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Dimeric Copper(II) Complexes with an Aminoalcohol and Halogenobenzoic Acids. The Crystal and Molecular Structures of Bis[2-Br-benzoato-μ-(2-diethylamino-ethanolato-N,μ-O)copper(II)] and Bis[3-Br-benzoato-μ-(2-diethylaminoethanolato-N,μ-O)copper(II)]

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Abstract

Dimeric copper(II) complexes with 2-diethylaminoethanol and with 2-Cl-, 2-Br-, 2-I- and 3-Br-benzoic acids have been investigated.

The electronic spectra in Nujol and in solutions show a shoulder at about 27 500 cm^{-1} and in Nujol broad flat bands at about 18 200–14 700 cm^{-1} for 2-Cl-, 2-Br- and 2-I-benzoato and 18 800–14 900 cm^{-1} for 3-Br-benzoato complex. The broad bands are attributed to d–d transitions for square-planar coordination and the shoulders 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 crystal and molecular structures of $[Cu_2(2\text{-}Br\text{-}C_6H_4COO)_2(C_6H_{14}NO)_2]$ and $[Cu_2(3\text{-}Br\text{-}C_6H_4COO)_2(C_6H_{14}NO)_2]$ were determined by three dimensional X-ray crystallography. The 2-Br-benzoato complex crystallizes in the monoclinic space group $P2_1/c$ with $a = 12.228(9)$, $b = 8.633(5)$, $c = 14.297(8)$ Å, $\beta = 97.63(6)°$, $Z = 2$, and the 3-Br-benzoato complex in the triclinic space group $P\bar{1}$ with $a = 8.263(5)$, $b = 8.759(5)$, $c = 10.552(6)$ Å, $\alpha = 87.54(4)$, $\beta = 80.74(5)$, $\gamma = 87.45(5)°$, $Z = 1$. The structures were solved by direct methods and refined to the R values 0.078 and 0.055 using 1851 and 1629 independent reflections for the 2-Br- and 3-Br-benzoato complex, respectively. Some of the C atoms of the aminoethanolato ligands are disordered, having one or more rotational orientation.

Each Cu(II) ion has a square-planar environment. Two ethanolato O atoms, a benzoato O atom and an amino N atom form a square plane with Cu–O bonds of 1.891–1.924 Å and a Cu–N bond of 2.017–2.029 Å. The Cu–Cu′ distances are 2.946(2) Å for the 2-Br-benzoato complex and 3.005(2) Å for the 3-Br-benzoato complex.

The IR spectra show the carboxylate frequency ν(COO)(asym) as a broad band at 1615 with a shoulder at 1600 cm^{-1} for the 2-Br-benzoato complex and as a band at 1613 cm^{-1} for the 3-Br-benzoato complex. The ν(COO)(sym) vibrations appear as a broad band at 1372 and 1373 cm^{-1} with a shoulder at 1360 and 1365 cm^{-1} for the two complexes, respectively.

Introduction

A great number of copper(II) complexes with 2-dialkylaminoethanols (abbreviated as DR-noH) have been reported and their structures and magnetic properties extensively studied [1–4]. The structures are typically dimeric, polymeric with dimeric units of cubane-like tetramers distorted into different types [1]. By contrast, complexes containing the carboxylate ion as a second ligand exhibit widely different structures in the solid state, e.g. mononuclear [5], dinuclear [1, 6], trinuclear [1], tetrameric [1–5], hexanuclear [1, 5] and nonanuclear [5].

In the present work, we have prepared the series of dimeric copper(II) complexes and have investigated two molecular and crystal structures of them, namely $[Cu_2(2\text{-}Br\text{-}C_6H_4COO)_2(C_6H_{14}NO)_2]$ and $[Cu_2(3\text{-}Br\text{-}C_6H_4COO)_2(C_6H_{14}NO)_2]$.

Experimental

Preparation of the Complexes

These compounds were made by a method described earlier [6] using 2-Cl-, 2-Br-, 2-I- and 3-Br-benzoic acid (X-ben; AGA).

Spectral Studies

Copper analyses were carried out by atomic absorption spectroscopy using a Perkin-Elmer 2380 spectrometer.

