

The Crystal and Molecular Structure of a Dinuclear Cu(II)-Complex Tetrakis[μ -(3-chloropropionato)]-bis(4-picoline)- dicopper(II)

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The structure of the title compound has been determined by X-ray crystallographic methods. The crystals are triclinic, space group $P\bar{1}$, $a=8.475(3)$ Å, $b=8.903(3)$ Å, $c=10.204(5)$ Å, $\alpha=97.27(3)^\circ$, $\beta=92.45(4)^\circ$ and $\gamma=93.72(3)^\circ$. The structure was solved by direct methods and refined to an R value of 0.038 for 3509 reflections.

The structure consists of centrosymmetric dinuclear units in which the two Cu(II) ions are bridged by four carboxyl groups in *syn-syn* configuration so that the Cu-Cu distance is 2.675(2) Å. The Cu-coordination is elongated octahedral with the carboxyl oxygen atoms in the basal plane (Cu-O \approx 1.97 Å) and a 4-picoline molecule (Cu-N=2.170(2) Å) and copper(II) ion in the terminal positions. The structural data are discussed in comparison with the known structures of copper(II) propionates.

The carboxylato-bridged transition-metal dimers $M_2(\text{RCOO})_4L_2$ have been studied extensively. The metal-metal interactions vary from very weak single bonds to exceptionally strong multiple bonds.^{1,2} Previous reviews of dinuclear copper(II) tetracarboxylates consisting of four triatomic bridges have concentrated on structural, spectral and magnetic data.^{3,4} Some of the copper(II) carboxylates show antimicrobial effects.⁵

In the preceding papers^{6,7} we have reported preparations, spectral and magnetic properties of copper(II) 3-chloropropionate monohydrate and

copper(II) 3-chloropropionate with 4-picoline and proposed that the compounds have structures similar to that of copper(II) acetate monohydrate.⁸ To verify our conclusions and because practically no work of X-ray has been done on copper(II) halogenopropionate compounds we further carried out on X-ray analysis for $\text{Cu}_2(3\text{-ClC}_2\text{H}_4\text{COO})_4(4\text{-pic})_2$.

EXPERIMENTAL

A light green complex $\text{Cu}_2(3\text{-ClC}_2\text{H}_4\text{COO})_4(4\text{-pic})_2$ was prepared by treating 4-picoline with copper(II) 3-chloropropionate monohydrate as described previously.⁷ A single crystal, 0.41 \times 0.40 \times 0.12 mm was used for the measurements of crystal and intensity data.

The unit cell parameters and the orientation matrix were determined by a least-squares refinement based on 15 centered reflections measured at 20 °C on a Nicolet R3m diffractometer. Intensity data were collected ($3^\circ < 2\theta < 60^\circ$) in the ω -scan mode, using graphite-monochromatized $\text{MoK}\alpha$ radiation. The scan range was $\pm 0.5^\circ$ and the scan speed varied from 2.55 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 $\text{MoK}\alpha$ -peak. Each background was measured for half the scan time. The intensity of a standard reflection, recorded after every 99 measurements, remained essentially constant. The intensities were corrected for Lorentz and polarization effects and for absorp-

tion from empirical ψ -scan data from 8 reflections. Of the 4441 reflections collected, 3509 had $|F_o| > 5\sigma_{F_o}$ and were used in subsequent calculations.

CRYSTAL DATA

$\text{Cu}_2(3\text{-ClC}_2\text{H}_4\text{COO})_4(\text{NC}_6\text{H}_7)_2$,
 $\text{Cu}_2\text{Cl}_4\text{O}_8\text{N}_2\text{C}_{24}\text{H}_{30}$
 Space group: $P\bar{1}$ (No. 2),
 $a=8.475(3)$ Å, $b=8.903(3)$ Å, $c=10.204(5)$ Å,
 $\alpha=97.27(3)^\circ$, $\beta=92.45(4)^\circ$, $\gamma=93.72(3)^\circ$,
 $V=761.1$ Å³, $Z=1$, $F(000)=378$,
 $\mu(\text{MoK}\alpha)=18.5$ cm⁻¹, $\lambda(\text{MoK}\alpha)=0.71069$ Å,
 $D_x=1.62$ g cm⁻³.

STRUCTURE DETERMINATION

Direct methods (SOLV)⁹ gave the positional parameters of the copper atom. All remaining non-hydrogen atoms were located on subsequent Fourier maps.

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 positional parameters of hydrogen atoms were refined.

