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Synthesis, Structure and Magnetism of Two Hexameric Copper(II) Complexes: Diaquabis[μ-(4-bromobenzoato-*O,O'*)]-tetrakis(4-bromobenzoato)hexakis-[μ-(2-dimethylaminoethanolato)]hexacopper(II) and Bis[μ_3-(2-dibutylaminoethanolato)-μ-(2-dibutylaminoethanolato)]tetrakis-(μ-dichloroacetato-*O,O'*)-bis(dichloroacetato)-di-μ_3-hydroxo-hexacopper(II)

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Abstract

The title compounds, 1 and 2, have been crystallized and examined by spectroscopy, magnetism and X-ray diffraction techniques. The 4-bromobenzoate compound crystallizes in the triclinic space group $P\bar{1}$, with $a = 10.897(4)$, $b = 12.496(6)$, $c = 16.260(11)$ Å, $\alpha = 69.33(4)$, $\beta = 95.59(4)$, $\gamma = 102.00(4)°$, $Z = 1$, $M_r = 2146.2$, $D_x = 1.76$ g cm^{-3}, $V = 2025(2)$ Å^3 and $R = 0.047$ for 4015 observed reflections. The centrosymmetric overall structure is composed of three dimers, which are bridged into a hexametallic unit by carboxylato oxygen atoms with apical Cu–O distances of 2.575(7) and 2.651(5) Å. Of the three ethanolato-bridged dimers, one is centrosymmetric and the other two are non-centrosymmetric. Within the Cu_2O_2 dimeric units the Cu–O–Cu angles are 96.7(2) and 97.5(3) for the non-symmetric dimer and 102.1(3)° for the symmetric dimer and the Cu–Cu distances are 2.896(2) and 2.988(2) Å, respectively.

The dichloroacetate compound 2 crystallizes in the triclinic space group $P\bar{1}$, with $a = 10.414(7)$, $b = 13.884(9)$, $c = 15.809(9)$ Å, $\alpha = 109.96(6)$, $\beta = 106.76(6)$, $\gamma = 78.21(6)°$, $Z = 1$, $M_r = 1872.2$, $D_x = 1.52$ g cm^{-3}, $V = 2042(2)$ Å^3 and $R = 0.052$ for 3257 observed reflections. The crystal structure consists of discrete hexameric complex molecules, considered as tetrahedral Cu_4 units sharing a common edge, arranged in a distorted octahedral geometry. The copper atoms in the centrosymmetric molecule are linked together by carboxylate groups, ethanolato oxygen atoms and triply bridging hydroxo oxygen atoms. The distances between the hydroxo O and Cu atoms are 1.972(5)–2.003(5) Å and the Cu–O–Cu angles are 99.8(3)–130.4(3)°. The six Cu–Cu distances in the distorted tetrahedral units vary between 3.037(1) and 3.608(1) Å.

The spectroscopic and magnetic properties of both compounds agree with the observed X-ray structures. For 1 the coordinated water molecules can be distinguished in the IR spectra, as can the OH groups in compound 2. The ligand-field spectra show broad bands, in agreement with different coordination geometries for the several copper compounds.

Magnetic exchange in both compounds is quite strong, and only in the 80–300 K temperature range is the Curie–Weiss law observed. In 1 and 2 the values of θ are -72 and -153 K, respectively. The magnetic moment of 1 varies from 1.30 to 1.53 BM between 80 and 300 K, whereas in 2 the magnetic moment varies almost linearly from 1.0 BM at 4 K, to 1.4 BM at 300 K, indicating a complicated exchange mechanism in the hexanuclear unit. The high-temperature magnetic moments obtained by extrapolation for 1 and 2 are 1.70 and 1.75 BM, respectively, in agreement with $S = \frac{1}{2}$ systems.

EPR powder spectra show weak signals, and only at 77 K can some hyperfine splitting (probably due to minute amounts of paramagnetic species) be seen on top of the broad lines originating from the hexanuclear clusters.

Introduction

The coordination chemistry of aminoalcohols and carboxylic acid with transition metal ions has received considerable attention [1,2] in recent years. The attractiveness of aminoalcohols and carboxylic acids as ligands is based on the strong tendency of the aminoalcohol oxygen atom and the carboxylate group to form bridges between metal

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atoms, allowing the formation of a wide variety of magnetochemically interesting polynuclear complexes. So far, copper(II) and aminoalcohols containing carboxylate groups have been shown to yield monomeric, dimeric, trimeric, tetrameric, hexameric, nonameric and polymeric species [1–11].

Earlier [5], we have prepared and reported the tetrameric crystal structure of copper(II) dichloroacetate with 2-dibutylaminoethanol in which the Cu and bridging ethanolato O atoms form cubane-type Cu_4O_4 cores. The short Cu–O(ethanolato) bonds within the cores form eight-membered rings folded in a boat-like conformation with Cu–Cu distances of 3.134(5)–3.824(5) Å.