Electron absorption spectra were measured in the region 300–850 nm with a Shimadzu UV-240 spectrophotometer and the infrared spectra in the

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TABLE I. Crystal Data, Data Collection and Refinement Data

Compound	2-Br-ben	3-Br-ben
Formula	$C_{26}H_{36}Br_2Cu_2N_2O_6$	$C_{26}H_{36}Br_2Cu_2N_2O_6$
Formula weight	759.48	759.48
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (A)	12.228(9)	8.263(5)
b (A)	8.633(5)	8.759(5)
c (A)	14.297(8)	10 552(6)
α (°)		87.54(4)
β (°)	97.63(6)	80.74(5)
γ (°)		87.47(5)
V (A^3)	1496	753
Z	2	1
D_c (g cm^{-3})	1.62	1.66
D_o (g cm^{-3})	1.69	1.67
Linear absorption coefficient (cm^{-1})	43.5	43.2
Crystal size (mm)	0.12 × 0.22 × 0.25	0.15 × 0.21 × 0.26
Data collection method	ω	ω
2θ range (°)	2.0–55.0	3.0–50.0
Scan rate (° min^{-1})	2.5–29.3	2.5–29.3
Number standard reflections	1	1
Variation in standard intensities	±1%	±1%
Reflections collected	2984	2653
Reflections used in refinements $I > 2.5\sigma(I)$	1851	1629
Number of variables	244	232
R $(=\Sigma\Delta/\Sigma\lvert F_o\rvert)^a$	0.078	0.055
R_w $(=\Sigma\Delta\sqrt{w}/\Sigma\lvert F_o\rvert\sqrt{w})^b$	0.078	0.052
Residual electron density (e A^{-3})	0.98	0.71
$F(000)$ (e)	764	382
T (K)	293	293

$^a\Delta = \lVert F_o\rvert - \lvert F_c\rVert$. $^bw^{-1} = \sigma^2(F_o) + 0.0005\lvert F_o\rvert^2$.

region 200–4000 cm^{-1} with a Perkin-Elmer 1330 spectrometer.

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-centered 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 (λ = 0.71069). 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.

Structure Determination

The structures were 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(3)* for 3-Br-ben [7].

The disorder of the carbon 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 carbon atoms showed severe dispersion of the electron density. The atoms were given a site occupation factor of 0.5, and refined the corresponding bond length pairs of the atoms fixed together. The two disordered positions of atoms C(2), C(3) and C(5) for 2-Br-ben and atoms C(3) and C(5) for 3-Br-ben refined well, giving site occupation factors of about 0.6 and 0.4 for 2-Br-ben and 0.75 and 0.25 for 3-Br-ben. These were considered fixed in subsequent calculations. The disorders were judged to arise from the mixture of two possible configurations of the DEt-no ligand in one or more rotational orientations of the ethyl groups and the amine around the N–Cu axis.

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

The calculations were performed on a Nicolet R3m diffractometer system with SHELXTL software for minicomputer (Nova 3) [7]. The program uses neutral atom scattering factors from ref. 8 and takes anomalous dispersion into account. The figures were drawn with the 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 Tables II and III. Bond distances and angles are given in Table IV.

TABLE II. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\times 10^3$) for $[Cu(Et_2\text{-no})(2\text{-Br-ben})]_2$

Atom[a]	*x*	*y*	*z*	*U*
Cu	976(1)	102(2)	722(1)	41(1)
O(1)	−365(7)	1146(9)	325(6)	66(3)
N	1448(7)	2086(11)	1403(6)	40(3)
C(1)	−405(10)	2719(13)	579(9)	55(4)
C(2)	355(19)	2930(25)	1451(17)	56(8)
C(2)*	805(27)	3282(37)	848(33)	69(15)
C(3)	2143(17)	3001(22)	780(17)	57(8)
C(3)*	2702(21)	2458(36)	1485(21)	46(10)
C(4)	3091(11)	2197(20)	476(11)	77(6)
C(5)	2228(24)	1953(29)	2262(19)	75(10)
C(5)*	1260(49)	2111(46)	2355(20)	100(21)
C(6)	1639(16)	1006(22)	3014(11)	106(9)
Br	3820(1)	−3095(2)	172(1)	70(1)
O(2)	2261(5)	−1090(8)	1185(5)	43(3)
O(3)	1181(7)	−2770(10)	1778(6)	62(3)
C(7)	2088(9)	−2310(13)	1617(7)	39(4)
C(8)	3068(8)	−3277(10)	1967(7)	33(3)
C(9)	3916(8)	−3661(11)	1450(7)	38(4)
C(10)	4816(10)	−4494(15)	1852(9)	54(5)
C(11)	4901(11)	−4969(16)	2746(10)	67(5)
C(12)	4119(12)	−4622(15)	3288(9)	64(5)
C(13)	3202(11)	−3835(14)	2901(8)	51(4)

