Crystal and Molecular Structure and Spectral Properties of the Dimeric Alkoxo-oxygen Coordinated Copper(II) Complex Formed with 2-Diethylaminoethanol and 3-Hydroxobenzoic Acid

KIMMO SMOLANDER

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

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Abstract

The crystal and molecular structure of $[Cu_2(C_6H_{14}NO)_2(3\text{-}OH\cdot C_6H_4COO)_2]$ has been determined by three dimensional X-ray crystallography. The complex crystallizes in the monoclinic space group $P2_1/n$ with $a = 8.733(5)$, $b = 21.670(19)$, $c = 15.270(10)$ Å, $\beta = 96.14(5)°$, $Z = 4$. The structure was solved by direct methods and refined to the R values 0.057 and 0.052 using 2043 independent reflections. The C atoms of the 2-diethylaminoethanolato ligands are disordered through having one or more rotational orientations.

Each Cu(II) ion has a distorted elongated square-pyramidal environment (4 + 1). Two alkoxo O atoms, a benzoato O atom and an amino N atom form the basal plane with Cu–O bonds of 1.885–1.935 Å and a Cu–N bond of 1.984(8)–2.023(6) Å, and the axial site is occupied by a phenolic O atom with a Cu–O distance of 2.562(6) or 2.808(6) Å. The Cu–Cu distance in the non-centrosymmetric dimer is 2.958(2) Å.

The dimers are joined into a one-dimensional polymeric chain in the direction of the c-axis by phenolic O atoms. These form long bonds to the Cu(II) ions and strong hydrogen bonds to the uncoordinated carboxylate O atoms.

The electronic spectrum in Nujol shows a broad flat band, centred at about 16000 cm^{-1} with a shoulder at 27000 cm^{-1}. The broad band is attributed to d–d transitions and the shoulder to charge transfer from a p_π orbital of the bridging O atom to the unfilled d orbital of the Cu(II) ion. The latter is a characteristic feature of the alkoxo-bridged structure.

The IR spectrum shows the carboxylate stretching frequency ν(COO)(asym) as a broad band at 1550 cm^{-1}, and ν(COO)(sym) as a broad band at 1390 cm^{-1} with a shoulder at 1375 cm^{-1}.

The known structures of copper(II) 2-dialkylaminoethanolato complexes are tabulated.

Introduction

Though the alkoxo-bridged copper(II) complexes have received considerable attention in recent years and their structural, magnetic and spectral properties have been extensively studied, much less attention has been paid to their mixed ligand complexes. In most of these the main ligand has been an amino- or amino-thioalcohol and the second ligand a halogen or pseudo-halogen ion. Structures are typically dimeric, polymeric with dimeric units or cubane-like tetrameric [1–5].

The possibilities for complicated structures increase if the second ligand is a carboxylate ion, which is able to coordinate to metal ions in a number of different ways. Structures can vary from uncoordinated ionic via unidentate to bidentate, with several combinations of these [6].

Many interesting copper(II) structures formed with dialkylaminoethanols (DR-no) and carboxylate ions have been shown to be in the solid state, e.g. mononuclear [7], dimeric [1], trinuclear [1], tetrameric [1], hexanuclear [1] and even nonanuclear [8]. When we further take as the carboxylato ligand a hydroxobenzoic acid anion that can coordinate to metal ion through a variety of dentation modes, the possibilities for variation become still more numerous. In this study we report the details of the molecular and crystal structure and the electronic and infrared spectral properties of $[Cu_2(DEt\text{-}no)_2(3\text{-}OH\text{-}C_6H_5COO)_2]$.

Experimental

Preparation of the Complex

The 3-hydroxobenzoic acid (3-OH-ben; Fluka 54620) was first converted to its sodium salt with sodium hydroxide in molar ratio of 1:1 in warm water. Copper(II) sulphate pentahydrate (Merck 2790) in water was then added to this solution so

0020-1693/87/$3.50

TABLE I. Crystal Data, Data Collection and Refinement Data

Formula	$C_{26}H_{38}Cu_2N_2O_8$
Formula weight	633.68
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	8.733(5)
b (Å)	21.670(19)
c (Å)	15.270(10)
β (°)	96.14(5)
V (Å^3)	2873.2
Z	4
D_c (g cm^{-3})	1.47
D_o (g cm^{-3})	1.47
λ (Å) (Mo Kα)	0.71069
Monochromator	graphite
Linear absolute coefficient (cm^{-1})	15.9
Crystal size (mm)	0.20 × 0.31 × 0.34
Diffractometer	Nicolet R3m
Data collection method	ω
2θ range (°)	3.0–50.0
Scan rate (° min^{-1})	2.5–29.3
Number of standard reflections	1
Variation in standard intensities	±1%
Reflections collected	4986
Reflections used in refinement $I > 2.5\sigma(I)$	2043
Number of variables	466
R (= $\Sigma\Delta/\Sigma\lvert F_o\rvert$)[a]	0.057
R_w (= $\Sigma\Delta w^{1/2}/\Sigma\lvert F_o\rvert w^{1/2}$)[b]	0.052
Residual electron density (e Å^{-3})	0.61
T (K)	293
$F(000)$ (e)	1328
h range	0–11
k range	0–25
l range	−19 to 19