Recently, we succeeded in preparing two new types of copper(II) carboxylate complexes with 2-dialkylaminoethanols, and present here the crystal structures and results of spectroscopic and magnetic studies (EPR, magnetic susceptibility and ligand field) of the hexameric complexes $[Cu_6(C_7H_4BrO_2)_6(C_4H_{10}NO)_6(H_2O)_2]$ (1) and $[Cu_6(C_2HCl_2O_2)_6(C_{10}H_{22}NO)_4(OH)_2]$ (2).

Experimental

Preparation

The copper(II) carboxylates were prepared from $CuCO_3$ and 4-bromobenzoic and dichloroacetic acids, respectively. Solid complexes were obtained upon slow evaporation of ethanol solution of the copper(II) carboxylates and 2-dialkylaminoethanols at room temperature in the molar ratio 1:1 and 2:3 for compounds **1** and **2**. The complexes analyse as indicated in the title.

X-ray Data Collection and Refinement

Crystal data and refinement details are given in Table I. Each data set was corrected for Lorentz-polarization effects and absorption from Φ-scan data. Structures were solved by direct and Fourier methods using MULTAN 80 and XRAY 76 programs [12, 13]. The least-squares refinement, minimizing $\Sigma w(\Delta F)^2$, with anisotropic temperature factors for non-H atoms and isotropic temperature factor for the H atoms of the water molecule and the OH^- ion, gave R values of 0.047 and 0.052 for compounds **1** and **2**, with $w = 1/\sigma^2(F_o)$. The other H atoms were included at idealized positions (C–H = 1.0 Å) with $U = 0.08$ and held fixed. No chemically significant peaks were observed on the final difference maps. Residual electron densities were within ±0.8 e $Å^{-3}$ and the largest Δ/σ was 0.7. Scattering factors, including anomalous dispersion were taken from ref. 14. Atomic positions are listed in Tables II and III. Interatomic distances and angles are given in Tables IV and V. See also 'Supplementary Material'.

TABLE I. Crystal and Diffraction Data for Complexes $[Cu_6(C_7H_4BrO_2)_6(C_4H_{10}NO)_6(H_2O)_2]$ (**1**) and $[Cu_6(C_2HCl_2O_2)_6(C_{10}H_{22}NO)_4(OH)_2]$ (**2**)

Complex	**1**	**2**
M_r	2146.2	1872.2
Space group	$P\bar{1}$	$P\bar{1}$
Crystal system	triclinic	triclinic
a (Å)	10.897(4)	10.414(7)
b (Å)	12.496(6)	13.884(9)
c (Å)	16.260(11)	15.806(9)
α (°)	69.33(4)	109.96(6)
β (°)	95.59(4)	106.76(6)
γ (°)	102.00(4)	78.21(6)
V ($Å^3$)	2025(2)	2042(2)
Z	1 (hexamer)	1 (hexamer)
D_{meas} (Mg m^{-3})	1.76	1.52
D_{calc} (Mg m^{-3})	1.76	1.52
$F(000)$	1070	958
2θ range (°)	4–48	4–45
Significant reflections ($I > 3\sigma(I)$)	4015	3257
μ (cm^{-1})	48.1	20.4
Final R value ($\Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$)	0.047	0.052
Final R_w value ($(\Sigma w\Delta F^2/\Sigma wF_o^2)^{1/2}$)	0.048	0.047
Weighting scheme	$1/\sigma^2(F_o)$	$1/\sigma^2(F_o)$
Diffractometer	Nicolet P3	Nicolet P3
Radiation	Mo Kα	Mo Kα
Scanning type	ω-scan	ω-scan
Scan speed (°/min)	2.5–29.3	2.5–29.3

TABLE II. Fractional Atomic Coordinates (× 10^4) and Equivalent Isotropic Temperature Factors for **1**

	x	y	z	U_{eq} ($Å^2$)^a
Cu(1)	2041(1)	2471(1)	2649(1)	0.036
Cu(2)	−488(1)	1783(1)	3298(1)	0.039
Cu(3)	3599(1)	4797(1)	−61(1)	0.044
Br(1)	8807(1)	7305(1)	3186(1)	0.093
Br(2)	−7258(1)	−3371(1)	3389(1)	0.095
Br(3)	−3111(1)	−218(1)	−308(1)	0.082
O(1)	1162(6)	1478(5)	4675(4)	0.069
O(11)	665(5)	1186(4)	2815(3)	0.042
O(12)	3408(5)	3751(4)	2576(3)	0.044
O(13)	3316(5)	3327(5)	4024(4)	0.059
O(21)	632(4)	3195(4)	2691(3)	0.044
O(22)	−1765(5)	353(4)	3736(3)	0.045
O(23)	−2295(6)	1130(5)	2338(4)	0.065
O(31)	4994(5)	5846(5)	195(4)	0.059
O(32)	2254(5)	3783(5)	−452(4)	0.055
O(33)	2134(5)	2936(5)	980(4)	0.063
N(1)	3162(6)	1261(6)	2835(4)	0.047
N(2)	−1276(7)	2833(6)	3750(4)	0.052
N(3)	2598(6)	5951(6)	5(5)	0.059
C(11)	1036(8)	101(7)	3109(6)	0.059
C(12)	2302(9)	283(7)	2694(7)	0.063
C(13)	4214(8)	1699(9)	2211(7)	0.067

