Exchange Interaction in a Linear Trinuclear Copper(II) Cluster Complex with a Single Oxygen Bridge between Neighboring Copper(II) Ions. Crystal Structure of Bis[μ-(2-amino-2-methyl-1-propanolato)]-bis(2-amino-2-methyl-1-propanol)-tetrakis(phenylacetato)-tricopper(II)

Heikki Muhonen[a]* and William E. Hatfield[b]

[a]Department of Division of Inorganic Chemistry, University of Helsinki, SF-00100 Helsinki 10, Finland, and
[b]Department of Chemistry, University of North Carolina, Chapel Hill, N.C. 27514, USA

Muhonen, Heikki and Hatfield, William E. 1986. Exchange Interaction in a Linear Trinuclear Copper(II) Cluster Complex with a Single Oxygen Bridge between Neighboring Copper(II) Ions. Crystal Structure of Bis[μ-(2-amino-2-methyl-1-propanolato)]-bis(2-amino-2-methyl-1-propanol)-tetrakis(phenylacetato)-tricopper(II). – Acta Chem. Scand. A 40: 41–51.

The structure was solved from single crystal X-ray data. $[Cu_3(C_4H_{10}NO)_2(C_8H_7O_2)_4(C_4H_{11}NO)_2]$, triclinic, $P\bar{1}$, $a = 10.177(3)$, $b = 11.143(2)$, $c = 11.599(2)$ Å, $\alpha = 95.05(2)$, $\beta = 96.09(2)$, $\gamma = 97.80(2)°$, $V = 1288.7(5)$ Å^3, $Z = 1$. The least-squares refinement led to an R value of 0.051. In the structure three copper atoms form a centrosymmetric linear array with neighboring Cu...Cu distances of 3.477(1) Å. The middle and terminal copper atoms are joined by only a single alkoxo-oxygen bridge, with a Cu–O–Cu bridging angle of 128.3(2)° and Cu–O distances inside the bridge of 1.911(4) and 1.952(4) Å. The middle copper atom has planar coordination from nitrogen [Cu–N = 1.969(5) Å] and oxygen [Cu–O = 1.911(4) Å] atoms of the bridging aminoalcohol ligands. The terminal copper atoms have highly distorted octahedral coordination. The equatorial plane of the octahedron is made up by the bridging aminoalcohol oxygen atom [Cu–O = 1.952(4) Å], the nitrogen atom from the nonbridging aminoalcohol ligand [Cu–N = 2.002(5) Å], and two carboxylate oxygen atoms from two different phenylacetato ligands [Cu–O = 1.976(4) and 1.975(3) Å]. One axial position is occupied by an oxygen atom from the nonbridging aminoalcohol ligand and the other axial position has a carboxylate oxygen atom from one of the phenylacetato ligands. The axial Cu–O distances are 2.499(5) and 2.676(5) Å. Magnetic susceptibilities, measured in the temperature range 4.2–300 K, reveal that the ground state is a spin doublet. The exchange coupling constant between middle and terminal copper atoms was found to be $J = -169$ cm^{-1}. Molecules are packed in chains parallel to c and there is a weak intertrimer ferromagnetic interaction of $zJ' \sim 4$ cm^{-1}.

Complexes of aminoalcohols with transition metal ions have received much attention in recent years, especially with respect to their structures and magnetic properties. For the most part, complexes of copper(II) have been made with a variety of N-substituted aminoalcohols being used as ligands. The desirability of aminoalcohols as ligands is a consequence of the strong tendency of the aminoalcohol oxygen atom to form bridges between metal atoms resulting in many different kinds of polynuclear complexes. The reported complexes have been shown to be monomeric, dimeric, trimeric, tetrameric, hexameric and polymeric although the vast majority are di-μ-alkoxo-oxygen bridged dimers or Cu_4O_4-cubane type tetramers. Thus far, all of the systematic studies of the magnetic properties of aminoalcohol complexes have concentrated on

*To whom correspondence should be addressed.

exchange interactions in (a) di-μ-alkoxo-oxygen bridged dimers,[1-5] (b) Cu_4O_4-cubane type tetramers,[1-5] and (c) hydrogen-bonded dimers.[3,6]

Our aim is to determine what kind of complexes the N-unsubstituted aminoalcohol, 2-amino-2-methyl-1-propanol, will form with copper(II). We especially wish to obtain completely new polynuclear systems that will permit the study of less explored magnetic interactions. To accomplish this goal we are proceeding along two paths. First, we want to find if the complexes formed by 2-amino-2-methyl-1-propanol in the presence of small counter ions are structurally similar to those formed by N-substituted aminoalcohols. Second, we want to determine the effect of steric hindrance in the inner and outer coordination spheres of copper(II) on complex formation. Therefore we selected the benzoate ion as the generic counter ion since a variety of derivatives is available for the planned systematic studies. In this paper we describe the structure and magnetic properties of a compound with the phenylacetate ion as the counter ion. In phenylacetate ion, compared to benzoate ion, the phenyl ring is displaced one aliphatic C–C bond length away from the carboxylate group, and there is more space in the immediate environment of the copper(II) ion.