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

that the acid–copper molar ratio was 2:1. The pH was adjusted with the 3-OH-ben acid to between 5 and 5.5. The solution was then heated to boiling temperature, filtered and left to stand at ambient temperature. The green product that precipitated was collected and recrystallized from ethanol. The complex was prepared by combining a warm acetone solution of the copper(II) 3-hydroxobenzoate with 2-diethylaminoethanol (DEt-no; Fluka AG) in molar ratio of 1:1.1. The solution was refluxed, filtered and left to evaporate slowly at ambient temperature. After a few days very dark blue crystals were collected, washed with cold methanol/ether mixture and dried in a desiccator.

Spectral Studies

The electronic spectrum was measured in the region 300–850 nm with a Shimadzu UV-240 spectrophotometer, and the infrared spectrum in the region 200–4000 cm^{-1} with a Perkin-Elmer 1330 spectrophotometer. In both cases the Nujol suspension technique was used.

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 25 well-centred reflections measured at 20 °C with a Nicolet R3m diffractometer.

Intensity data were collected with the same diffractometer, using graphite-crystal monochromated Mo Kα radiation (λ = 0.71069 Å), by the ω-scan technique. The intensity of one check reflection recorded after every 99 measurements remained essentially constant throughout the data collection. The intensities were corrected for Lorenz and polarization effects but not for absorption.

Structure Determination

The structure was solved by direct methods and Fourier techniques, and refined by blocked-cascade full-matrix least-squares with anisotropic temperature factors for all non-hydrogen atoms except C(22) [9].

The disorder of the C atoms of the DEt-no ligands was evident in the distances involving these atoms and in the shape and size of their thermal ellipsoids. A difference map calculated without the disordered C atoms showed severe dispersion of the electron density. The disordered atoms were therefore given a site occupation factor of 0.5. The corresponding bond length pairs of the atoms were fixed together and refined as such. The two disordered positions of atoms C(22), C(23), C(24) and C(25) refined well, giving site occupation factors of about 0.5, and in subsequent calculations they were considered fixed. The disorders were concluded to arise from a mixture of one or more rotational orientations of the DEt-no ligand around the N–Cu axis (as shown in Fig. 3). Attempts to resolve the orientation disorder of atoms C(12), C(13), C(14), C(15) and C(16) by creating two half-weighted carbon atoms near the ends of the major ellipsoid axis failed.

The H atoms bonded to C atoms were included at calculated positions with fixed bond lengths (C–H = 0.96 Å) and constrained angles. The isotropic thermal parameters for the H atoms were set at 1.2 times the equivalent isotropic thermal parameter for the corresponding C atom. The positional parameters of H atoms of the benzoato groups were refined.

The phenolic H atoms could not be clearly located from a regular difference Fourier map. Consequently, a second and a third difference map were calculated using approximately one-third and one-fourth of the data respectively. These maps showed peaks near the phenolic O atom O(24) and carboxyl O atom O(23) and the H atoms were accordingly given these positions.

The calculations were done with a Nicolet R3m diffractometer system with SHELXTL software for minicomputer (Nova 3) [9]. The program uses neutral atom scattering factors from ref. 10 and takes anomalous dispersion into account. The figures were drawn with SHELXTL program on a Zeta-plotter.

The final atomic coordinates and thermal parameters with their e.s.d.s for non-hydrogen atoms are given in Table II. Bond distances and angles are given in Table III.

TABLE II. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\times 10^3$) for [Cu$_2$(DEt-no)$_2$(3-OH-ben)$_2$]

