2)	1.501(4)	1.511(6)	1.511(4)	1.510(3)	1.503(4)
C(*n*2)–F(*n*)	1.372(6)	1.374(7)	1.374(3)	1.375(3)	1.385(3)
Cu–O(*n*1)–C(*n*1)	124.1(2)	124.4(3)	121.5(1)	122.4(1)	132.9(2)
Cu–O(*n*2)–C(*n*1)	122.4(2)	120.2(2)	124.2(1)	123.4(1)	
O(*n*1)–C(*n*1)–O(*n*2)	126.0(3)	127.6(4)	126.9(2)	126.9(2)	124.1(2)
O(*n*1)–C(*n*1)–C(*n*2)	115.3(4)	117.6(4)	114.1(2)	114.9(2)	114.9(2)
O(*n*2)–C(*n*1)–C(*n*2)	118.7(4)	114.8(3)	119.0(2)	118.2(2)	120.9(2)
C(*n*1)–C(*n*2)–F(*n*)	111.0(4)	111.1(3)	111.4(2)	112.4(2)	112.2(2)

The diethyl-(2-hydroxyethyl)ammonium ion, II

O–C(1)	1.404(4)	O–C(1)–C(2)	114.1(2)
C(1)–C(2)	1.504(4)	C(1)–C(2)–N	116.0(2)
N–C(2)	1.504(3)	C(2)–N–C(3)	114.2(2)
N–C(3)	1.496(3)	C(2)–N–C(5)	110.6(2)
N–C(5)	1.513(3)	C(3)–N–C(5)	113.2(2)
C(3)–C(4)	1.498(5)	N–C(3)–C(4)	113.2(2)
C(5)–C(6)	1.502(4)	N–C(5)–C(6)	114.7(2)
H–N	0.87(3)	H–N–C(2)	105(2)
H–O	0.81(4)	H–N–C(3)	105(2)
O•••N	3.22	H–N–C(5)	108(2)
		H–O–C(1)	107(3)

Symmetry code (i): $-x, -y, 1-z$ for **I** $-x, 1-y, 1-z$ for **II**

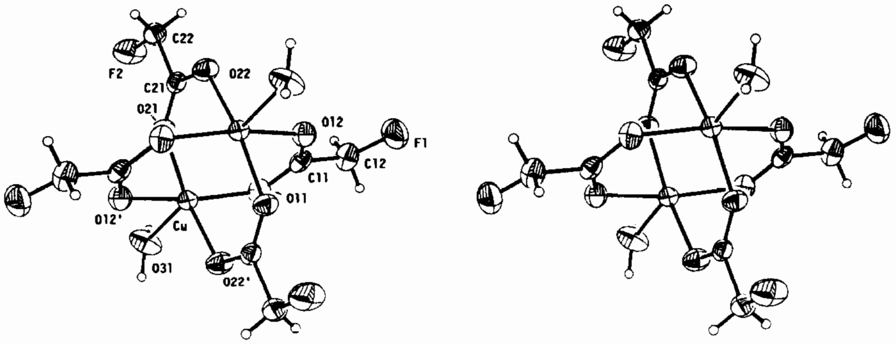

Fig. 1. Stereoview of $Cu_2(FH_2CCOO)_4(H_2O)_2$.