Experimental

Preparation and analysis of the complex. Copper(II) phenylacetate, which was used as starting material in the complex preparation, was prepared following the procedure described by Orama *et al.*[7] for the preparation of copper(II) *m*-bromobenzoate. The title complex was synthesized by adding 18 g solid copper(II) phenylacetate, which was used without prior analyses, in small portions to a warm solution of 9.5 g 2-amino-2-methyl-1-propanol in about 150 ml ethanol. The solution was allowed to evaporate to dryness at room temperature yielding a noncrystalline precipitate. The precipitate was redissolved by heating in 2-propanol, divided into smaller fractions, and these solutions were allowed to evaporate to dryness at room temperature. One of the fractions yielded about 70 mg of a dark blue, crystalline product which precipitated over a white substance which evidently was phenylacetic acid. Other fractions exclusively yielded solid phenylacetic acid, which had been colored blue by the complex. The dark blue, crystalline product was mechanically separated from the surface of the phenylacetic acid precipitate.

X-ray analysis. Structure determination. The unit cell parameters were obtained by least-squares fit of 17 centred and indexed reflections in the range $6 < 2\theta < 16°$. The details concerning crystallographic data collection and the results are summarized in Table 1. Intensities were corrected for Lorentz and polarization effects. Three high electron density maxima, of which one was clearly smaller than the other two, were obtained by MULTAN80[8] supposing no kind of symmetry. These maxima were used as copper atom positions in the first step of the Fourier synthesis. The structure was solved by an iterative process and Fourier and least-squares refinements were carried out in each step. When the *R* factor was 0.14, it seemed evident that the molecule possessed a center of symmetry. That being the case, calculations were started in the centrosymmetric space group. The molecule was moved in the *c* direction so that the middle copper atom sat on the center of symmetry while supposing, based on the low value of the *R* factor that the orientation of the molecule was correct. After moving of the molecule to the right place in the unit cell, refinement in the space group $P\bar{1}$ converged rapidly. Difference syntheses calculated during the refinement provided the location of all hydrogen atoms and their parameters were introduced into the refinement. Final refinement by full-matrix least-squares method using anisotropic temperature factors for the nonhydrogen atoms and isotropic temperature factors for the hydrogen atoms converged to the *R* value of 0.051. The highest peaks in the difference Fourier map calculated at the end of the refinement were less than 0.35 e $Å^{-3}$. All calculations except the phase determination were carried out with the programs of the X-RAY 76 system.[9] The atomic scattering factors were those of the program system. Dispersion correction was applied for copper atoms.[10] A Univac 1108 computer was used for calculations, and figures were drawn by the PLUTO[11] program.

Magnetic measurements. Magnetic susceptibility measurements in the range 77–300 K were performed on a powdered sample weighing about 15 mg with use of a Faraday type balance consisting of a Chan 2000 electrobalance equipped with

Table 1. Crystal data and details of the structure determination.

formula	$[Cu_3(C_4H_{10}NO)_2(C_8H_7O_2)_4(C_4H_{11}NO)_2]$
formula weight	1085.7
crystal system	triclinic
a	10.177(3) Å
b	11.143(2) Å
c	11.599(2) Å
α	95.05(2)°
β	96.09(2)°
γ	97.80(2)°
space group	$P\bar{1}$
V	1288.7(5) Å^3
Z	1
D_c	1.40 g/cm^3
D_m	1.41 g/cm^3
diffractometer	Syntex $P2_1$
crystal dimensions	0.46×0.13×0.13 mm
radiation	λ = 0.7107 Å (Mo *K*α)
absorption coeficient	13.4 cm^{-1}
data collected	$4.0 < 2\theta < 50.0°$
scan type	ω
scan speed	2.1–29.3°/min
scan range	[2θ(Mo $K\alpha_1$)–1.0]–[2θ(Mo $K\alpha_2$) + 1.0]°
background time/scan time	0.5
number of standard reflections	2 (no significant variation)
absorption correction	not made
number of reflections collected	5334
number of observed reflections	2859 [$F > 5\sigma(F)$]
weighting scheme	$w = 1.0/[\sigma^2(F_o) + 0.00025F_o^2]$
number of parameters refined	445
$R = \Sigma(\|F_o\|-\|F_o\|)/\Sigma\|F_o\|$	0.051
$R_w = [\Sigma w(\|F_o\|-\|F_o\|)^2/\Sigma w\|F_o\|^2]^{1/2}$	0.051

an Anac 3472 HA electromagnet and 502 Lewis coils from George Associates, Berkeley, California. Automatic data collection was achieved with use of the peripherals that have been described elsewhere.[12] At low temperatures, from about 4.2 to 100 K, magnetic susceptibility data were collected on a powdered sample weighing about 50 mg with use of a Princeton Applied Research Model 155 vibrating sample magnetometer (VSM) operating at field strength of 10 kOe with use of procedures that have been described previously.[13] Both instruments were calibrated with $HgCo(NCS)_4$. Susceptibilities were corrected for the diamagnetism, which was estimated to be -203×10^{-6} cgsu/Cu and for the temperature independent paramagnetism, Nα, of copper(II), which was estimated to be 60×10^{-6} cgsu/Cu atom.