Atom[a]	*x*	*y*	*z*	*U*
Cu(1)	−901(1)	−882(1)	−3071(1)	50(1)
Cu(2)	−125(1)	206(1)	−1940(1)	56(1)
O(11)	−1626(6)	−452(3)	−2103(4)	55(2)
N(1)	−3027(9)	−1209(3)	−3307(5)	75(3)
C(11)	−3175(12)	−561(5)	−2006(7)	70(5)
C(12)	−3738(17)	−1053(10)	−2497(11)	203(11)
C(13)	−2962(19)	−1811(2)	−3303(13)	262(14)
C(14)	−3667(24)	−2342(5)	−3312(11)	315(17)
C(15)	−3881(16)	−993(12)	−4102(13)	207(12)
C(16)	−3382(19)	−715(11)	−4781(10)	200(13)
O(12)	−4(7)	−1215(3)	−4063(3)	54(2)
O(13)	1433(8)	−1978(3)	−3445(4)	77(3)
O(14)	2327(8)	−742(3)	−6814(4)	79(3)
C(17)	1025(10)	−1629(5)	−4057(6)	47(4)
C(18)	1792(9)	−1668(4)	−4889(5)	40(3)
C(19)	1705(10)	−1204(4)	−5484(5)	48(3)
C(110)	2457(10)	−1233(4)	−6241(5)	54(4)
C(111)	3269(11)	−1747(5)	−6399(6)	61(4)
C(112)	3388(11)	−2221(5)	−5796(6)	65(4)
C(113)	2651(10)	−2183(4)	−5047(5)	52(3)
O(21)	692(7)	−307(3)	−2783(4)	82(3)
N(2)	1885(8)	665(2)	−1977(4)	58(3)
C(21)	2058(13)	−134(5)	−3077(8)	81(5)
C(22)	2298(20)	541(2)	−2859(5)	58(5)
C(22)*	2945(9)	315(11)	−2459(16)	140(16)
C(23)	2059(32)	1295(7)	−1713(12)	89(12)
C(23)*	1470(29)	1201(10)	−2491(26)	216(30)
C(24)	897(24)	1663(10)	−2366(16)	155(12)
C(24)*	2827(29)	1656(13)	−2596(31)	261(29)
C(25)	3100(21)	332(8)	−1404(9)	68(8)
C(25)*	2506(35)	939(2)	−1119(6)	260(25)
C(26)	2822(14)	418(3)	−425(7)	127(7)
O(22)	−822(7)	678(3)	−998(4)	63(3)
O(23)	−3110(7)	985(3)	−1635(3)	68(4)
O(24)	−394(7)	1669(3)	1979(3)	57(3)
C(27)	−2104(10)	962(4)	−1013(5)	51(3)
C(28)	−2371(10)	1285(4)	−171(6)	45(3)
C(29)	−1263(11)	1307(4)	540(6)	44(3)
C(210)	−1534(10)	1620(4)	1290(6)	45(3)
C(211)	−2942(12)	1889(5)	1354(6)	67(4)
C(212)	−4029(12)	1876(6)	655(8)	96(6)
C(213)	−3757(11)	1570(6)	−125(7)	82(5)
H(024)	−2727	993	−2247	73
H(025)	−1050	1869	2551	59

[a] Site occupation factors for the disordered atoms are 0.50.

Discussion

Spectral Results

The electronic absorption spectrum of the title complex shows a shoulder at 27 000 cm^{-1}. This is a characteristic feature of the alkoxo-bridged structure and is assigned to charge transfer from a p_π orbital of the bridging oxygen atom to the unfilled d orbital of the copper(II) ion [4]. The band is found between 24 000 and 29 000 cm^{-1} for aminoalcoholato dimers ([Cu$_2$(DR-no)$_2$X$_2$] and [Cu$_2$(DR-nno)$_2$X$_2$] [11–14] which is a little higher than for thioalcoholato dimers [Cu$_2$(R-so)$_2$X$_2$] [15] 22 000–24 000 cm^{-1} and thioaminoalcoholato dimers [Cu$_2$(R-sno)$_2$X$_2$] [13] about 24 000 cm^{-1}.

The broad flat band at 14 900–17 400 cm^{-1} and centred at about 16 000 cm^{-1} is attributable to d–d transitions.

The infrared spectrum shows the carboxylate stretching frequencies ν(COO)(asym) and ν(COO)(sym), the first as a broad band at 1550 cm^{-1} and the second as a broad band at 1390 cm^{-1} with a shoulder at 1375 cm^{-1}. Deacon and Phillips [6] reported that the separation between the ν(COO) frequencies of carboxylato complexes depends on the coordination of the carboxylate RCOO$^-$ ion. The separation is over 200 and 260 cm^{-1} in unidentate acetato and trifluoroacetato complexes and less than 150 and 200 cm^{-1} in the corresponding bidentate (chelating or bridging) complexes. In ionic compounds it is about 165 and 230 cm^{-1} for acetate and trifluoroacetate, respectively. The ν(COO)(asym) band is reported sensitive to the electron-withdrawing effect of R in carboxylate ions, which increases the frequency [16]. The same effect is observed for the corresponding acids RCOOH but is less marked. The effect of the substituent on the ν(COO)(sym) stretching is quite different: there is no correlation between this frequency and the polar effect of R [16].