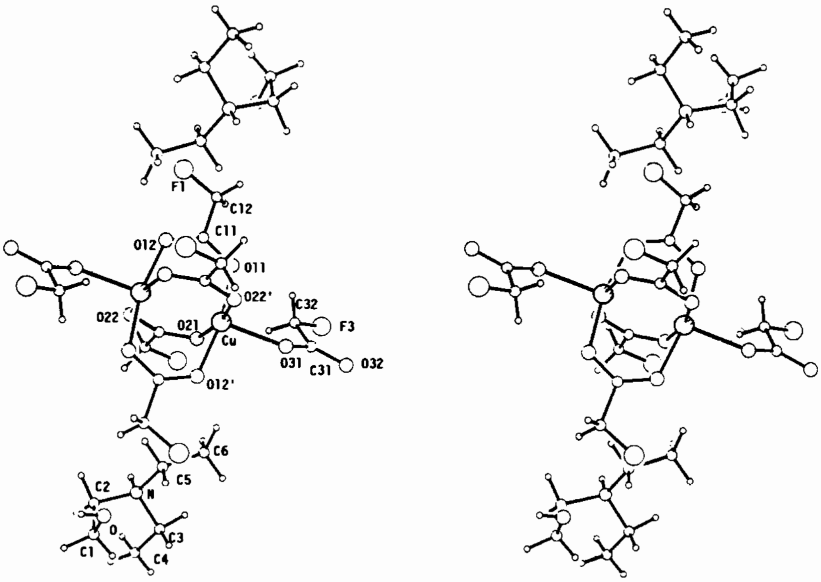

Fig. 2. Stereoview of $(C_6H_{16}NO)_2[Cu_2(FH_2CCOO)_4(FH_2CCOO)_2]$.

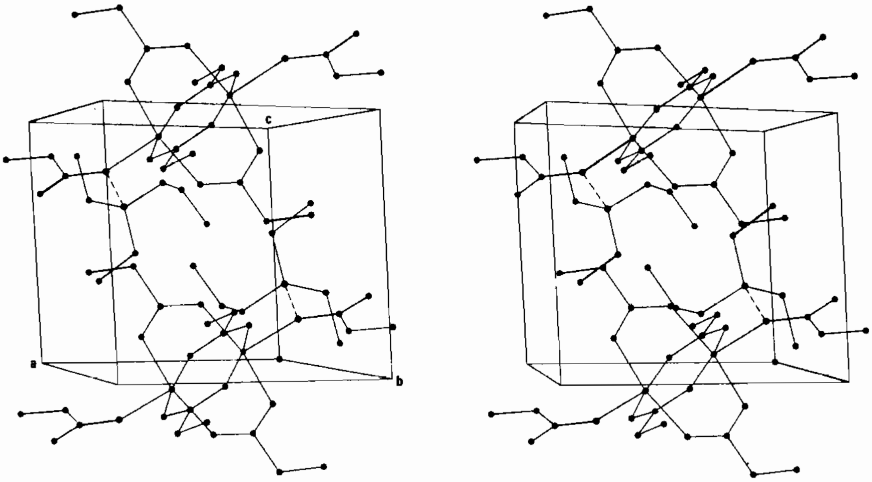

Fig. 3. Stereoview of the packing in $(C_6H_{16}NO)_2[Cu_2(FH_2CCOO)_4(FH_2CCOO)_2]$.

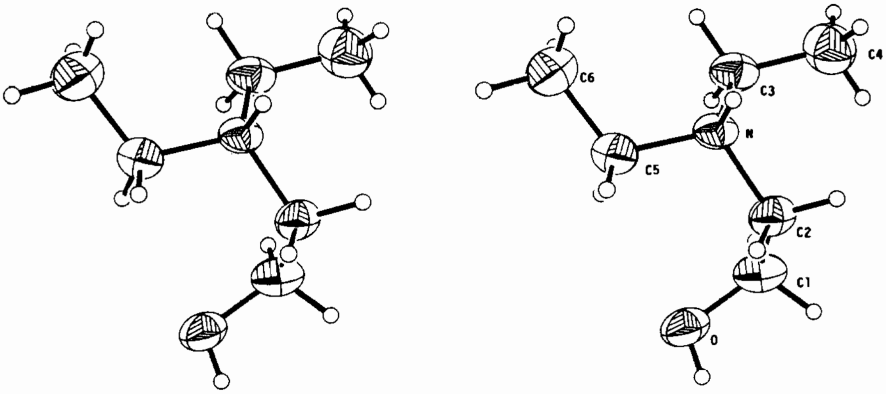

Fig. 4. Stereoview of the $(Et_2NHCH_2CH_2OH)^+$ cation.

The basal plane consists of four oxygen atoms O(11), O(21), O(12′) and O(22′) at distances of 1.952–1.982 Å. The apical Cu–O bond lengths of 2.131(4) and 2.135(1) Å are short, but agree with the values reported for similar structures.