(continued)

TABLE II. *(continued)*

	x	y	z	U_{eq} (Å^2)^a
C(14)	3688(10)	905(9)	3743(7)	0.070
C(15)	3830(7)	3870(6)	3296(5)	0.038
C(16)	5029(7)	4721(6)	3256(5)	0.035
C(17)	5534(8)	4937(7)	4006(5)	0.047
C(18)	6645(8)	5704(7)	3995(6)	0.052
C(19)	7250(7)	6258(7)	3205(6)	0.051
C(110)	6790(8)	6084(7)	2447(5)	0.053
C(111)	5662(7)	5302(7)	2480(5)	0.044
C(21)	559(9)	4143(7)	2941(7)	0.065
C(22)	−395(18)	3884(12)	3494(16)	0.217
C(23)	−1424(16)	2381(14)	4684(8)	0.124
C(24)	−2477(15)	2969(16)	3361(11)	0.143
C(25)	−2469(7)	352(7)	3046(5)	0.043
C(26)	−3570(7)	−635(6)	3157(5)	0.040
C(27)	−4062(7)	−1314(7)	3977(5)	0.045
C(28)	−5124(8)	−2130(7)	4047(6)	0.054
C(29)	−5762(8)	−2277(7)	3300(7)	0.058
C(210)	−5237(9)	−1657(9)	2483(7)	0.062
C(211)	−4165(8)	−827(8)	2409(6)	0.056
C(31)	4768(8)	6873(7)	232(6)	0.056
C(32)	3508(14)	6970(17)	−133(25)	0.316
C(33)	1759(20)	6290(15)	−746(9)	0.165
C(34)	1895(17)	5549(12)	749(8)	0.149
C(35)	1744(7)	3000(7)	229(5)	0.044
C(36)	602(7)	2185(7)	74(5)	0.044
C(37)	−63(7)	1385(7)	802(5)	0.049
C(38)	−1150(7)	671(7)	678(6)	0.051
C(39)	−1563(7)	740(7)	−162(6)	0.044
C(310)	−915(8)	1510(8)	−890(6)	0.057
C(311)	172(8)	2239(7)	−766(5)	0.050

[a] $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j$.

TABLE III. Fractional Atomic Coordinates (× 10^4) and Equivalent Isotropic Temperature Factors for 2

	x	y	z	U_{eq} (Å^2)^a
Cu(1)	−366(1)	1629(1)	1586(1)	0.047
Cu(2)	1139(1)	−473(1)	1894(1)	0.047
Cu(3)	−1475(1)	−122(1)	−85(1)	0.043
Cl(1)	190(5)	3083(4)	4951(2)	0.195
Cl(2)	−9(12)	854(7)	4804(6)	0.169
Cl(20)	−1360(14)	1583(10)	4509(8)	0.244
Cl(3)	−1127(9)	−3265(4)	1709(5)	0.176
Cl(30)	−241(22)	−3145(14)	2543(19)	0.180
Cl(4)	−2550(4)	−1873(4)	3043(4)	0.205
Cl(5)	−5017(3)	2574(2)	1849(2)	0.128
Cl(6)	−5956(3)	2068(3)	−123(3)	0.143
O(1)	−621(5)	144(3)	1248(4)	0.045
O(2)	−663(6)	1960(4)	2803(4)	0.068
O(3)	1045(7)	843(5)	3273(4)	0.078
O(4)	304(5)	−1383(4)	2222(4)	0.056
O(5)	−1773(5)	−543(4)	2220(4)	0.076
O(6)	−3213(5)	441(4)	188(4)	0.057
O(7)	−2687(5)	2049(4)	983(4)	0.067
O(8)	−3(5)	1217(3)	366(4)	0.043
O(9)	2069(5)	183(4)	1365(4)	0.047
N(1)	207(6)	3042(4)	1794(4)	0.044
N(2)	3020(6)	−1047(5)	2488(5)	0.050
C(1)	62(10)	1512(6)	3366(6)	0.066
C(2)	−189(17)	1870(10)	4339(9)	0.128
C(3)	−879(9)	−1251(6)	2336(6)	0.055
C(4)	−1104(10)	−2109(8)	2679(9)	0.098
C(5)	−3442(8)	1393(6)	672(6)	0.051
C(6)	−4906(9)	1655(6)	804(6)	0.071
C(7)	827(9)	2848(6)	998(6)	0.056
C(8)	47(9)	2138(6)	162(6)	0.055
C(9)	−966(8)	3869(6)	1740(6)	0.053
C(10)	−1664(10)	4209(7)	2532(7)	0.070
C(11)	−2978(10)	4887(7)	2319(9)	0.091
C(12)	−3681(13)	5294(9)	3088(11)	0.134
C(13)	1235(8)	3337(6)	2689(6)	0.055
C(14)	1805(10)	4359(7)	2910(7)	0.077
C(15)	2773(13)	4600(8)	3856(10)	0.135
C(16)	3255(14)	5592(11)	4163(10)	0.151
C(17)	3751(9)	−132(7)	2683(7)	0.061
C(18)	3466(9)	181(7)	1817(7)	0.064
C(19)	3593(9)	−1970(7)	1829(6)	0.062
C(20)	2988(10)	−2967(7)	1625(7)	0.072
C(21)	3504(12)	−3833(8)	863(8)	0.072
C(22)	2895(15)	−4816(9)	613(9)	0.097
C(23)	3092(10)	−1232(6)	3384(6)	0.146
C(24)	4462(10)	−1556(8)	3925(8)	0.062
C(25)	4388(12)	−1672(8)	4825(8)	0.091
C(26)	5693(15)	−2152(9)	5316(9)	0.145