The refinement converged to an R value of 0.038 and to a weighted discrepancy factor $R_w = \frac{\sum |F_o| - |F_c|}{\sqrt{w} \sum |F_o| \sqrt{w}}$ of 0.039 with the weighting scheme $w^{-1} = \sigma_{F_o}^2 + 0.0005 |F_o|^2$.

The structure was refined by the blocked-cascade full-matrix least-squares method.⁹ The

Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^3$) for non-hydrogen atoms with e.s.d.'s in parentheses.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ^a
Cu	578(1)	374(1)	-1124(1)	31(1)
O1	-177(2)	-1730(2)	-1828(2)	46(1)
O2	-1106(2)	-2364(2)	57(2)	45(1)
C1	-808(3)	-2650(3)	-1141(2)	38(1)
C2	-1288(4)	-4232(3)	-1809(3)	50(1)
C3	-801(5)	-4515(4)	-3211(3)	62(1)
C11	-1789(2)	-6196(1)	-4057(1)	107(1)
O3	2505(2)	-426(2)	-395(2)	42(1)
O4	1535(2)	-1058(2)	1475(2)	48(1)
C4	2585(3)	-1035(3)	646(2)	37(1)
C5	4077(3)	-1788(3)	950(3)	44(1)
C6	4807(3)	-2527(3)	-255(3)	49(1)
C12	3525(1)	-4053(1)	-1093(1)	80(1)
N	1670(2)	942(2)	-2899(2)	37(1)
C7	1753(4)	-59(3)	-3972(3)	60(1)
C8	2524(5)	258(4)	-5070(3)	68(1)
C9	3295(4)	1653(4)	-5088(3)	52(1)
C10	3200(4)	2696(4)	-3984(3)	62(1)
C11	2377(4)	2305(3)	-2936(3)	53(1)
C12	4186(5)	2029(6)	-6255(4)	76(2)

^aEquivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

neutral atom scattering factors have been taken from Ref. 10.

The calculations were performed on a Nicolet R3m diffractometer system with SHELXTL⁹ software for minicomputer (Nova 3). The figures were drawn with SHELXTL⁹ programs on a Zeta-plotter. The final atomic positional and

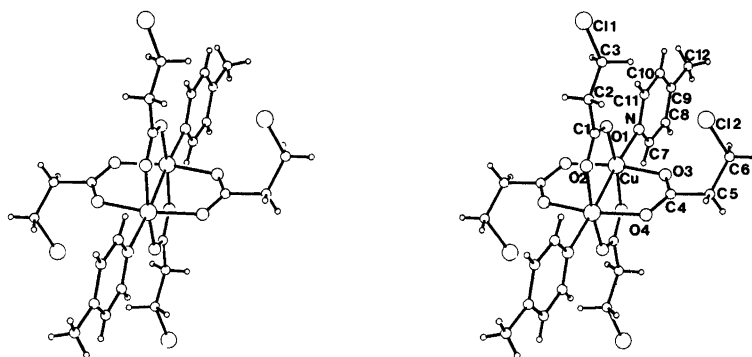


Fig. 1. Stereoview of $\text{Cu}_2(3\text{-ClC}_2\text{H}_4\text{COO})_4(4\text{-pic})_2$.

Table 2. Fractional atomic coordinates ($\times 10^3$) and isotropic thermal parameters ($\times 10^3$) for hydrogen atoms.

Atom	x	y	z	U
H1(C2)	-229(4)	-433(4)	-184(3)	60
H2(C2)	-88(4)	-488(4)	-131(3)	60
H1(C3)	-107(4)	-369(4)	-381(4)	74
H2(C3)	37(4)	-450(4)	-324(4)	74
H1(C5)	374(3)	-254(3)	150(3)	52
H2(C5)	478(4)	-101(3)	135(3)	52
H1(C6)	495(4)	-198(4)	-94(3)	59
H2(C6)	575(4)	-295(4)	-5(3)	59
H1(C7)	128(4)	-100(4)	-399(3)	70
H1(C8)	260(4)	-44(4)	-573(4)	80
H1(C10)	362(4)	374(4)	-401(4)	73
H1(C11)	221(4)	294(4)	-229(3)	62
H1(C12)	456(5)	305(5)	-616(4)	91
H2(C12)	371(5)	184(5)	-700(5)	91
H3(C12)	502(5)	158(5)	-625(4)	91

thermal parameters with their e.s.d.'s for non-hydrogen atoms are given in Table 1 and for hydrogen atoms in Table 2. Bond distances and angles are given in Table 3.

