A Mononuclear Copper(II) Complex with an Aminoalcohol. The Crystal and Molecular Structure of Bis(2-amino-2-methyl-1-propanol)copper(II) Dibenzoate

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The crystal structure of $[Cu(C_4H_{11}NO)_2](C_7H_5O_2)_2$ has been determined from three-dimensional X-ray diffraction data collected by counter methods. The compound crystallizes in the space group $P2_1/c$, with $Z=2$ and the cell dimensions $a=5.654(2)$ Å, $b=22.974(11)$ Å, $c=9.166(4)$ Å and $\beta=101.66(3)°$. The structure was solved by heavy-atom Patterson and Fourier methods and refined by full-matrix least-squares techniques. The final R-value, based on 1394 reflections, was 0.063.

The structure consists of discrete $[Cu(C_4H_{11}NO)_2]^{2+}$-cations and $C_7H_5O_2^-$-anions. Cu(II) has a square-planar coordination with $Cu-O$ and $Cu-N$ distances of 1.933(5) and 1.972(5) Å, respectively. The $N-Cu-O$ angle is 84.7(2)°. The benzoate ions connect the cations by means of hydrogen bond contacts in the direction of the a-axis.

The transition metal complexes of aminoalcohols have received considerable attention lately as a result of the current interest in the magnetic properties of polynuclear complexes. Uhlig and Staiger studied copper(II) complexes of the type Cu(AO)X, where AOH = aminoalcohol and X = halide ligand, and divided them into three categories on the basis of their room temperature magnetic moments.[1,2] Later Nishida and Kida measured the temperature dependence of magnetic susceptibilities of copper(II) complexes of the type Cu(R₂AO)X, where $R_2AOH = N,N$-dialkylaminoalcohol and X = Cl⁻, Br⁻ or NCS⁻, and proposed a new criterion for the classification of polynuclear copper(II) aminoalcohol complexes.[3,4] Other investigators too have studied the magnetic properties,[5,6] and several structures have been determined by X-ray diffraction to support the magnetic classifications and to explicate further the mechanisms of metal-metal interaction in alkoxo-bridged copper(II) complexes.[6-13] We know only one copper(II) aminoalcohol complex in which the benzoate group has been used as a ligand, and a dimeric structure has been proposed for this complex.[14]

The crystal and molecular structure of $[Cu(C_4H_{11}NO)_2](C_7H_5O_2)_2$ which we describe here is exceptional in that the alkoxo oxygen does not form a bridge between the metal atoms. It is the first structure reported for a complex with this aminoalcohol. Work is also in progress on additional (2-amino-2-methyl-1-propanol)copper(II) complexes.

EXPERIMENTAL

Crystal preparation. Copper(II) benzoate was prepared by the method described elsewhere for the preparation of copper m-bromobenzoate[15] and was used without prior analysis. $[Cu(C_4H_{11}NO)_2](C_7H_5O_2)_2$ was then prepared according to the method of Hein et al.,[14] with commercially obtained 2-amino-2-methyl-1-propanol (Merck). Violet crystals formed within a few days. After purification from coprecipitates under a microscope, the crystals were suitable for X-ray measurement. IR-spectra indicated the presence of aminoalcohol in the crystals.

Crystal data and space group. Oscillation and equi-inclination Weissenberg photographs revealed the crystals to be monoclinic. The space group, from systematic absences, is $P2_1/c$. The cell parameters were refined by the least-squares method, using data obtained from a powder photograph taken

with a camera of Guinier-Hägg type. $CuK\alpha$ radiation ($\lambda = 1.5418$ Å) was employed and calcium fluoride ($a = 5.4630$ Å) was the internal standard. The calculated density of 1.378 g cm^{-3}, based on two formula units in the cell, is in agreement with that of 1.38 g cm^{-3} obtained by the flotation method in a mixture of carbon tetrachloride and dioxan. Crystal data for $[Cu(C_4H_{11}NO)_2]$-$(C_7H_5O_2)_2$ are:

$a = 5.654(2)$ Å $V = 1166.1$ Å^3
$b = 22.974(11)$ Å $FW = 484.04$
$c = 9.166(4)$ Å $Z = 2$
$\beta = 101.66(3)°$ Space group $P2_1/c$