Results and discussion

Description of the structure. The molecule is shown in Fig. 1. The final atomic positional parameters are given in Table 2, and bond lengths and angles are listed in Table 3. The structure consists of three copper atoms arrayed in a straight line, with separations of 3.477(1) Å. The middle copper atom, Cu2, lies at the center of symmetry. Neighboring copper atoms are linked by a single alkoxo-oxygen bridge. Within the bridge the Cu–O distances are 1.952(4) Å for Cu1–O1 and 1.911(4) Å for Cu2–O1. The bridge angle Cu2–O1–Cu1 is 128.3(2)°. The coordination around the middle Cu2 atom is planar with the bond lengths being 1.911(4) Å for Cu2–O1 and 1.969(5) Å for Cu2–N1. The coordination around the terminal copper atoms is highly distorted oc-

Table 2. Final fractional coordinates, and U_{eq} ($\times 10^2$) and U_{iso} ($\times 10^2$) values for nonhydrogen and hydrogen atoms, respectively.

$U_{eq} = \frac{1}{3} \cdot \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j \cos\alpha_{ij}$.

	x	*y*	*z*	U_{eq} or U_{iso} (Å^2)
Cu1	.02119(7)	−.02493(7)	.29788(6)	3.03(4)
Cu2	.00000	.00000	.00000	3.47(6)
N1	.0426(5)	.1717(4)	−.0285(4)	3.9(3)
N2	.0089(4)	−.1395(4)	.4211(4)	3.1(2)
O1	.0498(4)	.0599(3)	.1603(3)	3.9(2)
O2	.1494(4)	−.1900(4)	.2344(4)	4.4(2)
O3	−.1645(4)	−.0809(4)	.2262(3)	3.9(2)
O4	−.1955(4)	.0665(4)	.3561(4)	5.2(2)
O5	.1706(4)	.0792(3)	.3973(3)	3.5(2)
O6	.3353(4)	−.0112(4)	.3316(4)	6.5(3)
C1	.1053(7)	.1855(6)	.1766(5)	4.6(3)
C2	.0432(6)	.2515(5)	.0824(5)	3.9(3)
C3	−.1001(8)	.2615(8)	.0980(7)	7.3(5)
C4	.1242(8)	.3758(6)	.0774(6)	6.4(4)
C5	.1537(6)	−.2635(6)	.3285(6)	4.5(3)
C6	.0277(6)	−.2690(5)	.3878(5)	3.9(3)
C7	.0488(7)	−.3332(6)	.4990(6)	5.8(4)
C8	−.0939(7)	−.3328(6)	.3080(6)	5.4(4)
C9	−.2365(6)	−.0085(5)	.2705(5)	3.6(3)
C10	−.3789(6)	−.0141(6)	.2135(6)	4.6(3)
C11	−.4332(6)	−.1258(6)	.1324(5)	3.9(3)
C12	−.5100(7)	−.2232(7)	.1700(6)	5.4(4)
C13	−.5600(8)	−.3273(7)	.0961(7)	6.8(5)
C14	−.5394(8)	−.3360(8)	−.0159(7)	7.2(5)
C15	−.4644(7)	−.2390(7)	−.0596(6)	6.0(4)
C16	−.4138(7)	−.1363(7)	.0173(6)	6.0(4)
C17	.2928(6)	.0652(5)	.3954(5)	3.8(3)
C18	.3926(6)	.1546(6)	.4816(6)	4.9(4)
C19	.4457(6)	.2635(5)	.4240(5)	3.7(3)
C20	.3697(7)	.3585(7)	.4069(6)	5.6(4)
C21	.4162(9)	.4580(7)	.3572(7)	6.4(5)
C22	.5430(9)	.4712(7)	.3241(6)	6.4(5)
C23	.6192(7)	.3797(8)	.3398(6)	6.0(4)
C24	.5722(6)	.2779(6)	.3890(6)	4.6(4)
H1	.084(6)	.242(5)	.270(5)	6(2)
H2	.190(5)	.185(5)	.172(4)	3(2)
H3	−.107(9)	.316(8)	.169(8)	14(3)
H4	−.148(6)	.185(6)	.098(5)	9(2)
H5	−.140(7)	.301(6)	.029(6)	8(2)
H6	.077(7)	.434(6)	.026(6)	9(2)
H7	.204(6)	.362(6)	.058(5)	7(2)
H8	.117(6)	.428(5)	.159(5)	7(2)
H9	−.015(4)	.192(4)	−.073(3)	2(1)
H10	.108(7)	.172(6)	−.046(5)	7(2)
H11	.207(5)	−.140(5)	.250(5)	2(2)
H12	.168(6)	−.352(5)	.299(5)	6(2)
H13	.230(4)	−.231(4)	.383(4)	2(1)
H14	.087(6)	−.407(6)	.472(5)	6(2)
H15	.118(7)	−.294(6)	.544(6)	7(2)
H16	−.026(5)	−.334(5)	.535(4)	3(2)
H17	−.160(6)	−.339(5)	.350(5)	7(2)
H18	−.111(5)	−.291(4)	.245(4)	3(1)
H19	−.078(5)	−.421(5)	.289(5)	4(2)
H20	−.066(5)	−.142(4)	.455(4)	2(1)
H21	.058(5)	−.098(4)	.495(4)	3(1)
H22	−.384(6)	.066(5)	.170(5)	7(2)