The absorption bands of [Cu$_2$(benzoato)$_4$(dimethylsulphoxide)$_2$] [17] are at 1630 and 1400 cm^{-1} with a separation of 230 cm^{-1}. The complex has the common acetato structure where the Cu–O bond lengths are symmetrical about 1.95 Å. In [Cu$_2$(DEt-no)$_2$(benzoato)$_2$], the absorption bands are at 1610 and 1355 cm^{-1} with a separation of 255 cm^{-1}, the benzoato ligand is unidentate and the Cu–O distances are 1.888(4) and 2.907(4) Å [1]. The bands are broader in the title compound, where the carboxyl group is bidentate bridged, forming a strong coordination bond to the Cu(II) ion and a strong hydrogen bond to the phenolic O atom (Cu–O = 1.918 and O···O = 2.59 Å). The band separation is between 160 and 185 cm^{-1}, which differs somewhat from the separations observed for two compounds introduced for comparison.

TABLE III. Interatomic Distances (Å) and Angles (°) with Estimated Standard Deviations in Parentheses

	$n = 1$ $m = 2$	$n = 2$ $m = 1$
The copper(II) environments		
Cu(n)–O(n1)	1.912(6)	1.896(7)
Cu(n)–O(n2)	1.919(6)	1.917(6)
Cu(n)–N(n)	1.984(8)	2.023(6)
Cu(n)–O(m1)	1.885(6)	1.935(6)
Cu(n)–O(m4)	2.562(6)′	2.808(6)″
Cu(n)–O(n3)	3.220(7)	3.182(7)
Cu(n)–Cu(m)	2.958(2)	
O(n1)–Cu(n)–N(n)	86.2(3)	83.1(3)
O(n1)–Cu(n)–O(n2)	172.1(3)	174.2(3)
O(n1)–Cu(n)–O(m1)	78.1(3)	77.3(3)
N(n)–Cu(n)–O(n2)	100.1(3)	95.9(3)
N(n)–Cu(n)–O(m1)	158.7(3)	159.5(2)
O(n2)–Cu(n)–O(m1)	94.6(3)	103.0(2)
Cu(n)–O(n1)–Cu(m)	100.5(3)	102.9(3)
O(m4)–Cu(n)–N(n)	102.7(3)′	108.1(3)″
O(m4)–Cu(n)–O(n1)	88.9(2)′	79.2(3)″
O(m4)–Cu(n)–O(n2)	94.3(2)′	92.2(3)″
O(m4)–Cu(n)–O(m1)	91.5(3)	93.6(2)″
	$n = 1$	$n = 2$
The 2-diethylaminoethanolato ligands		
O(n1)–C(n1)	1.40(1)	1.37(1)
C(n1)–C(n2)	1.36(2)	1.51(1)
N(n)–C(n2)	1.48(2)	1.46(1)
N(n)–C(n3)	1.31(1)	1.43(2)
N(n)–C(n5)	1.43(2)	1.49(2)
C(n3)–C(n4)	1.30(2)	1.56(3)
C(n5)–C(n6)	1.31(3)	1.55(2)
Cu(n)–N(n)–C(n2)	103.5(7)	103.6(6)
Cu(n)–N(n)–C(n3)	108.4(9)	122.0(12)
Cu(n)–N(n)–C(n5)	115.5(9)	108.1(8)
C(n2)–N(n)–C(n3)	104.2(13)	114.1(10)
C(n2)–N(n)–C(n5)	114.0(11)	102.9(9)
C(n3)–N(n)–C(n5)	110.4(14)	104.5(12)
N(n)–C(n2)–C(n1)	118.6(13)	109.9(7)
N(n)–C(n3)–C(n4)	149.4(17)	105.4(15)
N(n)–C(n5)–C(n6)	129.2(13)	109.4(12)
O(n1)–C(n1)–C(n2)	111.7(10)	107.3(10)
C(n1)–O(n1)–Cu(n)	113.8(6)	117.7(6)
C(n1)–O(n1)–Cu(m)	139.6(6)	138.7(7)
	$n = 1$	$n = 2$
The benzoato ligands		
O(n2)–C(n7)	1.269(12)	1.276(6)
O(n3)–C(n7)	1.226(11)	1.225(10)
C(n7)–C(n8)	1.500(12)	1.503(12)
C(n8)–C(n9)	1.353(12)	1.376(12)
C(n9)–C(n10)	1.391(12)	1.372(12)
C(n10)–C(n11)	1.355(14)	1.375(13)
C(n11)–C(n12)	1.377(14)	1.351(14)
C(n12)–C(n13)	1.373(13)	1.405(15)
C(n13)–C(n8)	1.380(12)	1.367(14)
C(n10)–O(n4)	1.376(11)	1.372(10)
Cu(n)–O(n2)–C(n7)	127.5(5)	126.4(4)
O(n2)–C(n7)–O(n3)	122.4(7)	126.1(2)
O(n2)–C(n7)–C(n8)	114.4(8)	115.2(2)
O(n3)–C(n7)–C(n8)	119.4(8)	118.7(2)
C(n7)–C(n8)–C(n9)	121.9(8)	122.1(8)
C(n7)–C(n8)–C(n13)	119.6(8)	118.3(8)
C(n8)–C(n9)–C(n10)	121.8(8)	120.5(9)
C(n9)–C(n10)–C(n11)	119.2(8)	120.3(8)
C(n10)–C(n11)–C(n12)	119.9(9)	119.5(9)
C(n11)–C(n12)–C(n13)	120.2(9)	120.8(10)
C(n13)–C(n8)–C(n9)	118.4(8)	119.6(9)
C(n12)–C(n13)–C(n8)	120.5(8)	119.2(9)
O(n4)–C(n10)–C(n9)	118.6(8)	120.2(8)
O(n4)–C(n10)–C(n11)	122.1(8)	119.6(6)

