Copper(II) Complexes of 3-Aminopropanols. Synthesis and Structure of Trimeric Tetrakis(3-aminopropanolato)tricopper(II) Nitrate

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The crystal and molecular structure of the dark-blue crystals of $Cu_3(ap)_4(NO_3)_2$ (ap = the 3-amino-1-propanolato ion) has been determined from single-crystal X-ray data and refined to a final *R*-value of 0.028 for 2603 reflections. The compound crystallizes in the monoclinic space group *C2/c* with eight trimeric molecules in a cell of dimensions $a = 2082.8(8)$, $b = 1306.4(2)$, $c = 1933.7(8)$ pm and $\beta = 119.87(2)°$. The structure is formed of almost linear alkoxobridged copper(II) trimers in which the Cu–Cu–Cu angle is 175.04(2)° and the Cu···Cu distances are 295.16(5) and 301.06(5) pm.

The nitrate ions are weakly coordinated to the copper(II) ion. One nitrate is tridentately bound to Cu(1) and Cu(2) within a trimer and to Cu(2) in the next trimer unit, forming Cu(2)–O–N–O–Cu(2) chains; the other nitrate has monodentate bonding to Cu(3). Two of the three copper(II) ions in a trimer have a distorted square pyramidal and the third has a tetragonally distorted octahedral coordination sphere. In the lattice the trimers are joined together by NH···O hydrogen bonds and Cu–O–N–O–Cu bridges.

The reaction of aminoalcohols with metal ions usually affords dehydrogenated complexes with coordinated alkoxy groups. Polynuclear complexes are easily formed.

We have tried to clarify the reactions of 3-amino-1-propanol (Hap) with the copper(II) ion. Complexes having the formulae Cu(ap)Fo and Cu(ap)(Hap)I (Fo = the formato ion and ap = the 3-amino-1-propanolato ion) have been isolated.[1,2] Both are alkoxybridged copper(II) dimers. When copper(II) nitrate was used as starting material both types of complex were obtained, with the formulae $Cu(ap)NO_3$ and $Cu(ap)(Hap)NO_3$.[3] However, further studies revealed the formation of a third compound from an ethanol solution of copper(II) nitrate and the 3-amino-1-propanolato anion. This new copper(II) complex has the empirical formula $Cu_3(ap)_4(NO_3)_2$, which according to X-ray analysis is a linear copper(II) trimer.

Trimeric complexes of first-row transition metals are well documented. The iron(II) ion forms a trinuclear sulfide–thiolate complex.[4] Cobalt(II,III) ions build linear trinuclear complexes with 2-aminoethanol, 2-aminoethanethiol and 3-amino-1-propanethiol as ligands.[5–7] A similar linear trichromium(III) cluster with 2-aminoethanethiol is reported.[8] The nickel(II) ion has been shown to form trinuclear complexes with 3-amino-1-thiol and 1,2-ethanethiol.[9,10]

The copper(I) ion forms a triangular trimer with 1,2-ethanedithiol,[11] whereas the copper(II) ion is known to form linear trinuclear complexes with macrocyclic and Schiff-base ligands with the central copper atom coordinated to four alkoxy oxygens.[12–15] Linear trimers of the copper(II) ion have also been reported,[16–19] but in these cases there is also a bridging anion such as OH^-, acetate or benzoate.

In this paper we describe the syntheses and the structure of a linear copper(II) trimer, the $[Cu_3(ap)_4]^{2+}$ cation, into which two nitrate anions are weakly coordinated.

Experimental

Preparation of $Cu_3(ap)_4(NO_3)_2$. A 1.8 mmol sample of $Cu(NO_3)_2 \cdot 3H_2O$ (Merck) was dissolved in 10 ml of ethanol. The solution was mixed with 5 ml of DME (1,2-dimethoxyethane) (Sigma) containing 3.7 mmol Hap (Aldrich) and 3.7 mmol triethylamine (Fluka). A dark-blue solution formed, and in few minutes a small amount of greenish-blue solid separated. To the solution was then added 1 ml of trifluoroethanol (Sigma), and all solids dissolved. On standing the solution overnight at room temperature, 266 mg of dark-blue crystals (71 %) were formed. The crystals were separated by filtration and washed with acetonitrile and ether. Cu, C and H analyses were carried out.