[a] $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j$. The site occupation factors are 0.5 for Cl(2), Cl(20) and 0.75 for Cl(3) and 0.25 for Cl(30).

TABLE IV. Selected Interatomic Distances (Å) and Angles (°) for 1

Cu(1)–O(11)	1.916(5)	Cu(1)–O(11)–Cu(2)	97.5(3)
Cu(1)–O(12)	1.924(5)	Cu(1)–O(21)–Cu(2)	96.7(2)
Cu(1)–O(21)	1.955(5)	Cu(3)–O(31)–Cu(3)^i	102.1(1)
Cu(1)–N(1)	2.060(8)	O(11)–Cu(1)–O(21)	78.7(2)
Cu(1)–O(33)	2.575(7)	O(11)–Cu(1)–N(1)	85.5(2)
Cu(1)–O(13)	2.922(7)	O(11)–Cu(1)–O(33)	94.7(2)
		O(21)–Cu(1)–O(12)	99.9(2)
Cu(2)–O(11)	1.936(6)	O(21)–Cu(1)–O(33)	100.4(2)
Cu(2)–O(21)	1.920(4)	O(12)–Cu(1)–N(1)	95.3(3)
Cu(2)–O(22)	1.972(5)	O(12)–Cu(1)–O(33)	89.7(2)
Cu(2)–N(2)	2.067(9)	O(13)–Cu(1)–O(11)	125.8(2)
Cu(2)–O(23)	2.571(7)	O(13)–Cu(1)–O(21)	88.7(2)
Cu(2)–O(1)	2.700(6)	O(13)–Cu(1)–O(12)	49.8(2)
		O(13)–Cu(1)–N(1)	94.4(4)
Cu(3)–O(31)	1.907(6)	O(13)–Cu(1)–O(33)	139.5(2)
Cu(3)–O(31)^i	1.935(7)	O(11)–Cu(2)–O(21)	79.1(2)
Cu(3)–O(32)	1.942(6)	O(11)–Cu(2)–O(22)	99.2(2)
Cu(3)–N(3)	2.017(9)	O(11)–Cu(2)–O(1)	84.0(2)
Cu(3)–O(33)	2.651(5)	O(21)–Cu(2)–N(2)	84.9(2)
		O(21)–Cu(2)–O(1)	88.0(2)
Cu(1)–Cu(2)	2.896(2)	O(22)–Cu(2)–N(2)	97.6(3)

(continued)

TABLE IV. *(continued)*

Cu(3)–Cu(3)^{i}	2.988(2)	O(22)–Cu(2)–O(1)	100.8(2)
		O(23)–Cu(2)–O(11)	90.6(2)
C(15)–O(12)	1.262(10)	O(23)–Cu(2)–O(21)	114.7(2)
C(15)–O(13)	1.257(9)	O(23)–Cu(2)–O(22)	56.2(2)
C(15)–C(16)	1.494(10)	O(23)–Cu(2)–N(2)	101.5(3)
C(19)–Br(1)	1.911(7)	O(23)–Cu(2)–O(1)	155.3(2)
C(25)–O(22)	1.296(8)	O(31)–Cu(3)–O(31)^{i}	77.9(3)
C(25)–O(23)	1.217(9)	O(31)–Cu(3)–N(3)	83.9(3)
C(25)–C(26)	1.504(10)	O(31)–Cu(3)–O(33)	131.4(2)
C(29)–Br(2)	1.907(8)	O(32)–Cu(3)–O(31)^{i}	99.0(3)
C(35)–O(32)	1.273(9)	O(32)–Cu(3)–N(3)	98.3(3)
C(35)–O(33)	1.234(10)	O(32)–Cu(3)–O(33)	54.5(2)
C(35)–C(36)	1.498(11)	O(31)^{i}–Cu(3)–O(33)	101.9(2)
C(39)–Br(3)	1.902(8)	O(33)–Cu(3)–N(3)	95.5(3)
O(1)···O(13)	2.910(8)	O(12)–C(15)–O(13)	124.7(7)
		O(22)–C(25)–O(23)	122.6(7)
		O(32)–C(35)–O(33)	122.3(7)

i = $-x + 1, -y + 1, -z$.

