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Copper(II) Complexes of 3-Aminopropanols. Synthesis and Structure of (3-Aminopropanolato)formatocopper(II)

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Abstract

The crystal and molecular structure of the title compound has been determined from single-crystal X-ray data and refined to a final *R* value of 0.030 for 971 reflections. The compound crystallizes in the monoclinic space group $P2_1/c$ with two dimeric molecules in a cell of dimensions $a = 856.9(1)$, $b = 887.7(1)$, $c = 837.0(1)$ pm and $\beta = 99.55(1)°$. The blue crystals of Cu(ap)(HCOO) (ap = 3-aminopropanolato ion) are made of centrosymmetric dialkoxy bridged dimers (Cu...Cu 296.4(1) pm). The dimers are polymerized along the *c* axis into chains via two NH–O hydrogen bonds (Cu...Cu 547.9(1) pm). These chains are joined together along the *b* axis by CuOCOCu bridges and NH–O hydrogen bonds (Cu...Cu 462.2(1) pm) forming layers, which are held together by van der Waals forces. Copper atoms have a distorted square-pyramidal coordination sphere.

Introduction

Copper(II) ion forms with aminoalcohols easily dimeric di-alkoxo-bridged complexes [1], which can be described by a general formula of $[Cu(ao)X]_2$, where ao^- is an aminoalcoholato ion and X^- is an anion. The aim of this study is to improve the syntheses of these dimeric copper(II) aminoalcoholato complexes by using copper(II)-trifluoromethanesulfonate as the copper source. The idea is that if at the beginning of the synthesis a $[Cu(ao)L]_2^{2+}$ unit could be obtained where L is a weakly coordinating solvent molecule or $CF_3SO_3^-$ ion, then L could be replaced by using a suitable compound of X^-. If the formed $[Cu(ao)X]_2$ complex is insoluble enough in the used solvent, then it is possible to isolate it.

This idea was tested by using compounds where ao^- is 3-aminopropanolato ion and X^- is a formato ion. The preparation and the crystal and molecular structure of Cu(ap)Fo is reported. This is a continuation of our investigations on copper(II) complexes with 3-aminopropanols [2].

Experimental

Preparation of Cu(ap)Fo

The synthesis was done according to the following reactions in ethanol:

$$2Cu(CF_3SO_3)_2 + 4HaP \rightleftharpoons [Cu(ap)EtOH]_2^{2+} + 2H_2ap^+ + 4CF_3SO_3^- \qquad (1)$$

$$[Cu(ap)EtOH]_2^{2+} + 2NH_4Fo \rightleftharpoons [Cu(ap)Fo]_2(s) + 2NH_4^+ \qquad (2)$$

A quantity of 2 mmol of $Cu(CF_3SO_3)_2$ was dissolved in 5 ml of EtOH. To this solution was added 4.2 mmol of 3-aminopropanol in 4.2 ml EtOH and 2.3 mmol of $HCOONH_4$ in 35 ml EtOH. The blue solution was allowed to stand at room temperature for one day. The formed blue crystals were filtered and washed with ethanol and acetone. A yield of 85% was obtained.

X-ray Measurements

Single-crystal X-ray measurements were done with an Enraf-Nonius CAD 4 diffractometer using Mo Kα radiation. The data obtained were corrected for Lorentz and polarization effects.

Crystal Data

$Cu[O(CH_2)_3NH_2](HCOO)$; $M_r = 182.67$; space group $P2_1/c$; $a = 856.9(1)$, $b = 887.7(1)$, $c = 837.0(1)$ pm; $\beta = 99.55(1)°$; $Z = 4$; $V = 627.9$ Å^3; $D_c = 1.93$ g/cm^3 : μ(Mo Kα) = 34.2 cm^{-1} and $T = 296$ K.