Intensity data. A crystal of dimensions $0.17 \times 0.29 \times 0.20$ mm was mounted along the a-axis. Intensity data from levels $0kl - 5kl$ were collected with a Stoe-Güttinger diffractometer equipped with a scintillation counter and a pulse height analyser and using Ni-filtered Cu radiation ($CuK\alpha$, $\lambda = 1.5418$ Å). The ω-scan, background – peak – background, technique was applied. The scan range was 3.0°. The scan speed 1°/min, and the scanning times were 30, 180 and 30 s. Of the 2130 recorded reflections, 1394 with $I > 3\sigma(I)$ were used for the structure analysis. The data were corrected for Lorentz and polarization factors but not for absorption $[\mu(CuK\alpha) = 16.8$ $cm^{-1}]$.

Structure determination and refinement. From a three-dimensional Patterson vector map the special positions $(0,0,0)$ and $(0,\frac{1}{2},\frac{1}{2})$ were found for the copper atoms. The approximate positions of the

four aminoalcohol atoms which form the ring with the copper atom were also determined from this vector map. Subsequent Fourier syntheses based on these atoms gave the positions of the other non-hydrogen atoms of the complex.

The structure was refined by full-matrix least-squares techniques. Initially the refinement was carried out with isotropic thermal parameters to the R-value of 0.132 and continued then with anisotropic thermal parameters to the R-value of 0.080. At this stage a difference electron density map was calculated and the probable positions of the hydrogen atoms were found. When their atomic positional and isotropic thermal factors were included as parameters, the refinement, after two cycles, gave a final R-value of 0.063 ($R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$). In the last cycle the average shift/error was 18 %. The weights were calculated according to the scheme $w = 1/(35 + | F_o |)$. The scattering factors for Cu^{2+} were taken from International Tables for X-Ray Crystallography,[16] those for O, N and C were from Cromer and Mann,[17] and those used for hydrogen atoms from Stewart et al.[18]

Calculations were carried out on a Univac 1108 computer using programs of the X-Ray systems.[19] The final parameters are given in Tables 1a and b. A list of the observed and calculated structure factors is obtainable on request from the authors.

Table 1a. Atomic positional and thermal parameters[a] multiplied by 10^4. Standard deviations are given in parentheses.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	0000	0000	0000	506(8)	378(6)	344(6)	91(7)	−22(5)	−48(7)
N(1)	3086(10)	260(3)	1238(6)	338(34)	286(29)	276(29)	82(26)	33(23)	−19(24)
O(1)	−1319(8)	688(2)	751(6)	319(25)	259(22)	332(24)	70(19)	−25(19)	−35(19)
O(2)	3344(10)	738(2)	−1718(6)	577(36)	505(33)	637(37)	46(27)	31(29)	292(29)
O(3)	6433(11)	1340(2)	−1116(6)	640(38)	459(32)	604(36)	107(28)	−239(30)	125(27)
C(1)	523(12)	1031(3)	1657(8)	363(40)	283(34)	420(38)	31(29)	50(30)	−102(31)
C(2)	2505(11)	638(3)	2451(7)	315(37)	346(33)	295(33)	−27(28)	28(27)	−43(27)
C(3)	1652(21)	248(5)	3560(10)	481(59)	652(57)	333(43)	−120(51)	6(39)	117(42)
C(4)	4643(16)	998(4)	3204(10)	374(49)	561(53)	426(48)	−97(40)	50(38)	−127(42)
C(5)	4389(14)	1197(3)	−1858(7)	507(48)	349(38)	330(36)	174(32)	62(33)	5(29)
C(6)	3206(12)	1634(3)	−3021(7)	405(40)	277(31)	287(31)	112(28)	71(28)	12(26)
C(7)	4484(15)	2103(3)	−3377(9)	348(46)	386(39)	500(44)	11(31)	−48(34)	47(34)
C(8)	3469(16)	2494(4)	−4451(9)	629(56)	384(40)	515(45)	−55(39)	90(40)	93(34)
C(9)	1132(16)	2423(4)	−5172(8)	590(52)	487(45)	369(41)	108(39)	−4(36)	137(36)
C(10)	−176(16)	1964(3)	−4807(9)	319(43)	553(44)	405(45)	38(40)	−47(33)	−51(37)
C(11)	858(13)	1566(3)	−3753(8)	430(44)	341(36)	377(37)	−17(32)	94(31)	−6(31)

[a] The anisotropic thermal parameters are of the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + \cdots + 2hka^*b^*U_{12} + \cdots)]$.