	x	y	z	U_{eq} or U_{iso} (Å^2)
H23	−.433(6)	−.004(5)	.253(5)	3(2)
H24	−.530(6)	−.216(5)	.257(5)	7(2)
H25	−.615(6)	−.390(5)	.132(5)	7(2)
H26	−.551(8)	−.399(7)	−.075(7)	14(3)
H27	−.435(6)	−.247(6)	−.145(5)	7(2)
H28	−.370(5)	−.080(5)	−.013(4)	5(2)
H29	.341(7)	.171(6)	.550(6)	8(2)
H30	.465(4)	.112(4)	.512(4)	3(1)
H31	.295(6)	.354(5)	.436(5)	7(2)
H32	.362(6)	.522(5)	.349(5)	7(2)
H33	.571(8)	.532(7)	.277(7)	10(3)
H34	.706(6)	.380(6)	.303(6)	7(2)
H35	.622(5)	.209(4)	.400(4)	3(1)

tahedral. The equatorial plane of the octahedron is made up of atoms O1, N2, O3 and O5, and the plane is tetrahedrally distorted with the deviations of the atoms O1, N2, O3 and O5 from the plane being −0.300(4), −0.288(4), 0.297(4) and 0.291(4) Å, respectively. The deviation of the Cu1 atom from the plane toward the axial O2 atom is only 0.086(2) Å, being less than those of the plane determining atoms. In the equatorial plane the coordination bond lengths vary for Cu–O bonds from 1.952(4) to 1.976(4) Å, while the Cu–N bond length is 2.002(5) Å. The axial Cu1–O2 bond distance involving the nonbridging aminoalcohol molecule is 2.499(5) Å, while the other axial Cu1–O4 bond distance to the carboxylate group coordinating both axially and equatorially is considerably longer, 2.676(5) Å. The angle O2–Cu1–O4 beetween the axial Cu–O bonds is 155.2(1)°. The angles, which the axial directions Cu1–O2 and Cu1–O4 form with the normal of the equatorial least-squares plane are 9.6(2) and 25.2(2)°, respectively. These three angles together with the axial bond lengths give an impression of the degree of axial distortion of the octahedron. The angle between the coordination planes [Cu2,O1,N1] and [O1,O3,O5,N2] around Cu2 and Cu1, respectively, is 42.2(2)°. The bridging aminoalcohol molecule gives rise exclusively to short copper – oxygen bonds and exists in the complex in the deprotonated form, while the nonbridging aminoalcohol molecule, in which the oxygen atom is in an axial coordination position, exists in the complex in the protonated form. The five membered aminoalcohol chelate rings have torsion angles O1–C1–C2–N1 and O2–C5–C6–N2 of −45.2(5) and −54.0(5)°, respectively, indicating that the aminoalcohol ligand that is coordinated to the middle copper atom is folded in to a lesser extent than the aminoalcohol coordinated to a terminal copper.

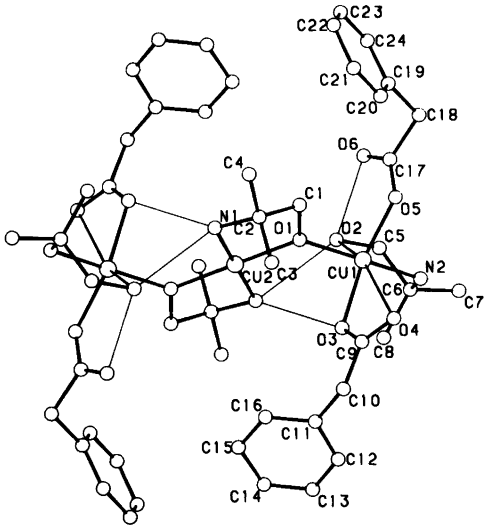


Fig. 1. View of the trinuclear copper(II) cluster molecule.

In the bidentate carboxylato ligand, the carboxylate group makes an angle of 77.5(5)° with the phenyl ring, and the angle C9–C10–C11 along the aliphatic chain connecting these planes is 115.8(5)°. The values for the respective angles in the unidentate carboxylato ligand are 69.5(5) and 110.7(5)°. The distance of the uncoordinated carboxylate oxygen atom O6 from Cu1 is 3.160(4) Å.

Table 3. Interatomic distances (Å) and angles (°).