RESULTS AND DISCUSSION

The crystal structure of tetrakis- $[\mu$ -(3-chloropropionato)]-bis(4-picoline)-dicopper(II), $\text{Cu}_2(3\text{-ClC}_2\text{H}_4\text{COO})_4(4\text{-pic})_2$ consists of centrosymmetric tetracarboxylato-bridged dimers, where the Cu-Cuⁱ distance is 2.675(1) Å. This is a molecular structure typical of carboxylato complexes, where the Cu-Cu distances are in the range 2.56–2.88 Å.³

The basal plane consists of four oxygen atoms O1, O3, O2ⁱ and O4ⁱ at distances of 1.962–1.977 Å. The fifth site is occupied by the second copper(II) ion and the sixth site by the nitrogen atom of the 4-picoline molecule. The apical Cu-N bond length of 2.170(2) Å and the Cu-O(carboxylic) bond lengths are in good agreement with those found in other dinuclear carboxylato complexes.³ The copper(II) ion is displaced 0.221 Å from the least-squares plane defined by the basal atoms toward the apical nitrogen atom. The sum of the bond lengths 11.39 Å in $\text{Cu}_2(3\text{-ClC}_2\text{H}_4\text{COO})_4(4\text{-pic})_2$ (the half value of the Cu-Cuⁱ distance is also included in the sum) agrees well with the values reported for

Table 3. Interatomic distances (Å) and angles (°) with e.s.d.'s in parentheses.

The copper(II) environment			
Cu-O1	1.974(2)	N-Cu-O1	96.8(1)
Cu-O2 ⁱ	1.973(2)	N-Cu-O2 ⁱ	96.1(1)
Cu-O3	1.977(2)	N-Cu-O3	94.3(1)
Cu-O4 ⁱ	1.962(2)	N-Cu-O4 ⁱ	98.6(1)
Cu-N	2.170(2)	N-Cu-Cu ⁱ	176.2(1)
Cu-Cu ⁱ	2.675(1)	Cu ⁱ -Cu-O1	83.5(1)
		Cu ⁱ -Cu-O2 ⁱ	83.6(1)
O1-Cu-O3	88.5(1)	Cu ⁱ -Cu-O3	81.9(1)
O1-Cu-O2 ⁱ	167.1(1)	Cu ⁱ -Cu-O4 ⁱ	85.2(1)
O1-Cu-O4 ⁱ	90.4(1)	O3-Cu-O2 ⁱ	90.7(1)
O3-Cu-O4 ⁱ	167.1(1)	O2 ⁱ -Cu-O4 ⁱ	87.6(1)
The 3-chloropropionato ligands			
O1-C1	1.252(3)	O3-C4	1.254(3)
O2-C1	1.257(3)	O4-C4	1.255(3)
C1-C2	1.508(3)	C4-C5	1.507(4)
C2-C3	1.501(4)	C5-C6	1.497(4)
C3-C11	1.771(3)	C6-C12	1.787(3)
Cu-O1-C1	123.6(2)	Cu-O3-C4	124.9(2)
C1-O2-Cu ⁱ	123.5(2)	C4-O4-Cu ⁱ	121.8(2)
O1-C1-O2	125.7(2)	O3-C4-O4	125.6(2)
O1-C1-C2	117.6(2)	O3-C4-C5	117.7(2)
O2-C1-C2	116.7(2)	O4-C4-C5	116.6(2)
C1-C2-C3	113.5(2)	C4-C5-C6	113.6(2)
C2-C3-C11	111.1(2)	C5-C6-C12	111.1(2)
The 4-picoline ligand			
N-C7	1.329(3)	Cu-N-C7	122.8(2)
N-C11	1.323(4)	C7-N-C11	116.2(2)
C7-C8	1.371(5)	N-C7-C8	123.4(3)
C8-C9	1.368(5)	C7-C8-C9	120.2(3)
C9-C10	1.375(4)	C8-C9-C10	116.6(3)
C9-C12	1.498(5)	C8-C9-C12	121.7(3)
C10-C11	1.371(5)	C10-C9-C12	121.7(3)
		C9-C10-C11	119.9(3)
		C11-N-Cu	120.8(2)
		N-C11-C10	123.7(3)
Symmetry code			
(i)	-x, -y, -z		

known dinuclear structures with the CuO_4N chromophores (11.38 Å).³

The 4-picoline molecule is planar, the greatest displacement from the least-squares plane being 0.018 Å (C8). In the ring the C-N bond lengths are slightly shorter than the C-C bond lengths. The bond angles vary from 116.2 to 123.7° and the bond lengths from 1.323 to 1.371 Å. These

Table 4. Selected structural data for the dinuclear copper(II) propionates with heterocyclic *N*-donor ligands.^a