[a] Site occupation factors for the disordered atoms are 0.60 and 0.40.

TABLE III. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\times 10^3$) for $[Cu(Et_2\text{-no})(3\text{-Br-ben})]_2$

Atom[a]	*x*	*y*	*z*	*U*
Cu	1501(1)	−356(1)	−963(1)	33(1)
O(1)	−639(7)	−1024(6)	−373(6)	43(2)
N	1775(11)	−2264(10)	−2015(8)	58(3)
C(1)	−992(14)	−2481(13)	−746(14)	80(5)
C(2)	243(19)	−2985(20)	−1746(20)	146(10)
C(3)	2685(21)	−3500(16)	−1266(21)	99(9)
C(3)*	3565(26)	−2930(50)	−2221(18)	59(11)[b]
C(4)	4297(18)	−3203(13)	−1116(12)	88(6)
C(5)	2703(22)	−2112(19)	−3269(15)	96(8)
C(5)*	1005(31)	−1992(39)	−3120(23)	104(25)
C(6)	1956(22)	−827(20)	−4110(14)	116(8)
Br	7530(1)	5975(1)	4512(1)	62(1)
O(2)	3634(7)	397(7)	−1450(6)	46(2)
O(3)	2554(8)	2409(8)	−2406(7)	60(3)
C(7)	3738(11)	1677(11)	−2077(9)	41(3)
C(8)	5450(11)	2244(11)	−2426(8)	39(3)
C(9)	6763(11)	1488(11)	−2015(9)	46(4)
C(10)	8301(12)	2081(12)	−2327(9)	50(4)
C(11)	8560(12)	3398(11)	−3048(9)	46(3)
C(12)	7193(11)	4167(10)	−3453(8)	38(3)
C(13)	5684(11)	3588(10)	−3195(8)	34(3)

[a] Site occupation factors for the disordered atoms are 0.75 and 0.25. [b] Isotropic temperature factor.

TABLE IV. Interatomic Distances (A) and Angles (°)[a]

	2-Br-ben	3-Br-ben
The copper(II) environments		
Cu–O(1)	1.891(8)	1.889(6)
Cu–O(2)	1.921(7)	1.895(6)
Cu–N	2.017(9)	2.029(9)
Cu–O(1)′	1.913(8)	1.924(6)
Cu–O(3)	2.897(8)	2.895(7)
Cu–Cu′	2.946(2)	3.005(2)
O(1)–Cu–N	85.5(7)	85.0(3)
O(1)–Cu–O(2)	174.7(7)	175.9(3)
O(1)–Cu–O(1)′	78.5(4)	76.0(3)
N–Cu–O(2)	96.9(3)	98.8(3)
N–Cu–O(1)′	155.9(4)	159.6(3)
O(2)–Cu–O(1)′	100.6(3)	100.1(3)
Cu–O(1)–Cu′	101.5(4)	104.0(3)
The 2-diethylaminoethanolato ligands[b]		
O(1)–C(1)	1.41(1)	1.41(1)
C(1)–C(2)	1.47(3)	1.42(2)
N–C(2)	1.53(3)	1.42(2)
N–C(3)	1.53(3)	1.55(2)
N–C(5)	1.46(3)	1.42(2)
C(3)–C(4)	1.47(3)	1.40(2)
C(5)–C(6)	1.60(3)	1.57(2)
Cu–N–C(2)	103.3(9)	105.8(9)
Cu–N–C(3)	107.6(9)	107.1(9)
Cu–N–C(5)	117.0(11)	116.0(8)
C(2)–N–C(3)	109.6(13)	94.3(11)
C(2)–N–C(5)	118.5(16)	123.5(13)
C(3)–N–C(5)	100.4(15)	106.9(11)
N–C(2)–C(1)	111.2(16)	120.8(15)