Cu1–N2	2.002(5)	Cu1–O4	2.676(5)
Cu1–O1	1.952(4)	Cu1–O5	1.975(3)
Cu1–O2	2.499(5)	Cu2–N1	1.969(5)
Cu1–O3	1.976(4)	Cu2–O1	1.911(4)
O1–Cu1–N2	167.9(2)	O2–Cu1–O5	97.0(1)
O1–Cu1–O2	92.7(2)	O3–Cu1–N2	93.4(2)
O1–Cu1–O3	87.9(2)	O3–Cu1–O4	54.2(1)
O1–Cu1–O4	99.0(2)	O3–Cu1–O5	157.8(2)
O1–Cu1–O5	93.8(1)	O4–Cu1–N2	91.4(2)
O2–Cu1–N2	75.3(2)	O4–Cu1–O5	103.8(1)
O2–Cu1–O3	105.0(1)	O5–Cu1–N2	89.6(2)
O2–Cu1–O4	155.2(1)	O1–Cu2–N1	84.7(2)
C1–O1	1.425(7)	C5–O2	1.421(8)
C1–C2	1.502(9)	C5–C6	1.514(9)
C2–N1	1.496(7)	C6–N2	1.503(8)
C2–C3	1.507(11)	C6–C7	1.538(10)
C2–C4	1.522(9)	C6–C8	1.516(8)
Cu2–O1–Cu1	128.3(2)	Cu1–O1–C1	118.5(3)
Cu2–O1–C1	112.9(3)	Cu1–O2–C5	104.5(3)
Cu2–N1–C2	109.3(4)	Cu1–N2–C6	117.3(3)
N1–C2–C1	105.2(5)	N2–C6–C5	106.7(5)
N1–C2–C3	107.3(5)	N2–C6–C7	109.1(5)
N1–C2–C4	110.5 (5)	N2–C6–C8	109.2(5)
C1–C2–C3	110.8(6)	C5–C6–C7	108.7(5)
C1–C2–C4	111.2(5)	C5–C6–C8	112.0(5)
C3–C2–C4	111.6(6)	C7–C6–C8	111.0(5)
C9–O3	1.273(7)	C17–O5	1.277(7)
C9–O4	1.237(7)	C17–O6	1.232(8)
C9–C10	1.518(8)	C17–C18	1.536(8)
C10–C11	1.495(8)	C18–C19	1.501(9)
Cu1–O4–C9	75.0(3)		
Cu1–O3–C9	106.7(3)	Cu1–O5–C17	123.4(3)
O3–C9–O4	123.2(5)	O5–C17–O6	126.1(5)
O3–C9–C10	117.8(5)	O5–C17–C18	114.9(5)
O4–C9–C10	119.0(6)	O6–C17–C18	118.9(5)
C9–C10–C11	115.8(5)	C17–C18–C19	110.7(5)
C10–C11–C12	121.1(6)	C18–C19–C20	121.0(6)
C10–C11–C16	122.6(6)	C18–C19–C24	122.1(6)
The range of variation for C–C bonds and C–C–C angles in phenyl rings:			
bidentate ligand			
1.336(12)–1.401(12)		116.2(6)–123.5(7)	
monodentate ligand			
1.347(11)–1.409(10)		116.8(6)–122.0(7)	

The packing of molecules of the 2-amino-2-methyl-1-propanol – phenylacetato complex is shown in Fig. 2. There are three intramolecular and two intermolecular hydrogen bonds, and the parameters for these are given in Table 4. The trinuclear cluster molecules form a chain which is parallel to *c*-axis. As shown in Table 4, the distance between neighboring trinuclear molecules in the chain is of the magnitude found for normal hydrogen bond distances.

Comparison with related structures. The structures of copper(II) complexes formed by the present aminoalcohol with benzoate[14], *o*-nitrobenzoate[15] and salicylate[16] ions as counter ions

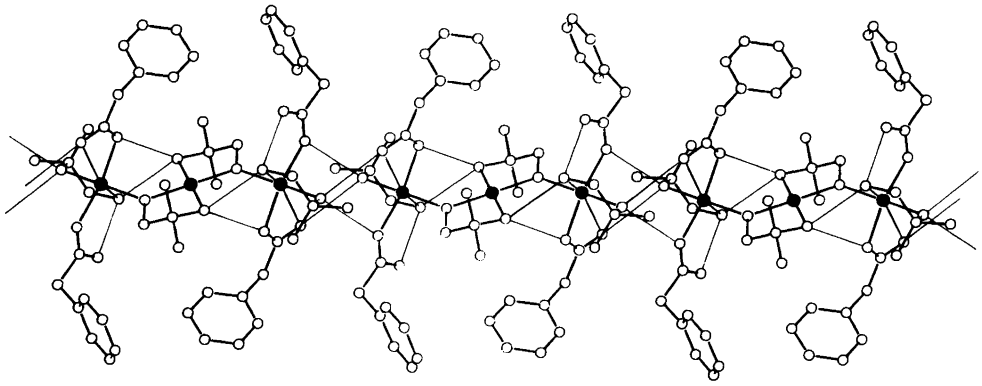


Fig. 2. Chain packing, which takes place in the *c* direction, is shown by three successive cluster molecules.

among carboxylates have been described earlier. Of the three complexes, the *o*-nitrobenzoato complex represents a typical monomeric bis-complex for copper(II) with two separate bidentate ligands. This means that in six-coordination one of the ligands is bidentate and the other is monodentate. Separate molecules are held together in the solid state via a hydrogen bonding network. The benzoate compound has a different type of structure in which the bis(aminoalcohol)copper(II) complex has a planar coordination arrangement of aminoalcohols around copper(II) ion. On both sides of this coordination plane there is abundant space for benzoate ions to coordinate, but coordination does not, however, take place. Instead of coordination the benzoate ion forms a very short hydrogen bond with the aminoalcohol ligand through the alcohol group. In the compound the hydrogen bonding O...O distance from the aminoalcohol oxygen atom to one of the carboxylate oxygen atoms is only 2.431(7) Å. Short hydrogen bonds have proved to be good pathways for the propagation of magnetic interaction between metal ions. In the benzoate compound the interaction pathway via the carboxylate bridge is not possible since the other carboxylate oxygen atom forms a hydrogen bond of normal length with a neighboring molecule. The Cu–O(carboxylate) axial distance is 3.184(6) Å, and the benzoate ions remain outside of the inner coordination sphere of copper.