Table 1b. Atomic positional ($\times 10^3$) and thermal ($\times 10^2$) parameters for the hydrogen atoms. Standard deviations are given in parentheses.

	x	y	z	U
H(1)	−218(17)	94(4)	30(10)	8(3)
H(2)	105(14)	133(4)	115(9)	6(2)
H(3)	−6(9)	125(2)	226(6)	1(1)
H(4)	42(14)	12(3)	321(8)	2(2)
H(5)	249(17)	5(4)	391(10)	5(3)
H(6)	145(12)	51(3)	434(8)	4(2)
H(7)	579(16)	78(4)	356(10)	6(3)
H(8)	414(17)	138(4)	383(11)	9(3)
H(9)	492(12)	114(3)	253(8)	3(2)
H(10)	356(13)	58(3)	37(9)	6(2)
H(11)	388(9)	3(3)	154(6)	1(1)
H(12)	573(13)	214(3)	−299(8)	3(2)
H(13)	423(19)	272(4)	−445(11)	8(4)
H(14)	50(16)	273(4)	−577(10)	7(3)
H(15)	−164(12)	195(3)	−525(7)	3(2)
H(16)	−4(12)	131(3)	−346(8)	3(2)

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure consists of discrete $[Cu(C_4H_{11}NO)_2]^{2+}$-cations and $C_7H_5O_2^-$-anions. The $C_7H_5O_2^-$-ions connect the cations by means of hydrogen bonds in the direction of the *a*-axis as shown in Fig. 1.

The aminoalcohol ligand and coordination around Cu(II). Cu(II) has a square-planar coordination with Cu−O and Cu−N distances of 1.933(5) and 1.972(5) Å, respectively. The Cu−O distance agrees with those found in polynuclear aminoalcohol complexes but the Cu−N distance is a little shorter than normal. Commonly the Cu−N distances in polynuclear cases vary in the range 2.02−2.09 Å,[6−14] though shorter distances are not unknown.[20]

Both the N−Cu−O angle of 84.7(2)° and the C−O distance of 1.431(8) Å agree with established values of polynuclear complexes. The mean amino-alcohol C−C distance is 1.509 Å and the three C−C distances are nearly equal (Table 2). The large benzoate anion has probably acted as a steric hindrance for the alkoxo-bridge formation between the metal atoms.

The ring has unsymmetrical *gauche* conformation, so that the ring carbon atoms C(1) and C(2) deviate 0.100 Å and −0.579 Å from the N−Cu−O plane, respectively. The dihedral angle between the planes O(1)−C(1)−C(2) and N(1)−C(2)−C(1) is 50.0°. The coordination around Cu(II) is shown in Fig. 2.

The benzoate anion and the hydrogen bond contacts. The Cu−O(2) distance is 3.184(6) Å and the
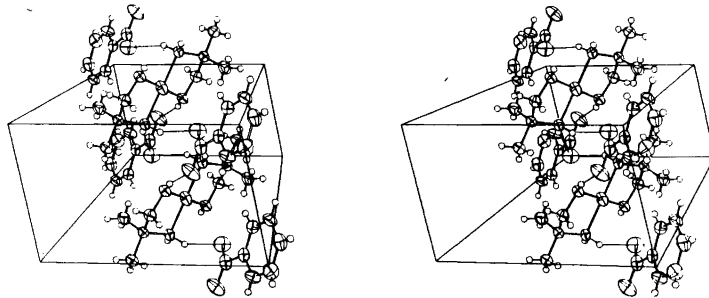

Fig. 1. A stereoscopic packing view of two complex units. The view direction is approximately along *b*; *c* is horizontal and *a* is approximately vertical.