(continued)

TABLE IV. *(continued)*

	2-Br-ben	3-Brben
N–C(3)–C(4)	116.8(15)	116.7(12)
N–C(5)–C(6)	107.7(19)	112.0(12)
O(1)–C(1)–C(2)	107.4(12)	109.9(11)
C(1)–O(1)–Cu	116.2(7)	116.4(6)
C(1)–O(1)–Cu′	136.1(7)	137.1(6)
The benzoato ligands		
O(2)–C(7)	1.253(13)	1.276(11)
O(3)–C(7)	1.228(14)	1.235(12)
C(7)–C(8)	1.492(14)	1.505(13)
C(8)–C(9)	1.391(15)	1.367(14)
C(9)–C(10)	1.376(15)	1.380(14)
C(10)–C(11)	1.334(19)	1.361(14)
C(11)–C(12)	1.342(20)	1.406(14)
C(12)–C(13)	1.364(18)	1.349(13)
C(13)–C(8)	1.409(15)	1.403(12)
C(9)–Br	1.879(11)	
C(12)–Br		1.903(8)
Cu–O(2)–C(7)	115.8(7)	116.6(6)
O(2)–C(7)–O(3)	125.5(10)	124.1(9)
O(2)–C(7)–C(8)	117.0(9)	114.8(8)
O(3)–C(7)–C(8)	117.5(10)	121.1(8)
C(7)–C(8)–C(9)	125.3(9)	121.8(8)
C(7)–C(8)–C(13)	119.8(10)	118.4(8)
C(8)–C(9)–C(10)	120.9(10)	119.6(9)
C(9)–C(10)–C(11)	121.2(12)	121.9(9)
C(10)–C(11)–C(12)	120.9(12)	117.7(9)
C(11)–C(12)–C(13)	119.2(12)	121.6(8)
C(13)–C(8)–C(9)	115.0(9)	119.9(8)
C(12)–C(13)–C(8)	122.7(12)	119.3(8)
Br–C(9)–C(8)	120.0(7)	
Br–C(9)–C(10)	119.0(9)	
Br–C(12)–C(11)		118.6(7)
Br–C(12)–C(13)		119.6(7)

[a]Symmetry code: (′) $-x$, $-y$, $-z$. e.s.d.s. are given in parentheses. [b]Site occupation factors 0.6 (2-Br-ben) and 0.75 (3-Br-ben) are tabulated for disordered atoms.

Results and Discussion

Spectral Results (Table V)

The electronic absorption spectra of the complexes (Fig. 1) show a shoulder at about 27 500 cm^{-1}. This is a characteristic feature of the dimeric 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 [9, 10].

The broad flat bands in Nujol at 18 200–14 400 cm^{-1} for 2-Cl-, 2-Br- and 2-I-benzoato complexes and 18 800–14 900 cm^{-1} for the 3-Br-benzoato complex are attributable to d–d transitions. The shape of the spectra is typical for square-planar coordination of the copper(II) ion [11].

The geometry around the copper(II) ions differs in acetone, chloroform and methanol solutions from that in the solid state. The shape and energy of the d–d bands from 14 700 to 15 200 cm^{-1} indicates that the coordination of copper(II) ions have a tetragonal six-coordinate structure in the solution state [11]. The very similar spectra of the 2-Cl-, 2-Br- and 2-I-benzoato complexes in the solid and solution state suggest the molecular structures and coordination spheres of these complexes are the same.

For the 2-Br- and 3-Br-benzoato complexes, respectively, the infrared spectra show the carboxylate stretching frequency ν(COO)(asym) vibration as a broad band at 1615 with a shoulder at 1600 cm^{-1} and at 1613 cm^{-1} and ν(COO)(sym) vibration as a broad band at 1372 with a shoulder at 1360 for 2-Br-ben and 1373 with a shoulder at 1365 cm^{-1} for 3-Br-ben. The separations of 243–255 and 240–248 cm^{-1} for the two complexes are about the same as for unidentate complexes [12].