The salicylate complex is composed of two monomeric fragments, namely of alternating copper(II) aminoalcohol and copper(II) salicylato fragments, which form a regular linear chain structure for the complex. The copper atoms are linked by a single carboxylate bridge, which alternates from one side of the *a*-axis to the other with the Cu...Cu separation of 5.042(7) Å. The aminoalcohol – phenylacetato complex may also be described as being built up of two monomeric fragments; a copper(II) aminoalcohol fragment (*A*) and a copper(II) mixed-ligand fragment in which the aminoalcohol and phenylacetate mole-

Table 4. Hydrogen bond distances (Å) and angles (°).[a]

A–H...B	A–H	H...B	A...B	(A–H...B)
O2–H11...O6	.75(5)	1.91(5)	2.636(6)	164(6)
N1–H9...O2^{i}	.81(4)	2.19(4)	2.961(6)	158(4)
N1–H10...O3^{i}	.72(7)	2.40(6)	2.891(6)	127(5)
N2–H21...O4^{ii}	.98(4)	2.08(4)	3.019(6)	159(4)
N2–H20...O5^{ii}	.89(5)	2.22(5)	3.020(6)	149(4)

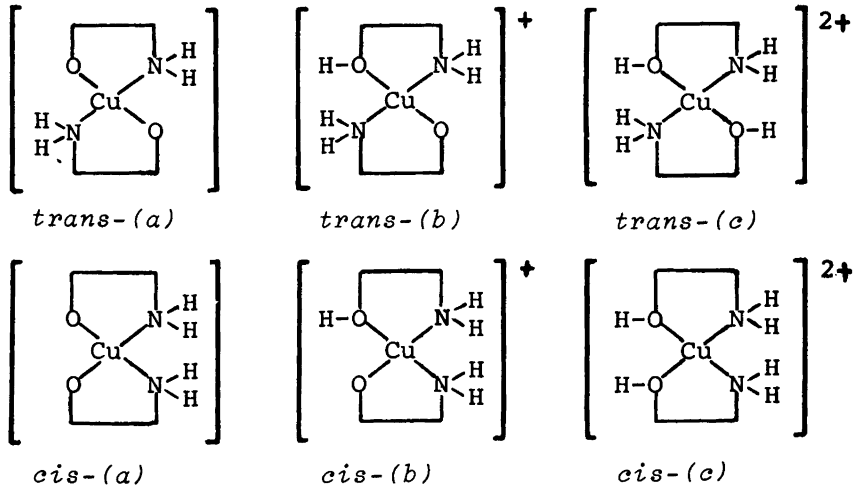
[a]Symmetry codes: $^{i}-x,-y,-z$; $^{ii}-x,-y,-z+1$

cules function as ligands (*B*). The two types of fragments are joined by the sharing of an aminoalcohol oxygen atom; the trinuclear molecule consisting of fragments *BAB*. The phenyl rings are far removed from the inner coordination spheres of copper atoms and steric hindrance associated with them affects the molecular packing rather than the coordination. In spite of the formal similarity between benzoate and phenylacetate ions, structures for the copper(II) complexes formed by 2-amino-2-methyl-1-propanol with the two carboxylate ions are completely different.

The structure of a complex formed between copper(II) benzoate and the N-substituted aminoalcohol, 2-dibutylaminoethanol, has been reported previously.[17] This complex is also a centrosymmetric linear copper(II) trimer. An essential structural difference between these trimers concerns the bridges between copper atoms. In the 2-dibutylaminoethanol – benzoato complex the benzoate ions are included in the inner coordination spheres of copper atoms, and one of the benzoate ions forms a carboxylate bridge between copper atoms. Because the alkoxo-oxygen atom also acts as bridging atom in this complex, there are two different bridging pathways between neighboring copper atoms. The Cu...Cu distance in the complex is 3.211(6) Å. The coordination geometries on the middle and terminal copper atoms are opposite to that found in the present phenylacetato complex.

Configurations of the bis-complexes formed by 2-amino-2-methyl-1-propanol with copper(II), which may exist as fragments in the structures. There are six different types of bis-complexes formed by 2-amino-2-methyl-1-propanol with copper(II), which may exist as fragments of the overall structure. As shown below, these are composed of *cis* and *trans* arrangements of the aminoalcohol ligands around copper(II) and of the protonated and deprotonated forms of the ligand. The benzoate, *o*-nitrobenzoate and salicylate compounds are all examples of the *trans-(c)* arrangement of ligands. Phenylacetato and monohydrate[18] complexes provide examples of *trans-(a)* configuration. No compound with the *trans-(b)* or *cis-(c)* configuration is known. We found one carboxylate compound which shows the *cis-(b)* arrangement of aminoalcohols, and we will discuss this configuration elsewhere. It appears that the *cis-(b)* arrangement is likely to lead to the formation of polynuclear complexes with hydrogen-bonded bridges, and there is an example of this arrangement in the nitrate compound.[6] A preliminary report of the structure of a complex which contains *cis-(a)* fragment has been presented.[19] The complex is not, however, a carboxylate compound. This configuration will be discussed in a forthcoming article in which the magnetic properties of the complex are explained in terms of its molecular structure.

