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Copper(II) Complexes of 3-Aminopropanols. Synthesis and Structure of 3-Aminopropanol(3-aminopropanolato)copper(II) Iodide

REIJO SILLANPÄÄ*, TEPPO LINDGREN

Department of Chemistry, University of Turku, SF-20500 Turku, Finland

and LASSI HILTUNEN

Department of Chemistry, Helsinki University of Technology, SF-02150 Espoo, Finland

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Abstract

Copper(II) trifluoromethanesulfonate was allowed to react with 3-aminopropanol (Hap) and lithium iodide in ethanol. The obtained blue crystals have the formula Cu(ap)(Hap)I, where ap is a 3-aminopropanolato anion. The space group of the complex is $P2_1/c$ with $Z = 4$. The unit cell parameters are a = 894.4(2), b = 1368.9(5) c = 1030.9(2) pm and β = 113.31(2)°. The structure was solved on 1322 unique Mo Kα reflections to $R = 0.045$. The compound is made up of alkoxo-bridged $[Cu(ap)(Hap)]_2$ dimers, which are polymerized through Hap molecules. Copper atoms have a distorted five-coordinated structure. Iodide ions are not coordinated to copper.

Introduction

The structures and magnetic properties of alkoxo-bridged copper(II) complexes have attracted considerable attention among chemists [1]. We have studied copper(II) chemistry of some 1,3-aminopropanols [2, 3]. Recently Haase *et al.* determined the crystal structures of three copper(II) complexes with *N*-alkylated 3-aminopropanols [4].

When $CuCl_2$ or $CuBr_2$ reacts with 3-aminopropanol (Hap) in molar ratio 1:2, green complexes of formula Cu(ap)Cl and Cu(ap)Br are formed. Spectroscopic data suggest that these complexes are dimers in solution but polymers in the solid state [2]. However, sometimes during these syntheses blue solutions and even blue solids were formed, especially when $CuBr_2$ was used as a copper source.

In order to get more information on copper(II) reactions with aminoalcohols an attempt was made to isolate the blue solids as crystals. The preparation and crystal structure of the blue compound, which according to analysis has the formula Cu(ap)(Hap)I, is reported.

Experimental

Synthesis of the Complex

One mmol of $Cu(CF_3SO_3)_2$ was dissolved in ethanol. After adding two mmol of 3-aminopropanol and one mmol of LiI, blue crystals were obtained at *ca.* 15 °C.

X-ray Measurements

Single crystal X-ray measurements were made with a Syntex $P2_1$ (Fortran version) automatic four-circle diffractometer employing graphite monochromatized Mo Kα radiation. The unit cell parameters were calculated by least-squares refinements of 25 reflections. The intensities were recorded using $\theta/2\theta$ scan technique with varying scan speed (1.5–29.5°/min). The systematic absences of the reflections indicated that the space group is $P2_1/c$.

Crystal Data

$Cu[O(CH_2)_3NH_2][HO(CH_2)_3NH_2]I$; $M_r = 339.66$ space group $P2_1/c$; $a = 894.4(2)$, $b = 1368.9(5)$, $c = 1030.9(2)$ pm, $\beta = 113.31(2)°$; $Z = 4$; $V = 1.159$ nm^3; $D_c = 1.95$ g/cm^3; D_m (flotation) = 1.88 g/cm^3; μ(Mo Kα) = 42.9 cm^{-1} and $T = 295$ K.

The intensity of one check reflection showed no loss of intensity. Corrections for Lp and absorption were applied. Out of 2061 independent reflections 1332 having $I > 2.5\sigma(I)$ were accepted as observed.

The structure was solved by direct methods [5], which gave positional parameters for Cu and I atoms. The atomic scattering factors and anomalous dispersion correction factors for heavy atoms were taken from International Tables [6]. The structure was refined with heavy atoms and hydrogen atoms having

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*Author to whom correspondence should be addressed.

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TABLE I. Atomic Positional Parameters and Equivalent Isotropic Temperature Factors for Cu(ap)(Hap)I[a]