TABLE V. Selected Interatomic Distances (Å) and Angles (°) for **2**

Cu(1)–O(1)	2.000(5)	O(1)–Cu(1)–O(2)	93.7(3)
Cu(1)–O(2)	1.922(7)	O(1)–Cu(1)–O(8)	83.7(2)
Cu(1)–O(8)	1.941(6)	O(1)–Cu(1)–O(7)	90.9(2)
Cu(1)–N(1)	2.059(7)	O(2)–Cu(1)–N(1)	95.2(3)
Cu(1)–O(7)	2.360(5)	O(2)–Cu(1)–O(7)	90.7(3)
		O(8)–Cu(1)–N(1)	87.1(3)
Cu(2)–O(1)	2.003(5)	O(8)–Cu(1)–O(7)	91.5(2)
Cu(2)–O(4)	1.944(7)	N(1)–Cu(1)–O(7)	96.4(2)
Cu(2)–O(9)	1.953(7)		
Cu(2)–N(2)	2.041(6)	O(1)–Cu(2)–O(3)	90.7(2)
Cu(2)–O(3)	2.331(5)	O(1)–Cu(2)–O(4)	94.0(2)
		O(1)–Cu(2)–O(9)	88.6(2)
Cu(3)–O(1)	1.972(5)	O(4)–Cu(2)–N(2)	91.3(3)
Cu(3)–O(6)	1.928(6)	O(4)–Cu(2)–O(3)	92.7(3)
Cu(3)–O(8^{i})	1.964(5)	O(9)–Cu(2)–N(2)	85.9(3)
Cu(3)–O(9^{i})	1.914(6)	O(9)–Cu(2)–O(3)	98.8(2)
Cu(3)–O(8)	2.438(6)	N(2)–Cu(2)–O(3)	90.7(2)
C(1)–O(2)	1.24(1)	O(1)–Cu(3)–O(6)	90.5(2)
C(1)–O(3)	1.24(1)	O(1)–Cu(3)–O(8^{i})	89.4(2)
C(1)–C(2)	1.53(2)	O(1)–Cu(3)–O(8)	72.3(2)
C(2)–Cl(1)	1.69(1)	O(6)–Cu(3)–O(9^{i})	94.9(2)
C(2)–Cl(2)	1.76(2)	O(6)–Cu(3)–O(8)	111.7(2)
		O(8)–Cu(3)–O(8^{i})	91.7(2)
C(3)–O(4)	1.26(1)	O(8)–Cu(3)–O(9^{i})	95.9(2)
C(3)–O(5)	1.23(1)	O(8^{i})–Cu(3)–O(9^{i})	90.0(2)
C(3)–C(4)	1.55(2)		
C(4)–Cl(3)	1.80(1)	Cu(1)–O(1)–Cu(2)	103.4(2)
C(4)–Cl(4)	1.70(1)	Cu(1)–O(1)–Cu(3)	99.8(3)
		Cu(2)–O(1)–Cu(3)	130.4(3)
C(5)–O(6)	1.29(1)		
C(5)–O(7)	1.21(1)	Cu(1)–O(8)–Cu(3)	87.0(2)
C(5)–C(6)	1.55(1)	Cu(1)–O(8)–Cu(3^{i})	118.7(3)
C(6)–Cl(5)	1.73(1)	Cu(3)–O(8)–Cu(3^{i})	88.3(2)
C(6)–Cl(6)	1.75(1)	Cu(2)–O(9)–Cu(3^{i})	120.6(3)
C(8)–O(8)	1.44(1)		
C(8)–C(7)	1.48(1)	O(2)–C(1)–O(3)	129(1)
N(1)–C(7)	1.50(1)	O(2)–C(1)–C(2)	118(1)
N(1)–C(9)	1.50(1)	O(3)–C(1)–C(2)	113(1)
C(9)–C(10)	1.52(2)		
C(10)–C(11)	1.52(1)	O(4)–C(3)–O(5)	127(1)
C(11)–C(12)	1.49(2)	O(4)–C(3)–C(4)	111(1)
N(1)–C(13)	1.49(1)	O(5)–C(3)–C(4)	122(1)
C(13)–C(14)	1.54(1)		
C(14)–C(15)	1.51(2)	O(6)–C(5)–O(7)	128(1)
C(15)–C(16)	1.44(2)	O(6)–C(5)–C(6)	111(1)
		O(7)–C(5)–C(6)	120(1)
C(18)–O(9)	1.42(1)		
C(18)–C(17)	1.51(2)	O(8)–C(8)–C(7)	109(1)
N(2)–C(17)	1.51(1)	C(8)–C(7)–N(1)	109(1)
N(2)–C(19)	1.49(1)	O(9)–C(18)–C(17)	111(1)
C(19)–C(20)	1.53(1)	C(18)–C(17)–N(2)	110(1)
C(20)–C(21)	1.52(1)		
C(21)–C(22)	1.50(2)		
N(2)–C(23)	1.50(1)		
C(23)–C(24)	1.51(1)		
C(24)–C(25)	1.51(2)		
C(25)–C(26)	1.51(2)		