The carboxylato-bridges are planar and perpendicular to each other. The bond lengths and angles agree with literature values [5–7, 10]. The C–O bond lengths of the unidentate carboxyl group in compound **II** differ from each other, being 1.278 for the coordinated and 1.228 Å for the uncoordinated oxygen atom, which has more double-bond character. Also the Cu–O–C angle 132.9° is wider than for the bidentate-bridge groups. The carbon atom C(32) of the axial fluoroactetato ligand makes a short intramolecular contact of 3.193 and 3.232 Å with oxygen atoms O(11) and O(21), respectively. The dihedral angle between the Cu–O–C–O–Cu bridge and the axial carboxyl group is 45.4°. The C–H bond lengths of the fluoroacetato groups vary from 0.78 to 1.02 Å.

The parameters of primary interest in dimeric carboxylato adducts are the Cu–Cu and Cu–L (axial) distances. A larger Cu–Cu distance is usually associated with greater displacement of copper(II) ions from the basal plane towards the axial ligand [5–7, 9]. The angular dimensions of the carboxylato framework, *viz.*, Cu–O–C and O–C–O angles, readjust themselves to accommodate the varying Cu–Cu distances [1], so that the bridge length (Cu–O–C–O–Cu) remains nearly constant, about 6.44 Å [1, 5].

Structural data for axial oxygen donor ligands of acetato and haloacetato compounds have been tabulated in Table VI. We can see that the Cu–Cu distances increase from 2.581 to 2.685 Å as the axial ligands become more basic or the parent acid of the bridging carboxylato groups more acid. The order of the increase in the displacement of copper(II) ion towards the axial ligand is the same as in the Cu–Cu distances, giving a linear relation between the Cu–Cu distances and the deviations from the basal plane.

The relations here for axial oxygen donor ligands are much more regular than for nitrogen donor ligands, where the Cu–Cu distances range from 2.576 to 2.671 Å for acetato compounds [16]. In haloacetato compounds the Cu–Cu distances are clearly longer (2.724–2.886 Å) [6]. The N-donor ligands are very different in size and shape. Some of them, e.g., pyrazine [17], 1,4-diazabicyclo-[2,2,2]octane [9] and hexamethylenetetramin-*N,N′*, [18], have two equivalent nitrogen donor atoms and form chain structures. In others; e.g., in 2-methylpyridine [19] and quinoline [20] adducts, steric effects associated with the bulky ligands cause elongation of the Cu–N(axial) distances.

The electronic spectra of dinuclear copper(II) carboxylato complexes show two bands, with maxima at *ca.* 28000 cm^{-1} (Band II) and *ca.* 14000 cm^{-1} (Band I) [7, 21]. Band I was assigned by Reimann *et al.* [21] to $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ transition. It is sensitive to the nature of both the ligands $RCOO^-$ and L [8, 21]. Absorption Band II, which appears as a shoulder, is assigned a local symmetry forbidden charge transfer from the carboxylato oxygen atoms to the metal ion, $np_\pi \rightarrow \sigma^*_{x^2-y^2}$ [22, 32]. The position of Band II is almost identical for all dimers [7, 22]. As can be seen in Table VII, the $\bar{\nu}_{max}$ values of Band I shift to higher energy as the axial ligand changes from fluoroacetato to water to dioxane (Fig. 5).