The structure was solved by direct methods and refined by least-squares techniques to an *R* value of 0.030 ($R_w = 0.033$) for 971 independent reflections having $I > 3\sigma(I)$. Hydrogen atoms were refined with

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

Atom	x	y	z	B_{eq}/B_{iso}
Cu	1.01336(7)	0.47320(7)	0.17650(6)	1.721(7)
O(1)	1.1323(3)	0.4394(4)	0.0011(3)	2.04(6)
O(2)	0.8579(4)	0.4642(4)	0.3293(3)	2.28(6)
O(3)	0.8551(5)	0.2264(4)	0.2468(5)	3.45(9)
N	1.1795(5)	0.3936(5)	0.3490(4)	2.10(7)
C(1)	1.2990(5)	0.4493(5)	0.0238(5)	1.94(8)
C(2)	1.3759(6)	0.3568(6)	0.1676(6)	2.34(9)
C(3)	1.3458(5)	0.4162(6)	0.3285(5)	2.23(8)
C(4)	0.8159(6)	0.3270(6)	0.3330(6)	2.7(1)
H(1C1)	1.335(7)	0.552(7)	0.045(7)	5.0
H(2C1)	1.341(7)	0.420(7)	−0.085(7)	5.0
H(1C2)	1.489(7)	0.359(7)	0.170(7)	5.0
H(2C2)	1.336(7)	0.261(8)	0.151(7)	5.0
H(1C3)	1.418(7)	0.365(7)	0.417(7)	5.0
H(2C3)	1.378(7)	0.528(8)	0.337(7)	5.0
H(C4)	0.750(7)	0.301(8)	0.396(7)	5.0
H(1N)	1.164(7)	0.319(7)	0.354(7)	5.0
H(2N)	1.169(7)	0.432(7)	0.445(7)	5.0

[a] The equivalent isotropic temperature factors for non-hydrogen atoms are of the form $B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}a_ia_j$.

isotropic parameter $B = 5.00$ Å^2 and also an empirical absorption correction was applied during refinements. All calculations were performed on an m-VAX computer using SDP-PLUS software [3]. Figures were drawn with ORTEP [4]. The final atomic positional coordinates and equivalent isotopic temperature factors are listed in Table I. See also 'Supplementary Material'.

Results and Discussion

The dimeric $[Cu(ap)Fo]_2$ unit is shown in Fig. 1. Each copper atom has a distorted square-pyramidal coordination (4 + 1). In the xy-plane around copper(II) ion there are two alkoxide oxygens, one amine nitrogen and one formato oxygen. The fifth coordination site is occupied by a formato oxygen from the adjacent dimer unit. Bond distances and angles are presented in Table II.

However the coordination sphere around the copper(II) ion could be considered also as octahedral (4 + 1 + 1) stereochemistry if the long Cu. . .O(3) distance (269.3(4) pm) is taken into account. In a bis(2,2′-bipyridyl)copper(II) complex with a bidentately coordinated formate ion there is also a long Cu. . .O distance (286.9 pm), but the coordination around the copper atom was described as *cis*-octahedral although the single-crystal ESR is in favour of square-pyramidal stereochemistry [5].

The formate ion ligation has an *anti–syn* configuration. The formato bridge links the dimeric units to a polymer with Cu. . .Cu distances of 462.2 pm (Fig. 2). The C–O bond parameters of the formate ion (C(4)–O(2) = 127.2(7) pm and C(4)–O(3) = 122.9(7) pm) are in good agreement with the parameters of C–O bonds of copper(II) formates [6, 7]. The asymmetry of C–O bonds of the formato group is a result of asymmetry in Cu–O(2) and Cu–O(3) bonds. A similar phenomenon is found in coordinated nitrato ions [8].

The C–H bond distances are from 92(7) to 107(7) pm in the 3-aminopropanolato ion. Upon coordination the 3-aminopropanolato ion adopts a chelated conformation with O–C–C–C and C–C–C–N torsion angles of −67.4(1)° and 70.5(2)°, respectively.