i = $-x, -y, -z$.

Measurements

Infrared spectra (as KBr discs) and ligand-field spectra (diffuse reflectance) of both compounds were recorded on routine Perkin-Elmer spectrometers, supplied with data stations. Magnetic susceptibilities were recorded on Faraday equipment (77–300 K) and on a vibrating sample magnetometer, as described previously [15].

Results and Discussion

Figure 1 shows a perspective view of the complex molecule **1**. The structure is composed of three dimers, which are bridged into a hexameric unit by carboxyl oxygen atoms with relatively weak Cu(1)–O(33) and Cu(3)–O(33) bonds of 2.575(7) and 2.651(5) Å, respectively. One of the three ethanolato-bridged dimers is centrosymmetric and the other two are non-centrosymmetric. Within the Cu_2O_2 dimeric units the bridging Cu–O–Cu angles are 96.7(2) and 97.5(3) for Cu(1), Cu(2) and 102.1(3)° for Cu(3) and the respective Cu–Cu distances are 2.986(2) and 2.988(2) Å.

The coordination around the Cu(1) and Cu(2) atoms is distorted octahedral, while the Cu(3) atom is five coordinated in a distorted square-pyramidal environment. Two ethanolato oxygen atoms, a carboxyl oxygen atom and an amino nitrogen atom form the equatorial coordination plane around the Cu(1) and Cu(2) atoms and the basal plane around

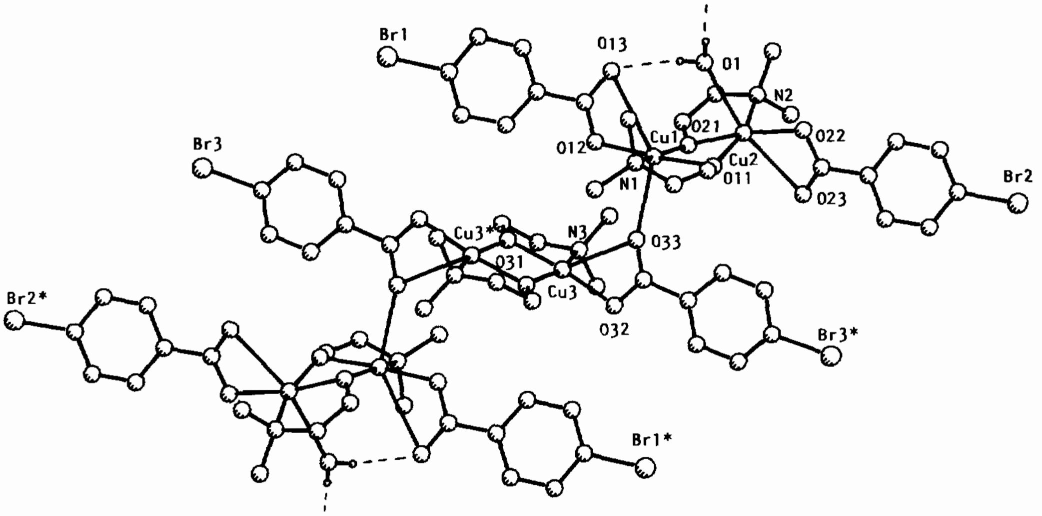

Fig. 1. Perspective view of the structure of $[Cu_6(C_7H_4BrO_2)_6(C_4H_{10}NO)_6(H_2O)_2]$ (1).