Magnetic properties. The temperature dependence of the reciprocal magnetic susceptibility and of the effective magnetic moment of the complex are shown in Fig. 3 where it may be seen that the μ_{eff} values (per copper ion) are near 1.2 B.M. in



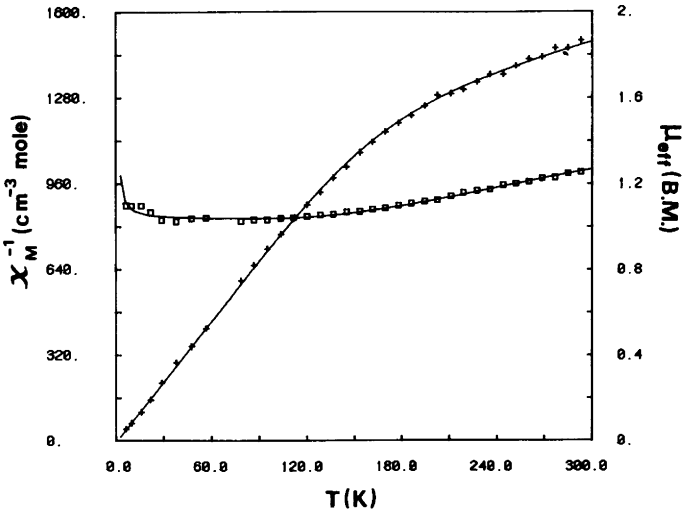


Fig. 3. Temperature dependence of the inverse magnetic susceptibility (+) and of the effective magnetic moment (□) for the compound. The solid curves represent theoretical values.

the temperature range 4.2–300 K. This observation suggests a strong antiferromagnetic interaction between neighboring copper(II) ions.

The Hamiltonian appropriate for the exchange coupling problem in a trinuclear entity is

$$H = -2(J_{12}\hat{S}_1 \cdot \hat{S}_2 + J_{23}\hat{S}_2 \cdot \hat{S}_3 + J_{13}\hat{S}_1 \cdot \hat{S}_3)$$

where the subscript 2 labels the central copper, and, as indicated from symmetry, $J_{12} = J_{23}$. The quartet state lies at $-(J_{12} + J_{13}/2)$ and the doublet states have energies $2J_{12} - J_{13}/2$ and $3J_{13}/2$. Substitution into the Van Vleck equation yields

$$X_M = \frac{Ng^2\beta^2}{3kT} \cdot \frac{5\exp[(J_{12} + J_{13}/2)/kT] + 0.5\exp[(-2J_{12} + J_{13}/2)/kT] + 0.5\exp(-3J_{13}/2kT)}{4\exp[(J_{12} + J_{13}/2)/kT] + 2\exp[(-2J_{12} + J_{13}/2)/kT] + 2\exp(-3J_{13}/2kT)}$$

where the susceptibility is expressed per copper. To account for the presence of intertrimer interaction, a mean field term was added the Van Vleck equation yielding

$$X_M^{corr} = X_M/(1 - 2zJ'X_M/Ng^2\beta^2)$$

The fitting of the calculated magnetic susceptibility to the experimental data was carried out with use of a Simplex routine where the criterion of best fit was the minimum value of the function

$$F = \sum_i (X_i^{obs} - X_i^{calcd})^2/(X_i^{obs})^2.$$

With any choice of reasonable starting values for the variables, the refinement always converged to the same minimum yielding g = 2.059, J_{12} = −168.8 cm^{-1}, J_{13} = −0.3 cm^{-1} and zJ' = 3.9 cm^{-1} with R, defined as square root of F, equalling 0.033.

The best fit magnetic parameters lead to the following conclusions. Each of the terminal copper ions is strongly antiferromagnetically exchange-coupled to the center copper ion of the trimetallic complex, but exchange coupling between the two terminal copper ions is essentially nonexistent. Furthermore, the best fit value of 3.9 cm^{-1} for zJ' indicates that the trimers are ferromagnetically coupled. In view of the chain-like structure of the compound, it would be appropriate to formulate the exchange coupling problem as a chain of trimers with the sequence of exchange parameters ...aabaabaab... (a = J_{12}, b = J').However, theoretical results for such chains are unavailable, and, in any event, the ratio J'/J suggests that the mean field treatment is appropriate.