Symmetry code: (′) $-x, -y, -z$; (″) $-x, -y, -1 - z$.

Description of the Structure of $[Cu_2(DEt\text{-}no)_2(3\text{-}OH\text{-}ben)_2]$

A stereoview of the molecular structure is shown in Fig. 1 and the packing in Fig. 2. The unit cell consists of four discrete non-centrosymmetric dimeric units of $[Cu_2(DEt\text{-}no)_2(3\text{-}OH\text{-}ben)_2]$. The dimers are joined into a one-dimensional polymeric chain in the direction of the c-axis by phenolic O atoms, which form long bonds to the Cu(II) ions and strong hydrogen bonds to the uncoordinated carboxylate O atoms, Figs. 3 and 4. The inversion centre lies between the dimers.

The Cu_2O_2 plane in the dimers is bent off the O–O axis by 10.2°, the Cu–Cu distance being 2.958(2) Å. In the two other non-centrosymmetric complexes known, monoclinic $[Cu_2(DMe\text{-}no)_2(NCS)_2]_n$ and orthorhombic $[Cu_2(DBu\text{-}no)_2Br_2]$, the Cu–Cu distances and dihedral angles are 2.950(1) Å, 17.6° and 3.019(4) Å, 3.5°, respectively (Table IV) [1]. In the centrosymmetric Cu_2O_2 cores of 2-dialkylaminoethanolato copper(II) complexes, the Cu–Cu distances range from 2.956(2) to 3.063(1) Å [1, 3].

The coordination around each of the Cu(II) ions is distorted elongated square-pyramidal (4 + 1). The two alkoxo O atoms, a benzoato O atom and an amino N atom form the basal plane with Cu–O bonds of 1.885(6)–1.935(6) Å and a Cu–N bond of 1.984(8)–2.023(6) Å, which are typical for coordination bonds [1]. The apical site is occupied by the phenolic O atom of the neighbouring molecule. The long Cu–O distances 2.562(6) and 2.808(6) Å for Cu(1)–O(24)′ ($-x$, $-y$, $-z$) and Cu(2)–O(14)″ ($-x$, $-y$,

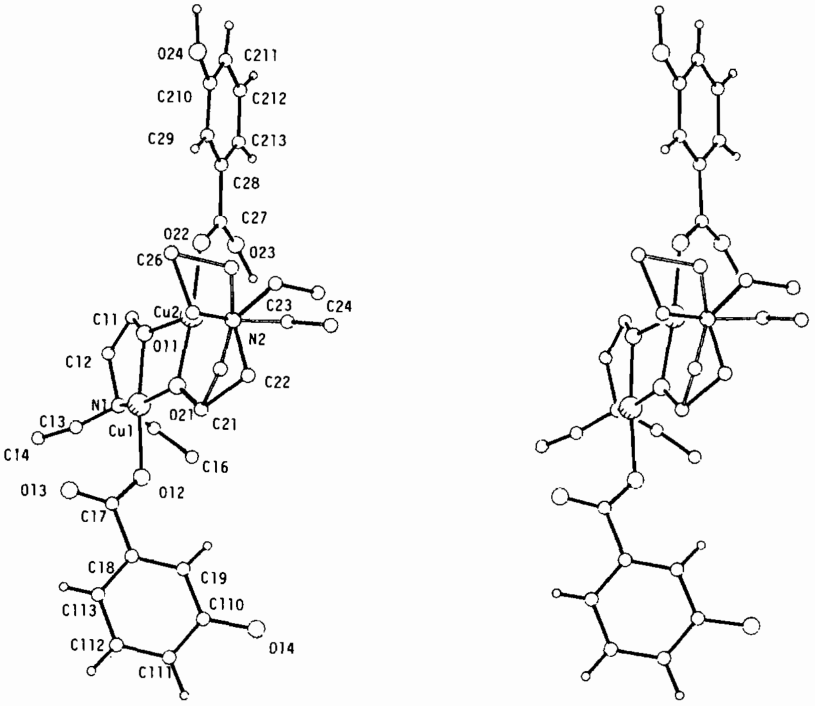

Fig. 1. Stereoview of $[Cu_2(DEt\text{-}no)_2(3\text{-}OH\text{-}ben)_2]$.