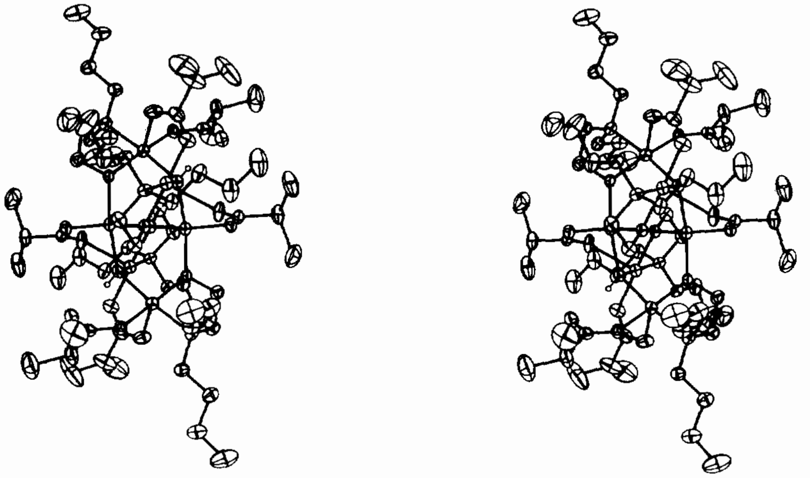

Fig. 2. Stereoview of the molecular structure of $[Cu_6(C_2HCl_2O_2)_6(C_{10}H_{22}NO)_4(OH)_2]$ (2).

the Cu(3) atom, with Cu–O bonds of 1.916(5)–1.974(5) Å and a Cu–N bond of 2.017(9)–2.067(9) Å. The apical site of the Cu(3) atom is occupied by the carboxyl oxygen O(33) atom, with a Cu–O distance of 2.651(5) Å. The axial sites of the Cu(2) atom are occupied by the water and carboxyl oxygen atoms and those of the Cu(1) atom by the carboxyl oxygen atoms. These Cu–O distances vary between 2.571(7) and 2.922(7) Å. However, due to the steric constraints of the carboxylate, the apical Cu–O makes an angle of about 50° with the coordination planes. The structure is stabilized by a weak intramolecular hydrogen bond between the carboxyl oxygen O(13) and the water oxygen O(1) atom; the distance O(1)...O(13) is 2.91(1) Å and the O(1)–H...O(13) angle is 168°. Moreover, a weak intermolecular hydrogen bond occurs from the second hydrogen atom of the water molecule to the O(22) atom of the carboxyl group; in the next unit the O(1)....O(22) (O(22) at $-x$, $-y$, $-z+1$) distance is 2.91(1) Å and the O(1)–H....O(22) angle is 166°. All other intermolecular contacts between non-hydrogen atoms are above 3.3 Å.

The crystal structure of compound 2 consists of discrete molecules, which are held in the crystal lattice by van der Waals forces. A view of the molecular structure is shown in Fig. 2 and the arrangement of the copper atoms with the Cu–Cu distances can be seen in Fig. 3.

The Cu atoms in the centrosymmetric molecule are linked by triply bridging ethanolato and hydroxo oxygen atoms, and by carboxylic and ethanolato oxygen bridges (Fig. 4). The Cu–O(hydroxo) distances of 1.972(5)–2.003(5) Å and the bridging Cu–O–Cu angles of 99.8(3)–130.4(3)° differ from the corresponding values in related hexameric [4] and nonameric [11] μ_3-hydroxo copper(II) complexes (1.934(11)–2.048(10) Å, 94.5(4)–130.4(5)°

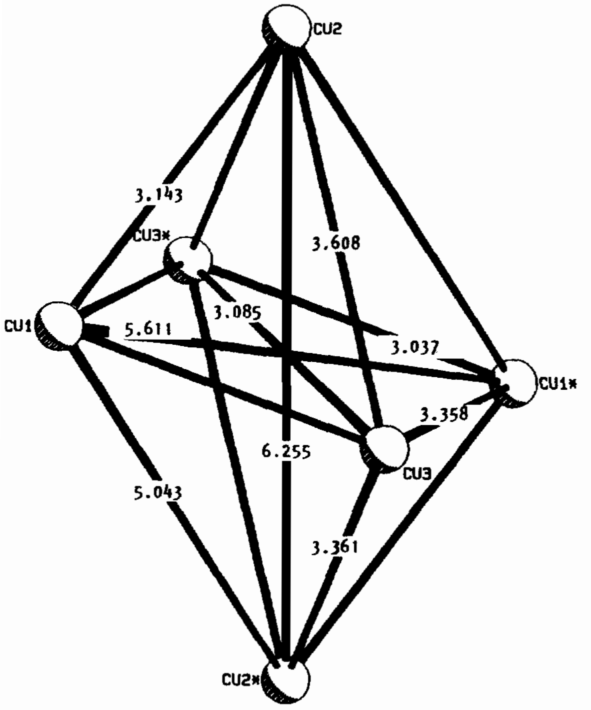

Fig. 3. The arrangement of the Cu atoms with Cu–Cu distances (Å) in structure **2**.