In addition to the CuOCOCu bridge there are hydrogen bonds holding the crystal together. Two

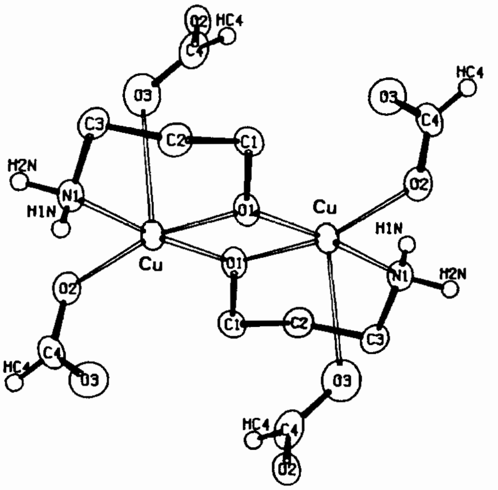

Fig. 1. The dimeric structural unit of $[Cu(ap)Fo]_2$ showing the atom numbering scheme. The CH-hydrogens of 3-aminopropanol are not shown.

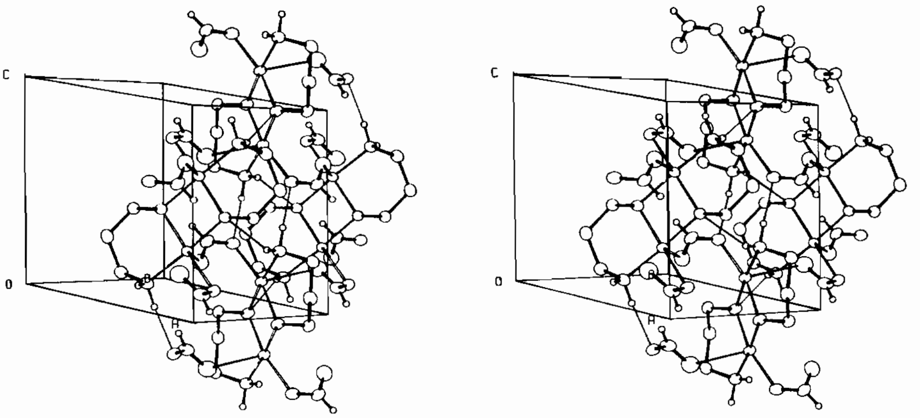

Fig. 2. A stereoscopic view of $[Cu(ap)Fo]_2$ showing the polymerization of the dimeric $[Cu(ap)Fo]_2$ molecules. The thin lines represent hydrogen bonds.

TABLE II. Bond Distances (pm) and Angles (°) for Cu(ap)Fo[a]

Distances			
Cu–O(1)	194.5(3)	C(1)–O(1)	141.2(5)
Cu–O(1^i)	193.8(3)	C(1)–C(2)	151.5(6)
Cu–N	198.2(4)	C(2)–C(3)	150.8(7)
Cu–O(2)	199.6(3)	C(3)–N(1)	147.6(6)
Cu–O(3)	269.3(4)	C(4)–O(2)	127.2(7)
Cu–O(3^{ii}))	254.8(4)	C(4)–O(3)	122.9(7)
Cu. . .Cu^i	296.4(1)	C(4)–H(C4)	86(7)
		N–H(1N)	68(7)
		N–H(2N)	89(6)
Angles			
O(1)–Cu–N	95.3(1)	O(1)–C(1)–C(2)	111.7(4)
O(1)–Cu–O(2)	165.2(1)	C(1)–C(2)–C(3)	113.8(4)
O(1)–Cu–O(1^i)	80.5(1)	C(2)–C(3)–N(1)	111.6(4)
O(1)–Cu–O(3^{ii})	93.5(1)	O(2)–C(4)–O(3)	125.1(5)
N–Cu–O(2)	89.7(2)	O(2)–C(4)–H(C4)	119(5)
N–Cu–O(1^i)	174.3(2)	O(3)–C(4)–H(C)	116(5)
N–Cu–O(3^{ii})	84.1(1)	H(1N)–N–H(2N)	106(6)
O(2)–Cu–O(1^i)	95.4(1)		
O(2)–Cu–O(3^{ii})	100.9(1)		
O(1^i)–Cu–O(3^{ii})	92.4(1)		
Cu–O(1)–Cu^i	99.5(1)		

[a]e.s.d.s in parentheses. Symmetry codes: (i) $2-x$, $1-y$, $-z$; (ii) $2-x, y+0.5, 0.5-z$.