As far as we know, there are no other examples of studies of magnetic properties of linear trinuclear copper(II) complexes bridged by only a single oxygen atom. The fairly large energy gap, $3J_{12}$ = −506 cm^{-1}, between the doublet and quartet states can be understood as a consequence of the large Cu1–O1–Cu2 bridge angle of 128.3(2)°. It is well known that exchange coupling is strongly dependent on the bridging angle

as has been documented, for example, by experimental and theoretical studies of di-μ-hydroxo-bridged copper(II) complexes.[20] The magnetic properties of the present compound can be explained in the following way. The d_{xy} orbitals are the magnetic orbitals on copper atoms in the complex. Combinations of these metallic orbitals can interact with symmetrically similar combinations of p_x or p_y orbitals of the bridging oxygen atoms. Complexes which possess only a single atom bridge between copper atoms and in which all the magnetic orbitals on copper atoms have the same symmetry, can display ferromagnetic superexchange interactions only in the very restricted bridging angle range near 90°. At angles near 180° the lobes of magnetic d_{xy} orbitals are parallel and the strongest antiferromagnetic interaction arises. In the present complex the large bridge angle of 128.3(2)°, suggests a large degree of overlap of the magnetic orbitals and those of the bridging oxygen atom, and as consequence of this overlap strong antiferromagnetic interactions result.

Another structural feature, which has been shown to have significant effect on the magnetic properties of di-μ-hydroxo-bridged copper(II) dimers, is the dihedral angle between the "coordination" planes [Cu1,O1,O2] and [Cu2,O1,O2] within the Cu1$<^{O1}_{O2}>$Cu2 unit.[21] Because the present complex, as a single bridged one, possesses only the Cu1$-^{O1}-$Cu2 bridging unit, the effect of the dihedral angle between the coordination planes around Cu1 and Cu2 on the magnetic properties is negligible. This can be understood by the following explanation. One of the d_{xy} orbital lobes on Cu1 is directed toward the O1 bridging atom and in the same way one of the d_{xy} orbital lobes on Cu2 is also directed toward the O1 bridging atom. If the d_{xy} orbital on Cu1 is kept immobile, and the d_{xy} orbital on Cu2 is rotated around the Cu2–O1 direction, then the dihedral angle between the coordination planes takes on all values from 0 to 90°. This kind of rotation does not cause any changes in the interaction pathway nor in the overlap with the bridging atom. We note that the dihedral angle between coordination planes around Cu1 and Cu2 is 42.2(2)°, and in spite of the large angle a strong antiferromagnetic interaction is found.

Acknowledgement. H.M. thanks the Heikki and Hilma Honkanen Foundation, and the Jenny and Antti Wihuri Foundation for their financial support.

References

1. Uhlig, E. and Steiger, K. *Z. Anorg. Allg. Chem. 346* (1966) 21 & *360* (1968) 39.
2. Nishida, Y. and Kida, S. *J. Inorg. Nucl. Chem. 38* (1976) 451.
3. Bertrand, J. A. and Eller, P. G. *Prog. Inorg. Chem. 21* (1976) 23.
4. Mergehenn, R. and Haase, W. *Acta Crystallogr. B 33* (1977) 1877.
5. Nieminen, K. *Ann. Acad. Sci. Fenn. Ser. A 2 197* (1983). This reference covers references for separate dimeric and tetrameric copper(II) aminoalcohol complexes.
6. Bertrand, J. A., Fujita, E. and VanDerveer, D. G. *Inorg. Chem. 19* (1980) 2022.
7. Orama, O., Huttner, G., Lorenz, H., Marsili, M. and Frank, A. *Finn. Chem. Lett.* (1976) 137.
8. Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J. P. and Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
9. Steward, J. M. Ed., *The X-Ray System, Version of 1976,* Technical Report TR-446, Computer Science Center, University of Maryland, College Park 1976.
10. *International Tables for X-Ray Crystallography,* Kynoch Press, Birmingham 1974, Vol IV p. 149.
11. Motherwell, W. D. S. and Clegg, W. (1978). *PLUTO Program for Plotting Molecular and Crystal Structures.* Univ. of Cambridge, England.
12. Weller, R. R. *The Cluster Approach to the Magnetic Susceptibilities of Low-Dimensional Copper Clusters,* Ph.D. Dissertation, University of North Carolina, Chapel Hill 1980.
13. Corvan, P. J., Estes, W. E., Weller, R. R. and Hatfield, W. E. *Inorg. Chem. 19* (1980) 1297.
14. Muhonen, H. and Hämäläinen, R. *Acta Chem. Scand. A 32* (1978) 121.
15. Muhonen, H. *Acta Crystallogr. C 39* (1983) 536,
16. Muhonen, H. *Acta Crystallogr. B 38* (1982) 2041.
17. Muhonen, H., Pajunen, A. and Hämäläinen, R. *Acta Crystallogr. B 36* (1980) 2790.
18. Muhonen, H. *Acta Crystallogr. B 37* (1981) 953.
19. Muhonen, H. and Hatfield, W. E. *Abstracts, 36th Southeastern Regional Meeting,* American Chemical Society, Raleigh, N. C., October 1984, no. 305.

20. see for instance, (a) Hatfield, W. E. *Comments Inorg. Chem. 1* (1981) 105. (b) Hay, P. J., Thibeault, J. C. and Hoffman, R. *J. Am. Chem. Soc. 97* (1975) 4884. (c) Kahn, O. *Inorg. Chim. Acta 62* (1982) 3. (d) Kahn, O. and Charlot, M. F. *Nouv. J. Chim. 4* (1980) 567.

21. Charlot, M. F., Jeannin, S., Jeannin, Y., Kahn, O., Lucrèce-Abaul, J. and Martin-Frère, J., *Inorg. Chem. 18* (1979) 1675.

Received June 11, 1985.