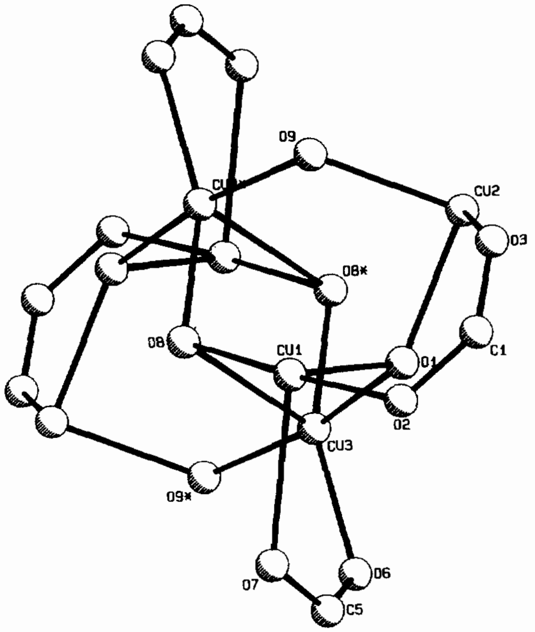

Fig. 4. View showing only the bridging system in **2**.

and 1.941(7)–2.149(7) Å, 97.5(3)–121.0(4)°, respectively).

The Cu....Cu contacts within the trinuclear unit (Fig. 3) are 3.143, 3.358 and 3.361 Å, whereas the intertrimer contacts are 3.037, 3.085 and 3.608 Å. Therefore, comparison with other trimers of this type [15, and refs. therein], is not useful.

The Cu–O distances for the triply bridging ethanolato oxygen atoms are 1.941(6), 1.964(5) and 2.438(6) Å, and the Cu–O–Cu bridging angles are between 87.0(2) and 118.7(3)°.

The environments of all six copper atoms may be described as a distorted square-based pyramid. The Cu(1) and Cu(2) atoms have a hydroxo oxygen, a carboxyl oxygen, an ethanolato oxygen and an amino nitrogen atom in the basal plane and a carboxyl oxygen atom in the apical position. The average deviation of O(1), O(2), O(8) and N(1) with regard to the mean plane is 0.04 Å and the Cu(1) atom is displaced toward the apical site by 0.08 Å. The corresponding values for Cu(2) are 0.09 and 0.11 Å, respectively. The apical position of the Cu(3) atom is occupied by an ethanolato oxygen atom, while two ethanolato oxygen atoms, a hydroxo oxygen atom and a carboxyl atom form the basal plane. The average deviation of these four atoms from the mean plane is 0.30 Å and Cu(3) is displaced toward the apical site by 0.11 Å. A relatively strong hydrogen bond exists between the hydroxo O(1) and the non-coordinated oxygen atom, O(5), of the carboxylate group; the distance O(1)....O(5) is 2.69(1) Å and the O(1)–H....O(5) angle is 177°.

Spectroscopy and Magnetism

The infrared spectra of both compounds show the spectral bands for the several ligand groups, the carboxylato groups (1605 cm^{-1} in **1**; 1660 cm^{-1} in **2**) and in addition O–H vibrations for the coordinated water (compound **1**) and hydroxo (compound **2**) ligands. In the hydroxo compounds the frequency at 3200 cm^{-1} agrees with the observed hydrogen bonding (*vide supra*). The water vibrations are observed at 3420 and 3400 cm^{-1} in compound **1** and are in agreement with the weaker hydrogen bonds seen from the O...O contacts (*vide supra*).

Ligand-field spectra for both compounds show broad bands at 14 800 (**1**) and 14 400 (**2**) cm^{-1}, and are in agreement with the found coordination geometries for the copper ions (4, 4 + 1, 4 + 1 + 1 coordination) in the clusters.

Magnetic susceptibility measurements for compound **1** show strong antiferromagnetism, as would be expected for the CuO_2Cu dimeric units. However, since the three dimers are also coupled mutually, a clear fit was not possible. Only in the 80–300 K region was a Curie–Weiss law observed with a θ value of -72 K; corresponding magnetic moments are 1.30–1.53 BM with a high-temperature extrapolation of 1.70 BM. No attempts were undertaken to fit the susceptibility with analytical expressions. Compound **2** also shows strong magnetic exchange, as reflected by a moment at 4 K of 1.0 BM, which regularly increases to 1.4 BM at room temperature. However, also in this case only between 80 and 300 K was a Curie–Weiss law observed, with a θ value of −153 K and high-temperature extrapolation of 1.75 BM. Apparently, the complicated magnetic exchange pathway possibilities do not allow fitting procedures; therefore, no attempts were undertaken to fit the observed curves.

EPR spectra of the powdered samples at room temperature show only broad, weak bands with maxima near $g = 2.08$. At liquid nitrogen temperature some weak signals with hyperfine lines appear, probably originating from paramagnetic monomeric Cu impurities which are always present in copper oligomers. Both compounds appear to contain two of such species, as deduced from their $g_\parallel$ values ($g_\parallel = 2.30$–2.37 with $A_\parallel = 135$–160 Gauss). These values are in the range for chromophores CuO_nN_m with $n > m$ and $n + m > 4$ [15].

Supplementary Material

Thermal parameters, hydrogen parameters and lists of F_{obs} and F_{calc} can be obtained from the authors.

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