Atom	x	y	z	U_{eq}/U_{iso}
I	0.67542(11)	0.45160(5)	−0.15693(7)	0.0579(3)
Cu	0.91287(14)	0.49334(7)	0.34062(11)	0.0356(4)
O(1)	0.9227(8)	0.4320(4)	0.5122(6)	0.040(2)
O(2)	0.8854(11)	0.8880(6)	0.1978(8)	0.059(3)
N(1)	0.7202(13)	0.4195(8)	0.2151(9)	0.056(3)
N(2)	0.9034(12)	0.5818(6)	0.1830(8)	0.042(3)
C(1)	0.8233(13)	0.3546(7)	0.5256(9)	0.044(3)
C(2)	0.6656(13)	0.3427(7)	0.4056(10)	0.049(3)
C(3)	0.6763(14)	0.3268(7)	0.2628(10)	0.054(3)
C(4)	0.7665(13)	0.8444(8)	0.0751(12)	0.055(4)
C(5)	0.8205(13)	0.7439(6)	0.0598(10)	0.046(3)
C(6)	0.8158(13)	0.6743(7)	0.1736(9)	0.045(3)
H(O2)	0.867(10)	0.904(7)	0.243(9)	0.06
H(1N1)	0.734(10)	0.418(8)	0.164(8)	0.06
H(2N1)	0.659(10)	0.455(7)	0.183(9)	0.06
H(1N2)	0.997(9)	0.606(6)	0.180(8)	0.06
H(2N2)	0.841(9)	0.566(7)	0.108(8)	0.06

[a] The equivalent isotropic temperature factors for non-hydrogen atoms are of the form $U_{eq} = (U_{11} + U_{22} + U_{33} + 2U_{13} \cos \beta)/3$.

TABLE II. Bond Distances (pm) and Angles (°) with Estimated Standard Deviations in Parentheses for Cu(ap)(Hap)I

Distances			
Cu–O(1)	192.8(6)	C(1)–O(1)	142.4(12)
Cu–O(1^{i})	193.5(6)	C(1)–C(2)	147.1(15)
Cu–N(1)	197.5(11)	C(2)–C(3)	152.8(15)
Cu–N(2)	200.1(8)	C(3)–N(1)	147.0(15)
Cu–O(2^{ii})	246.1(9)	C(4)–O(2)	142.2(14)
Cu•••Cu^{i}	303.4(1)	C(4)–C(5)	148.7(14)
		C(5)–C(6)	152.6(13)
		C(6)–N(2)	147.2(13)
Angles			
O(1)–Cu–N(1)	95.1(3)	O(1)–C(1)–C(2)	115.4(8)
O(1)–Cu–N(2)	168.6(3)	C(1)–C(2)–C(3)	114.9(10)
O(1)–Cu–O(1^{i})	76.5(3)	C(2)–C(3)–N(1)	109.0(8)
O(1)–Cu–O(2^{ii})	97.0(3)	O(2)–C(4)–C(5)	108.9(9)
N(1)–Cu–N(2)	91.8(4)	C(4)–C(5)–C(6)	112.8(9)
N(1)–Cu–O(1^{i})	168.4(4)	C(5)–C(6)–N(2)	114.3(9)
N(1)–Cu–O(2^{ii})	95.7(4)		
N(2)–Cu–O(1^{i})	95.3(3)		
N(2)–Cu–O(2^{ii})	91.3(3)		
O(1^{i})–Cu–O(2^{ii})	95.3(3)		
Cu–O(1)–Cu^{i}	103.5(3)		

Symmetry codes: (i) $2 - x$, $1 - y$, $1 - z$; (ii) $2 - x$, $y - 0.5$, $0.5 - z$.

anisotropic and isotropic temperature factors, respectively. The C–H hydrogen positions were calculated assuming the C–H distance to be 96 pm. Omission of 10 poorly agreeing reflections led to final $R = 0.045$ and $R_w = 0.045$, where $R = \Sigma\Delta/\Sigma F_o$, $R_w = \Sigma\sqrt{w\Delta}/\Sigma\sqrt{wF_o}$, $\Delta = |F_o - F_c|$ and $w = 2.91/[\sigma^2(F_o) + 0.000789 F_o^2]$.

Crystallographical calculations were performed with the SHELX-76 program [7] and the figures were drawn with ORTEP [8]. The final atomic positional coordinates and equivalent isotropic temperature factors are listed in Table I. See also 'Supplementary Material'.

Results and Discussion

The structure is composed of alkoxo-bridged $[Cu(ap)(Hap)]_2^{2+}$ dimers and iodide ions. A binuclear unit with labelled atoms is illustrated in Fig. 1. Intramolecular distances and angles are listed in Table II.

The halves of the binuclear units are related by crystallographic inversion symmetry. Each copper atom shows a distorted (4 + 1) square pyramidal coordination. The four short bonds are formed by two nitrogens (Cu–N(1) = 197.5(11) pm and Cu–N(2) = 200.1(8) pm) and by two oxygens (Cu–O(1) = 192.8(6) pm and Cu–O(1^{i}) = 193.5(6) pm). The long apical bond (Cu–O(2^{ii}) = 246.1(9) pm) is due to the bridging aminoalcohol molecule which binds the dimers to polymers as shown in Fig. 2.

The intramolecular Cu•••Cu distance is 303.4(1) pm and the bridge angle Cu–O–Cu is 103.5(3)°. The distances and angles within the Cu_2O_2 core are comparable with those of other alkoxo-bridged copper(II) complexes [4].