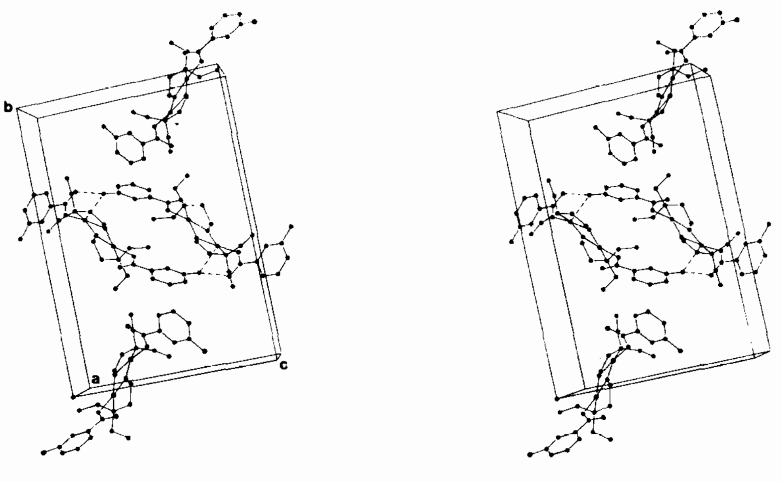

Fig. 2. Stereoview of the packing.

$-1-z$), as also the slight deviation from the basal plane (0.16 and 0.11 Å) toward the apical atom, indicate only weak interaction between those atoms [18].

The apical O atoms lie 6.5° and 14.9° off the z-axis, while the uncoordinated carboxylate O atoms are 50.2° and 56.7° at distances 3.220(7) and 3.182(7) Å for Cu(1) and Cu(2), respectively. These distances and angles deviate considerably from those of the $[Cu_2(DEt\text{-}no)_2(ben)_2]$ [1] complex, where the corresponding values are 45.4° and 2.907(4) Å. A shorter distance (by about 0.3 Å) than in the title complex is expected because the carboxyl group forms an unsymmetrical bidentate bridge between the Cu(II) ion and the phenolic O atom in *syn–syn* configuration.

The dihedral angles between the benzene ring plane and its carboxyl group deviate in molecules I

TABLE IV. Structural Features of the Dialkoxo-bridged Dimeric Copper(II) Complexes of 2-Dialkylaminoethanol

Compound[a]	Cu–Cu (Å)	Cu–O (Å)	Cu–O′ (Å)	Cu–O–Cu′ (°)	O–Cu–O′ (°)	Axial atom (Å)	$-2J$ (cm^{-1})	Molecular symmetry
$[Cu_2(DPr\text{-}no)_2(NCS)_2]_n$	2.956(2)	1.902(6)	1.930(10)	101.0(5)	79.0(5)	S 2.846(6)		C_i
$[Cu_2(DEt\text{-}no)_2(ONO)_2]$	2.976	1.904	1.916	102.3	77.7	O 2.584	361	C_i
$[Cu_2(DEt\text{-}no)_2(NCS)_2]_n$	2.981(2)	1.913(8)	1.937(8)	101.5(3)	78.5(3)	S 2.851(4)	279	C_i
β-$[Cu_2(DEt\text{-}no)_2Br_2]$	3.003(2)	1.900(4)	1.914(4)	103.9(2)	76.1(1)	Br 3.660(2)	744	C_i
$[Cu_2(DEt\text{-}no)_2I_2]$	3.007(1)	1.919(3)	1.907(3)	103.6(1)	76.4(1)	I 3.739(1)		C_i
$[Cu_2(DPr\text{-}no)_2(NCO)_2]$	3.010(1)	1.981(2)	1.924(2)	104.2(1)	75.8(1)		670	C_i
$[Cu_2(DEt\text{-}no)_2(ben)_2]$	3.011(1)	1.902(4)	1.925(4)	103.8(2)	76.2(2)			C_i
α-$[Cu_2(DEt\text{-}no)_2Br_2]$	3.026(2)	1.904(8)	1.924(8)	104.5(4)	75.5(4)		799	C_i
α-$[Cu_2(DEt\text{-}no)_2Br_2]$	3.033(5)	1.873(13)	1.949(13)	105.0(6)	75.0(6)		817	C_i
$[Cu_2(DEt\text{-}no)_2(NCO)_2]$[b]	3.044(1)	1.900(2)	1.944(2)	104.7(1)	75.2(1)		1056	C_i
$[Cu_2(DMe\text{-}no)_2Cl_2]_n$[b]	3.060(1)	1.921(2)	1.957(2)	104.2(1)	75.8(1)	Cl 2.905(1)	1020	C_i
$[Cu_2(DMe\text{-}no)_2Br_2]_n$[b]	3.063(1)	1.927(3)	1.963(3)	103.9(1)	76.1(1)	Br 3.127(1)	1065	C_i
$[Cu_2(DMe\text{-}no)_2(NCS)_2]_n$	2.950(1)	1.918(3)	1.920(2)	100.2(1)	77.2(1)	S 3.073(2)		C_1
		1.888(3)	1.928(2)	101.6(1)	77.7(1)	S 2.884(2)		
$[Cu_2(DEt\text{-}no)_2(3\text{-}OH\text{-}ben)_2]$[c]	2.958(2)	1.912(6)	1.885(6)	100.5(3)	78.1(3)	O 2.562(6)		C_1
		1.896(7)	1.935(6)	102.9(3)	77.3(3)	O 2.808(6)		
α-$[Cu_2(DBu\text{-}no)_2Br_2]$	3.019(4)	1.92(2)	1.93(2)	104.2(7)	75.7(6)		845	C_1
		1.92(2)	1.91(1)	103.8(7)	76.6(7)			