N – H2. . .O(2^{iii}) (iii = $2-x$, $1-y$, $1-z$) hydrogen bonds link the dimers together along the *c* axis (Fig. 2). The N. . .O(2^{iii}) distance is 303.8(5) pm and the N – H1. . .O(2^{iii}) angle is 156(6)°. There is also a weak hydrogen bond N – H1. . .O(1^{iv})(iv = x, $\frac{1}{2}-y$, $\frac{1}{2}+z$), which like the CuOCOCu bridge links the dimer chains along *b* axis. The N. . .O(1^{iv}) distance is 327.0(5) pm and the N–H1. . .O(1^{iv}) angle is 177(6)°. There is also a possibility for the existence of a C–H. . .O hydrogen bond as the C(4). . .O(3^{iii}) distance is 345.3(5) pm and the C(4)–H. . .O(3^{iii}) angle is 121(6)°. At least the C. . .O distance is quite near the C. . .O distances found in $[\{trans\text{-}Ir(CO)(CH_3CN)(PPH_3)_2\}\cdot 18C6]^{2+}$, where hydrogen bonded C. . .O distances are 324, 326 and 338 pm [9].

The structure of $[Cu(ap)(Fo)]_2$ is made up of van der Waals bonded layers along the *bc*-plane. There should also be an intensive interdimer magnetic interaction because there are two pathways for magnetic interaction: hydrogen bonds and a CuOCOCu bridge.

Conclusions

Dimeric $[Cu(ap)X]_2$ compounds can be prepared in two steps. In the first step a dimeric $[Cu(ap)L]_2$ unit is prepared using $Cu(CF_3SO_3)_2$ as starting material. In the second step the weakly coordinated L is replaced by an anion X.

Packing of the formed dimers is strongly dependent on anion X. Also the copper(II) ion being a plastic metal ion can modify its coordination sphere so that the best packing is obtained. As a result of this bonding parameters of the copper(II) ion and thus of the Cu_2O_2 bridge vary as anion X is changed.

Supplementary Material

Tables of anisotropic thermal parameters and observed and calculated structural factors can be obtained from the authors upon request.

References

1 M. Melnik, *Coord. Chem. Rev., 42,* 259 (1982).
2 R. Sillanpää, T. Lindgren and L. Hiltunen, *Inorg. Chim. Acta, 131,* 85 (1987).
3 B. A. Frenz, 'The Enraf-Nonius CAD 4 SDP', a real-time system for concurrent X-ray data collection and crystal structure determination, in H. Schenk, R. Olthof-Hazelkamp, H. van Koningsveld and G. C. Bassi (eds.), 'Com-

puting Crystallography', Delft University Press, Delft, 1978, pp. 64–71.

4 C. K. Johnson, 'ORTEP-II', a Fortran thermal-ellipsoid plot program for crystal structure illustrations, *Report ORNL-5138,* Oak Ridge National Laboratory, Tenn., 1976.

5 W. Fitzgerald and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.,* 567 (1981).

6 N. Burger and H. Fuess, *Solid State Commun., 34,* 699 (1980).

7 H. Tamura, K. Ogawa, W. Mori and M. Kishita, *Inorg. Chim. Acta, 54,* L87 (1981).

8 C. C. Addison, N. Logan, S. C. Wallwork and C. D. Carner, *Q. Rev., 25,* 289 (1971).

9 H. M. Colquhoun, J. F. Stoddart and D. J. Williams, *J. Am. Chem. Soc., 104,* 1426 (1982).