Description of the Structures

The structures of the two dimeric, centrosymmetric molecules [$Cu_2(2\text{-Br-}C_6H_4COO)_2(C_6H_{14}NO)_2$] and [$Cu_2(3\text{-Br-}C_6H_4COO)_2(C_6H_{14}NO)_2$] are shown in Figs. 2 and 3. The copper(II) ions are bridged by two 2-diethylaminoethanolato oxygen atoms forming a Cu_2O_2-core, where the Cu–Cu′ distances are 2.946(2) and 3.005(2) Å, respectively. The first distance is the shortest known in dimeric 2-dialkylaminoethanolato copper(II) complexes [1, 3, 6].

The coordination around each copper(II) ion is square-planar, with two alkoxo oxygens, a benzoato oxygen and an amino nitrogen atom in the square

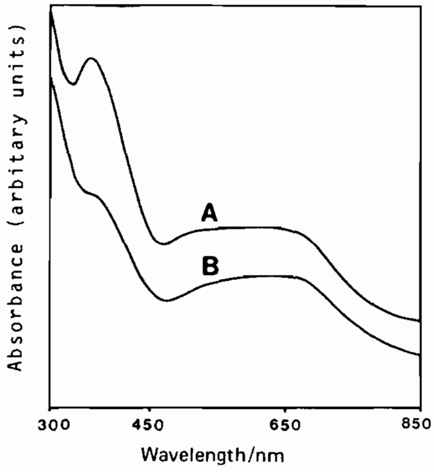

Fig. 1. Electronic absorption spectra of [$Cu_2(X\text{-}C_6H_4COO)_2(C_6H_{14}NO)_2$] in Nujol mulls. (A) X = 3-Br; (B) X = 2-Cl, 2-Br and 2-I.

TABLE V. Electronic Spectral Data[a]

Compound	Nujol	$CHCl_3$	Acetone	Methanol
$[Cu_2(DEt\text{-}no)_2(2\text{-}Cl\text{-}ben)_2]$	14.7–18.2	15.2 160	15.0 160	14.8 130
	27.3^b	27.3 1760	27.7 1360	28.6^b 1390
$[Cu_2(DEt\text{-}no)_2(2\text{-}Br\text{-}ben)_2]$	14.5–18.2	15.0 100	15.0 130	14.8 70
	27.8^b	27.3 1780	27.6 1280	28.6 1360
$[Cu_2(DEt\text{-}no)_2(2\text{-}I\text{-}ben)_2]$	14.7–18.2	15.1 150	14.9 140	14.9 120
	27.8^b	27.3 1660	27.5 1210	28.7 1280
$[Cu_2(DEt\text{-}no)_2(3\text{-}Br\text{-}ben)_2]$	14.9–18.8	14.9 150	14.7 150	14.7 140
	27.4	27.5 1830	27.9 1290	28.6 1540

[a] ν in 10^3 cm^{-1} and ϵ in dm^3 mol^{-1} cm^{-1}. [b] Shoulder.

plane. As can be seen in Table IV, the Cu–O and Cu–N bond lengths fall in the range 1.891–1.924 Å and 2.017–2.029 Å, respectively, which are quite normal for coordination bonds [1]. The coordination sphere of the copper(II) ion in the 2-Br-ben complex is more distorted than in the 3-Br-ben and benzoato [1] complexes. This is clearly seen from the dihedral angles between the Cu,O(1),O(1)' and Cu,N,O(2) planes and from the deviations from the square planes. The dihedral angles are 18.1°, 7.5° and 7.5° for the 2-Br-ben, 3-Br-ben and benzoato complexes, respectively.