TABLE VI. Structural Data for $Cu_2(RCOO)_4L_2$, where L is O Donor Ligand

R	L	Cu–Cu (Å)[a]	Cu–O (basal) (Å)	Cu–O (apical) (Å)	Cu–basal plane (Å)	Cu–O–C (°)	O–C–O (°)	References
CH_3	CH_3COOH	2.581(1)	1.967(2)	2.197(2)	0.18	122.9(2)	124.5(3)	9
CH_3	CH_3OH	2.597(1)	1.967(2)	2.159(7)	0.18	122.8(2)	124.9(3)	9
CH_3	dmf[b]	2.614(1)	1.964(3)	2.163(3)	0.20	123.2(3)	125.2(4)	9
CH_3	H_2O[c]	2.614(2)	1.969(2)	2.161(2)	0.19	123.0(1)	124.9(1)	26
CH_3	H_2O[d]	2.616(1)	1.969(3)	2.156(4)	0.19	123.1(3)	124.8(4)	27
$(CH_3)_{2.25}$ $(ClCH_2)_{1.75}$	urea	2.631	1.97	2.12	0.21	123.5(2)	124.5(3)	30
CH_3	urea, H_2O	2.625(2)	1.969(6)	2.130(7)	0.210	123.1(7)	125.8(9)	28
$ClCH_2$	urea	2.651	1.97	2.08	0.21		121.2	29
FCH_2	urea	2.657(3)	1.971(7)	2.099(7)	0.209	122.9(7)	126.3(9)	31
		2.674(3)	1.975(7)	2.105(7)	0.215	122.6(7)	127.1(9)	
FCH_2	H_2O	2.674(1)	1.969(2)	2.131(4)	0.214	122.8(2)	126.8(3)	This work
FCH_2	FCH_2COO^-	2.685(1)	1.976(2)	2.135(1)	0.219	122.9(1)	126.9(2)	This work

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. [b] *N,N*-dimethylformamide. [c] Neutron diffraction results. [d] X-ray diffraction results.

TABLE VII. Electronic Spectral Data for some $Cu_2(FH_2CCOO)_4L_2$ Complexes

Axial ligand	Band I	Band II[a]	References
L	$\bar{\nu}/10^3$ cm^{-1}	$\bar{\nu}/10^3$ cm^{-1}	
H_2O	13.7	28.0	25
H_2O	13.9	28.0	this work
FH_2CCOO^-	13.5	28.0	this work
dioxane	14.7	27.4	25

[a] Shoulder.

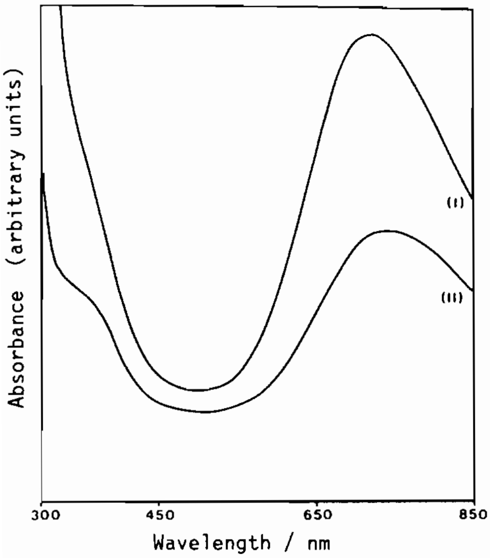

Fig. 5. Electronic absorption spectra of $Cu_2(FH_2CCOO)_4(H_2O)_2$ (I) and $(C_6H_{16}NO)_2[Cu_2(FH_2CCOO)_4(FH_2CCOO)_2]$ (II) in Nujol mulls.

The chelated 2-dialkylaminoethanolato ligands form a five-membered unsymmetric gauche conformation, where the torsion angles (OCCN) are from 43.4 to 47.8° for dimers (except $Cu_2(C_6H_{14}NO)_2(C_6H_5COO)_2$) and from 45.6 to 60.6° for tetramers. In hexanuclears the two five-membered rings are not equal.

In the ring containing the three-coordinate aminoethanol oxygen atom, the torsion angle is about 43° and the ring carbon atoms are on the same side of the CuON plane. In the ring containing the four-coordinate oxygen atom, the torsion angle is about 55° and the carbon atoms are now on different sides of the plane [10]. In the $(Et_2NHCH_2CH_2OH)^+$ cation the torsion angle (OCCN) 80.4° is 20–40° wider than in the rings. It is also much wider than in pure ethylenediamine [23] (64°) and in the free molecule (66.1°) in the $Cu(en)_3{\cdot}Cl{\cdot}0.75en$ [24] complex. Probable reasons for this are the steric hindrances of the alkyl groups and the hydrogen bonds.