[a] Ref. 1. [b] Ref. 3. [c] This work.

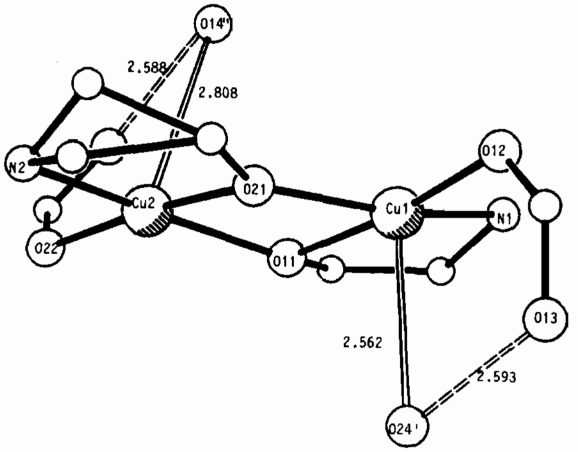

Fig. 3. Fragment of the molecule with the axial atoms and hydrogen bonds.

and II, being 16.9° and 3.8°, respectively. The phenolic O(24) has the maximum deviation from planarity 0.089 Å (except for O(12) and O(13)), due to the stronger interaction with the Cu(II) ion. It is noteworthly that the two C–O distances in each carboxyl group do not seem to be equal. The shorter, which should have more double bond character, involves the O atom hydrogen-bonded to the phenolic O atom. The average value of 1.374 Å for the phenolic C–O bond is somewhat greater ($>3\sigma$) than the corresponding values for salicylato copper(II) complexes having uncoordinated [19, 20], and coordinated [21, 22] phenolic O atoms, where the distances vary from 1.311(5) [22] to 1.335(4) [21] Å.

As mentioned above, the uncoordinated carboxyl O atom and the phenolic O atom form a strong hydrogen bond [23] and the latter also a long bond with the Cu(II) ion (Table V). According to the difference Fourier maps calculated with suppressed data, one of the involved H atoms is unexpectedly bonded to the carboxylic O(23) rather than the phenolic O(14)″. However the C–O carboxylic and phenolic bond lengths are as usually found in unidentate carboxyl groups and phenols (Table III). In bis(*N*′-isopropyl-2-methyl-1,2-propanediamine)Cu(II) salicylate complex where the H atom is at the carboxylic O atom rather than the phenolic O atom [20], the C–O bond lengths reflect this feature: the non-bonded carboxylic C–O bond (1.272(6) Å) is longer than the coordinated C–O bond (1.225(6) Å) and the phenolic C–O bond is about the same as the above reported values (1.325(6) Å) [20].

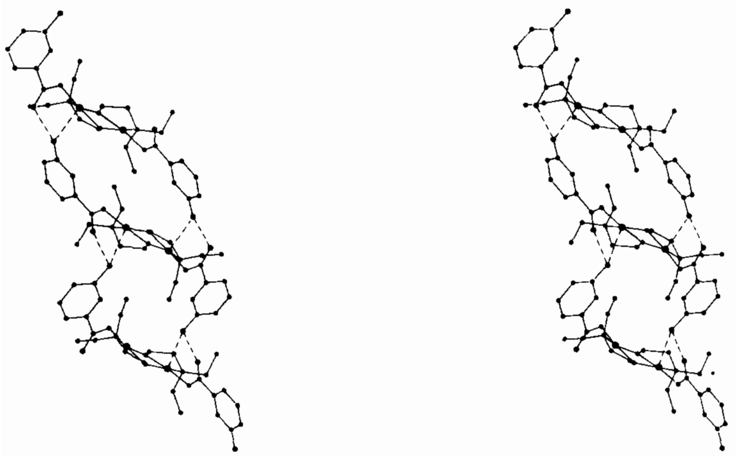

Fig. 4. Stereoview of the chain in the direction of the *c*-axis.