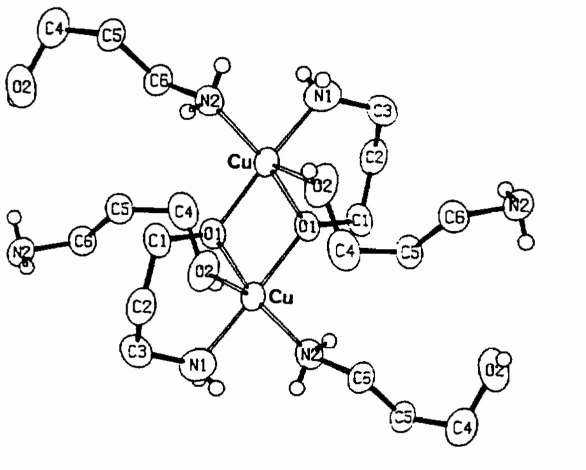

Fig. 1. The dimeric structural unit of [Cu(ap)(Hap)]I showing the atom numbering scheme. Iodide ions and CH-hydrogens are not shown.

The 3-aminopropanolato ion adopts a chelated conformation with O–C–C–C and C–C–C–N torsion angles 57(1)° and –73(1)°, respectively. On the contrary the neutral 3-aminopropanol molecule, which bridges the dimers to polymers, has a half linear conformation with O–C–C–C and C–C–C–N torsion angles 70(1)° and –166(1), respectively.

Iodide ions are not coordinated to copper(II) ions, but are hydrogen bonded by OH and NH protons. The parameters for possible hydrogen bonds are presented in Table III.

This structural study indicates that when the Cu(II) ion and 3-aminopropanol react in the molar ratio 1:2 dimeric $[Cu(ap)]_2^{2+}$ ions are formed. In these dimers the fourth ligand around copper in the *xy*-plane is a solvent molecule or a weakly coordinated anion. The way these dimers will then pack into the solid state depends on the anion and on the extra ligands present. The extra ligands can be an excess of aminoalcohol or other ligands which have been added in the solution of these dimers.

Supplementary Material

The supplementary material, including the rest of H-atom coordinates and anisotropic temperature factors (Table S1) as well as observed and calculated structure factors (Table S2), can be obtained upon request from R. Sillanpää.

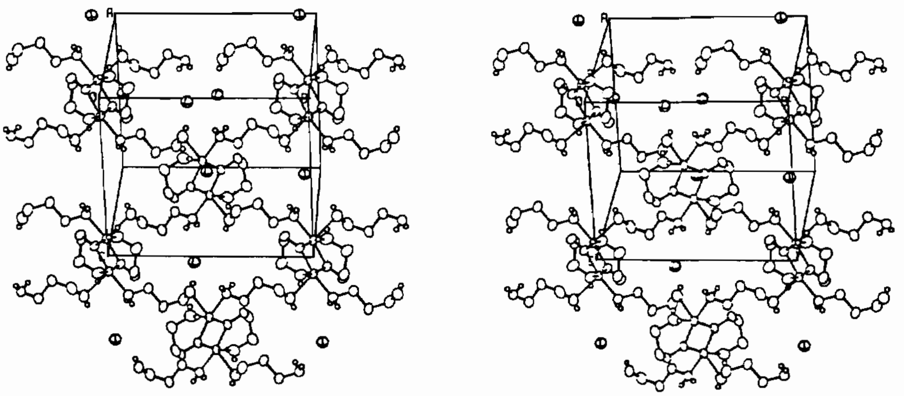

Fig. 2. A stereoscopic view of [Cu(ap)(Hap)]I showing the polymerization of the dimeric $[Cu(ap)(Hap)]_2^{2+}$ ions. The balls with principal ellipses represent iodide ions and CH-hydrogens are not shown.

TABLE III. Parameters for Possible Hydrogen Bonds

A–H···B	A–H (pm)	H···B (pm)	A···B (pm)	A–H···B (°)
O(2)–H(O2)···I^{iii}	60(9)	305(10)	358.1(9)	151(11)
N(1)–H(1N1)···I	58(9)	318(8)	372.1(9)	157(11)
N(1)–H(2N1)···I^{iv}	71(9)	316(9)	378.3(12)	148(9)
N(2)–H(1N2)···I^{v}	91(9)	313(9)	390.7(11)	144(7)
N(2)–H(2N2)···I	78(8)	298(8)	373.6(8)	162(8)

Symmetry codes: (iii) *x*, 1.5 – *y*, 0.5 + *z*;(iv) 1 – *x*, 1 – *y*, –*z*; (v) 2 – *x*, 1 – *y*, –*z*

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