The O•••N distance of 3.22 Å in the cation is about 0.5 Å longer than in the rings, where the mean values are 2.646 Å for dimers, 2.700 Å for pseudohalogen and halogen tetramers and 2.725 Å for haloacetato tetramers [10]. The bond lengths in the ion and the rings are about the same, excluding the C–O bond which is longer in tetramers. The angles N–C–C and O–C–C of 116.0 and 114.1° in the ion are 3–10° wider than in the chelate rings. In most cases the N–C–C angle is wider than the O–C–C angle in the rings, too [10]. The C–H bonds in the cation vary from 0.81 to 1.04 Å.

The molecules are held together by hydrogen bonds and van der Waals forces. The intermolecular hydrogen bonds as contacts less that 3.2 Å are tabulated in Table VIII. Least-squares planes are indicated in Table IX.

TABLE VIII. Intermolecular Contacts Below 3.2 Å in $Cu_2(FH_2CCOO)_4(H_2O)_2$ (I) and $(C_6H_{16}NO)_2[Cu_2(FH_2CCOO)_4(FH_2CCOOH)_2]$ (II)

Bond	Compound	A•••B	A–H	H•••B	A–H•••B	Symmetry code
O(31)–H1•••O(11)	I	2.866	0.88	1.99	171.6	$-x, y, 0.5-z$
O(31)–H1•••F(1)	I	3.010	0.88	2.59	124.4	$0.5+x, 0.5+y, z$
O(31)–H2•••O(12)	I	3.025	0.66	2.52	135.5	$0.5+x, 0.5+y, z$
C(12)–H2•••F(2)	I	2.969	1.00	2.91	83.4	$-0.5+x, 0.5+y, z$
C(11)•••F(2)	I	2.829				$-0.5+x, 0.5+y, z$
C(12)•••F(2)	I	2.969				$-0.5+x, 0.5+y, z$
F(1)•••F(2)	I	3.067				$-0.5+x, 0.5+y, z$
O(12)•••F(2)	I	3.115				$-0.5+x, 0.5+y, z$
O(22)•••F(1)	I	3.199				$0.5+x, -0.5-y, 0.5+z$
O–H•••O(32)	II	2.740	0.81	1.94	173.1	$1-x, -y, 1-z$
N–H•••O(31)	II	2.772	0.87	1.91	167.1	$1-x, 1-y, 1-z$
C(1)–H2•••O(12)	II	3.142	0.98	2.47	125.6	$1+x, y, z$
C(1)–H1•••F(3)	II	3.178	1.00	2.56	119.7	$1-x, -y, 1-z$

TABLE IX. Least-squares Planes (*; unit weights) and Deviations from the Planes (A)

(a) I $8.828x + 5.577y - 9.552z = -3.654$
II $3.298x - 4.545y + 7.389z = 2.545$

	I	II
Cu	0.214	0.219
O(11)*	−0.003	−0.001
O(12′)*	−0.003	−0.001
O(21)*	0.003	0.001
O(22′)*	0.003	0.001
O(31)	2.332	2.350

(b) I $-6.942x + 7.543y + 6.871z = 3.438$
II $6.526x + 5.431y + 1.723z = 3.580$

	I	II
Cu*	−0.002	0.005
Cu′*	−0.004	−0.011
O(11)*	0.011	0.003
O(12)*	0.013	0.022
C(11)*	−0.019	−0.020
O(31)	−0.303	0.149

(c) I $6.363x + 0.012y + 7.236z = 3.620$
II $-2.749x + 5.117y + 10.698z = 7.907$

	I	II
Cu*	−0.009	0.002
Cu′*	0.006	−0.002
O(21)*	0.017	−0.004
O(22)*	−0.001	−0.001
C(21)*	−0.012	0.003
O(31)	−0.028	0.076

(I) $a - b = 91.9$; $a - c = 91.0$; $b - c = 91.7°$; (′) $-x, -y, 1 - z$

(II) $a - b = 89.9$; $a - c = 88.7$; $b - c = 90.2°$; (′) $-x, 1 - y, 1 - z$.

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