Compound ^b	Cu–Cu Å	Cu–O (basal) Å	Cu–N (apical) Å	Ref.
Cu ₂ (C ₂ H ₅ COO) ₄ (3-pic) ₂	2.6312(4)	1.970(2)	2.167(2)	14, 15
Cu ₂ (C ₂ H ₅ COO) ₄ (py) ₂	2.642(2)	1.96(1)	2.17(1)	11
	2.619(2)	1.97(1)	2.13(1)	
Cu ₂ (C ₂ H ₅ COO) ₄ (3,5-lut) ₂	2.6447(6)	1.975	2.168(2)	16
Cu ₂ (C ₂ H ₅ COO) ₄ (2-pic) ₂	2.647(4)	1.97(1)	2.21(2)	17
Cu ₂ (C ₂ H ₅ COO) ₄ (4-pic) ₂	2.655(3)	1.971(9)	2.143(9)	13
	2.659(3)	1.971(9)	2.148(9)	
Cu ₂ (3-ClC ₂ H ₄ COO) ₄ (4-pic) ₂	2.675(1)	1.971(2)	2.170(2)	This work

^a Where more than one chemically equivalent distance is present, the mean value is tabulated. Estimated standard deviations in parentheses are average e.s.d.'s for the individual distance. ^b Abbreviations: 3-pic=3-picoline, py=pyridine, 3,5-lut=lutidine, 2-pic=2-picoline, 4-pic=4-picoline.

agree very well with the values reported for pyridine^{11,12} and 4-picoline¹³ complexes.

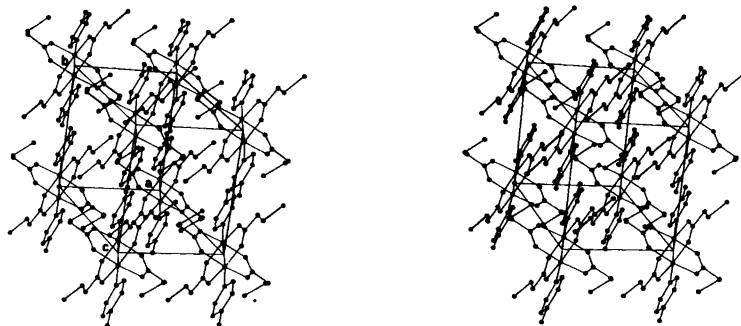
The carboxylato-bridges are planar and perpendicular to each other. Also here the bond lengths and angles agree with other values.^{11,13–17} The C–H bond lengths vary from 0.83(5) to 1.04(4) Å.

The 4-picoline molecule and one of the carboxylato-bridges are nearly coplanar, C12 having the greatest displacement (0.16 Å). The dihedral angles between 4-picoline and carboxylato-bridges are 8.8 and 86.2°. The 4-picoline is a weak π acceptor and could make a π back-bonding with the copper(II) ion. The Cu–N bond length 2.170(2) Å is somewhat longer or about the same than in other copper(II) propionato complexes with pyridine¹¹ and 4-picoline¹³ where the orientation of the pyridine rings are not the best for π back-bonding. The long Cu–N

bond length together with the dihedral angle 8.8° suggest that 4-picoline functions here almost entirely as a σ -donor base.

Table 4 contains selected structural data for copper(II) propionato complexes with heterocyclic *N*-donor ligands. In general the Cu–Cu distance is elongated when the acid strength increases.³ We can see from Table 4 for instance that the Cu–Cu distances of 2.655(3) and 2.659(3) Å found in Cu₂(C₂H₅COO)₄(4-pic)₂ are somewhat shorter than 2.675(1) Å found in Cu₂(3-ClC₂H₄COO)₄(4-pic)₂. This observation corresponds very well with the p*K*_a values of the respective acids 4.89 and 4.096, respectively.

Manohar *et al.*¹⁸ have found out that in Cu₂(CH₃COO)₄L₂ complexes the Cu–Cu distances lengthen as the ligands in the axial positions become stronger. Thus a stronger coordination tends to weaken the Cu–Cu interaction.

**Fig. 2.** Stereoview of the packing.

The more basic the axial ligands are the more they would lengthen the Cu–Cu distance. Also the propionato complexes show the same effect but not so clearly. The basic strength of the axial ligands changes in the series from pyridine < 3-picoline < 2-picoline \approx 4-picoline < to 3,5-lutidine.

The shortest intermolecular contact is 3.346 Å between C23 and O21 (1-x, -y, -z) atoms; other distances are longer than 3.45 Å.

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