TABLE V. Hydrogen Bonds and Intermolecular Contacts <3.2 Å

A–H···B	A···B	A–H	H···B	∢ A–H···B
O(23)–H(023)···O(14)″	2.588	1.025	1.607	158.5
O(24)–H(024)···O(13)′	2.593	1.177	1.461	158.8
O(11)···O(14)″	3.096			
O(11)···O(24)′	3.168			
C(14)···C(24)‴	3.154			

Symmetry code: (′) $-x, -y, -z$; (″) $-x, -y, -1-z$; (‴) $-0.5-x, 0.5+y, -0.5-z$.

A chelated 2-dialkylaminoethanolato ligand forms a puckered five-membered ring. In the title complex this ligand has one or more rotational orientations around the Cu–N bond. Many other complexes exhibit a similar disorder [1]. The angles and bond lengths of the aminoalcoholato ligand are normal.

Dioxygen-bridged Copper(II) Dimers

The structural features of all known dimeric and polymeric $[Cu_2(DR\text{-}no)_2X_2]$ complexes are summarized in Table IV. The values of Cu_2O_2 cores are tabulated together with the axial distances and coupling constants. In Fig. 5 the bridging angle Cu–O–Cu′ is plotted against the Cu–Cu′ distance for the centrosymmetric complexes of Table IV, for centrosymmetric di-μ-hydroxo complexes $[Cu_2(OH)_2L_2]$ and for 2-[2-(dialkylamino)ethylthio]-ethanolato (DR-nso) and *N*-(2-alkylthioethyl)-3-aminopropanolato (R-sno) complexes $[Cu_2(DR\text{-}nso)_2X_2]$ and $[Cu_2(R\text{-}sno)_2X_2]$ [1]. The least-squares fits are for the di-μ-hydroxo dimers $y = 54.50x - 59.54$ ($r = 0.96$), for the 2-dialkylaminoethanolato dimers $y = 54.76x - 60.98$ ($r = 0.96$) and for the DR-nso and R-sno dimers $y = 52.23x - 54.93$ ($r = 0.96$). As can be seen, the values of the Cu–Cu′ separation for the DR-no dimers, and even more so for the DR-nso dimers, fall in a smaller range than the corresponding values for the di-μ-hydroxo dimers. The straight line for the di-μ-hydroxo dimers lies about 0.7° above the DR-no line, which is about 1.5° above the DR-nso line. The three complexes $[Cu_2(DEt\text{-}no)_2(NCO)_2]$, $[Cu_2(DMe\text{-}no)_2Cl_2]_n$ and $[Cu_2(DMe\text{-}no)_2Br_2]_n$ deviate from the other 2-dialkylaminoethanolato dimers [3]. The Cu–O bond lengths are about the same for the di-μ-hydroxo and 2-dialkylaminoethanolato dimers and slightly greater for the DR-nso dimers, the average lengths being 1.915(16), 1.912(26) and 1.932(16) Å, respectively. The Cu–O–Cu′ angles deviate much more, as is seen in Fig. 5 and Table IV.

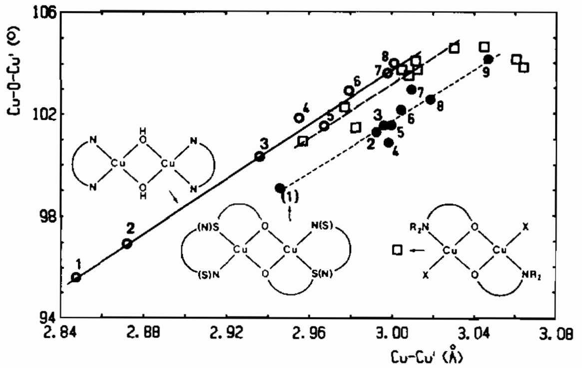

Fig. 5. Plot of the bridging angle Cu–O–Cu′ against the Cu–Cu′ distance for some centrosymmetric dioxygen-bridged copper(II) dimers. Di-μ-hydroxo dimers (○ and ——)[a]: $y = 54.50x - 59.54$, $r = 0.96$; DR-no dimers (□ and — — —)[b]: $y = 54.76x - 60.98$, $r = 0.96$; DR-nso and R-sno dimers (● and - - - -)[c]: $y = 52.23x - 54.93$, $r = 0.96$. [a]Ref. 24. [b]Table IV. [c]Ref. 25.

The dialkoxo-bridged complexes show increasing antiferromagnetic interaction with increase in the bridging angle, the singlet–triplet splitting being 96.3° [2]. The Cu–O–Cu′ angle would suggest strong antiferromagnetic interaction in this complex.

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