Though the phenyl ring is rotated around the C(7)–C(8) axis in 2-Br-ben, the Cu–O(3) distance and the angle between the square plane and the Cu–O(3) line remain about the same as in the 3-Br-

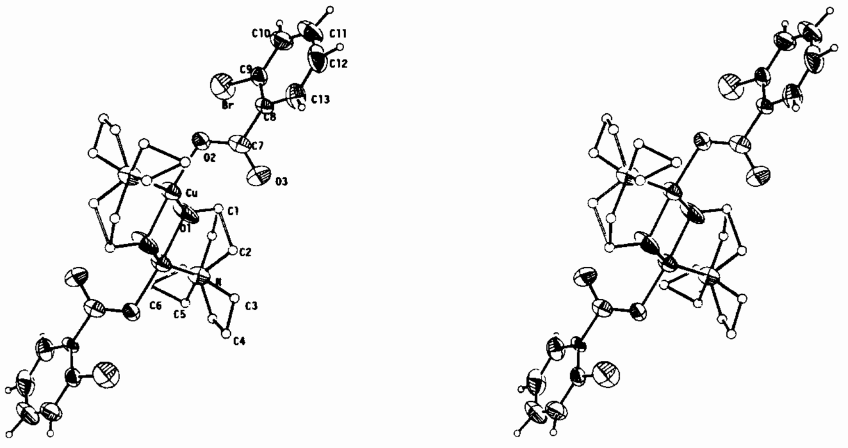

Fig. 2. Stereoview of $[Cu_2(2\text{-}Br\text{-}C_6H_4COO)_2(C_6H_{14}NO)_2]$.

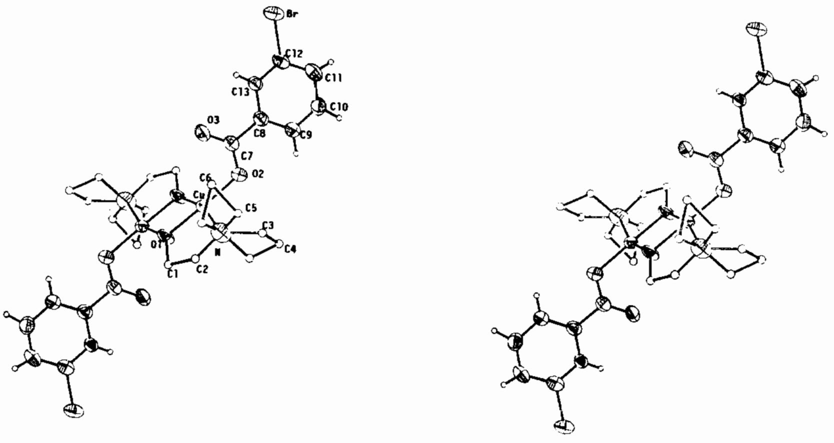

Fig. 3. Stereoview of $[Cu_2(3\text{-}Br\text{-}C_6H_4COO)_2(C_6H_{14}NO)_2]$.

ben and benzato complexes, *viz.* about 2.9 Å and 45°. But the dihedral angle between the phenyl ring and its carboxyl group is vastly different from that in the 3-Br-ben and benzoato complexes, the angles being 47.0°, 3.5° and 5.4°, respectively. This dramatic rotation of the 2-Br-ben ligand is caused by the steric effects of bromine in the *ortho* position.

The dimeric non-centrosymmetric [Cu_2(3-OH-$C_6H_4COO)_2(C_6H_{14}NO)_2$] [6] differs from the 2-Br-ben, 3-Br-ben and benzoato complexes. The Cu—O(3) distances are about 0.3 Å longer and the dihedral angles between the basal plane and the Cu—O(3) line clearly larger. The uncoordinated carboxyl oxygen atom O(3) and the phenolic oxygen atom each form a strong hydrogen bond, and the latter also forms a long bond to the Cu(II) ion as the axial bond in its elongated square-pyramidal (4 + 1) coordination sphere.

The chelated DEt-no ligand forms a puckered five-membered ring. In the title complexes the ligand has one or more rotational orientations around the Cu—N bond. Only one of the disordered forms is tabulated in Table IV; those with site occupation factors 0.6 and 0.75 for the 2-Br-ben and 3-Br-ben complexes, respectively. The angles and bond lengths of the aminoalcoholato ligands are normal [1].

The intermolecular contacts less than 3.5 Å are O(3)···C(5)* 3.382 Å $(-x, -\frac{1}{2}+y, -z)$ and O(3)···Br 3.01 Å $(1-x, 1-y, -1-z)$ for the two complexes respectively.

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

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