Table 2. Interatomic distances (Å) and angles (°). Standard deviations are given in parentheses. Distances involving hydrogen atoms vary between 0.67 and 1.16 Å.

Cation			
Cu−N(1)	1.972(5)	N(1)−Cu−O(1)	84.7(2)
Cu−O(1)	1.933(5)	Cu−N(1)−C(2)	107.5(4)
C(1)−O(1)	1.431(8)	Cu−O(1)−C(1)	111.7(4)
C(1)−C(2)	1.508(9)	O(1)−C(1)−C(2)	109.4(5)
C(2)−N(1)	1.497(9)	N(1)−C(2)−C(1)	104.0(5)
C(2)−C(3)	1.506(13)	N(1)−C(2)−C(3)	107.8(6)
C(2)−C(4)	1.512(11)	N(1)−C(2)−C(4)	112.4(6)
		C(1)−C(2)−C(3)	112.0(7)
		C(1)−C(2)−C(4)	109.8(6)
		C(3)−C(2)−C(4)	110.7(6)
Anion			
C(5)−O(2)	1.227(9)	O(2)−C(5)−O(3)	125.2(6)
C(5)−O(3)	1.261(9)	O(2)−C(5)−C(6)	119.3(6)
C(5)−C(6)	1.519(9)	O(3)−C(5)−C(6)	115.5(6)
C(6)−C(7)	1.373(10)	C(5)−C(6)−C(7)	120.5(6)
C(6)−C(11)	1.370(9)	C(5)−C(6)−C(11)	120.9(6)
C(7)−C(8)	1.369(11)	C(11)−C(6)−C(7)	118.6(6)
C(8)−C(9)	1.363(12)	C(6)−C(7)−C(8)	121.4(7)
C(9)−C(10)	1.368(12)	C(7)−C(8)−C(9)	119.7(8)
C(10)−C(11)	1.372(10)	C(8)−C(9)−C(10)	119.5(7)
		C(9)−C(10)−C(11)	120.7(7)
		C(10)−C(11)−C(6)	120.1(7)

Table 3. Hydrogen bond contacts (Å). Roman numerals refer to the following equivalent positions: I, x,y,z; II, $1-x,-y,-z$; III, $x-1,y,z$.

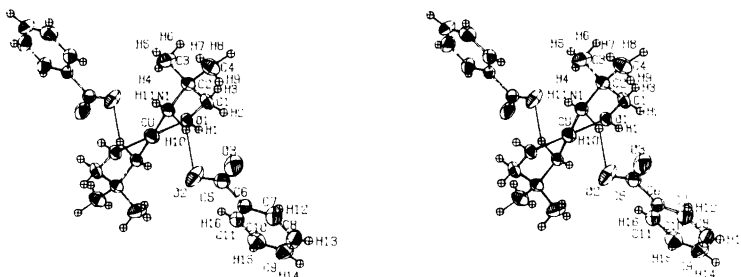| X−H···Y	X−H	H···Y	X···Y	∠(X−H···Y)
N(1)−H(10)···O(2)[I]	1.16(8)	1.93(8)	2.954(8)	146
N(1)−H(11)···O(2)[II]	0.72(5)	2.34(6)	3.029(8)	161
O(1)−H(1)···O(3)[III]	0.81(9)	1.66(9)	2.431(7)	160

Fig. 2. A stereoscopic view of the complex unit.

line joining the atoms makes an angle of 64.4° with the Cu−N(1)−O(1) plane. In Cu(II) complexes formed by 1,3-propanediamine with benzoate and different substituted benzoates this distance is about 2.5 Å.[21−24] The mean values of the ring C−C bonds and C−C−C angles are 1.369 Å and 120.0°,

respectively. The greatest deviation of a ring C atom from the least-squares plane of the benzene ring is 0.011 Å. The angle between the benzene ring and the carboxylate group is 10.5° and between the benzene ring and the $Cu-N(1)-O(1)$ plane, 65.7°. Each benzoate anion forms three hydrogen bonds and these are listed in Table 3. It is noteworthy that both of the amine hydrogen atoms have taken part in hydrogen bond formation and this may have had the effect of increasing the stability of the complex.

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