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Similar experiments were also performed with different Cu(II)-to-ap ratios [ap is the 3-amino-1-propanolato ion, generated by addition of $N(Et)_3$ to a THF (tetrahydrofuran) solution of Hap]. The concentrations of copper(II) nitrate varied from 1 to 2 mol l^{-1}. The solids formed were separated and analyzed by IR spectroscopy. These solids were $Cu(ap)NO_3$, $Cu_3(ap)_4(NO_3)_2$, $Cu(ap)(Hap)NO_3$ or their mixtures.

Spectral measurements. The solid-state UV–VIS spectrum of the compounds were recorded with a Cary 17D spectrometer using the Nujol mull technique. In the spectrum of $Cu_3(ap)_4(NO_3)_2$ there is a strong band at 353 nm (28300 cm^{-1}) and a very broad band with a much lower intensity at 615 nm (16300 cm^{-1}).

The solid-state IR spectra were recorded with a Perkin Elmer 180 grating infrared spectrophotometer using the Nujol mull technique. In the IR spectrum of $Cu_3(ap)_4(NO_3)_2$ the N–H stretchings are at 3306(s), 3274(sh), 3254(s), 3230(sh), 3173(m) and 3147(sh) cm^{-1}, combination bands are at 1746(w) and 1753(sh) cm^{-1}, NH_2 waggings are at 1604(s), 1594(s) and 1579(sh) cm^{-1} and a nitrate NO_3 stretching is at 1340(vs)(br) cm^{-1}.

Crystal structure determination. Single-crystal X-ray measurements were made with an Enraf–Nonius CAD4

Table 1. Crystal data and experimental details of the structure determination of $Cu_3(ap)_4(NO_3)_2$.

Formula	$Cu_3C_{12}H_{24}N_6O_{10}$
M_r	611.06
Space group	*C2/c*
Cell parameters at 291(1) K	
a/pm	2082.8(8)
b/pm	1306.4(2)
c/pm	1933.7(8)
β/°	119.87(2)
V/nm³	4.563
Calculated density g cm^{-3}	1.779
Z	8
μ (Mo *K*α)/cm^{-1}	28.4
Crystal description	Dark blue, prismatic
Crystal size/mm³	0.12×0.15×0.10
Instrument	Enraf–Nonius CAD4
Data collection	$\omega/2\theta$
Corrections	Lorentz-polarization
Maximum 2θ/°	50
hkl ranges	*h* = 0–24
	k = 0–15
	l = −22–19
No. of reflections measured	4202 unique
Reflections included	2603 with $I > 3\sigma(I)$
Solution	MULTAN 11/82
Parameters refined	376
Minimization function	$\Sigma w(\|F_o\| - \|F_c\|)^2$
Least-squares weights	$w = 1/(\sigma^2 F_o + 0.032 F_o^2)$
$R = \Sigma(\|F_o\| - \|F_c\|)/\Sigma\|F_o\|$	0.028
$R_w = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2]^{1/2}$	0.039
ESD of observations of unit weight	1.05
Max./min. in final difference map/e Å^{-3}	0.42(7)/−0.51(7)

Table 2. Atomic positional parameters and equivalent isotropic temperature factors for $Cu_3(ap)_4(NO_3)_2$. The equivalent isotropic temperature factors for non-hydrogen atoms are of the form $B_{eq} = 4/3\Sigma_i\Sigma_j\beta_{ij}a_ia_j$.

Atom	*x*	*y*	*z*	B_{eq}/B_{iso}
Cu(1)	0.14512(2)	0.08122(4)	0.62022(2)	2.63(1)
Cu(2)	0.26967(2)	−0.03804(4)	0.74425(2)	2.71(1)
Cu(3)	0.00925(2)	0.18925(4)	0.49433(2)	3.15(1)
O(1)	0.1826(1)	0.0346(2)	0.7277(1)	3.59(6)
O(2)	0.2201(1)	−0.0170(2)	0.6291(1)	2.74(5)
O(3)	0.1088(1)	0.1528(2)	0.5198(1)	3.36(6)
O(4)	0.0447(1)	0.1138(2)	0.5915(1)	3.82(6)
O(5)	0.2372(2)	0.2218(3)	0.6754(2)	7.0(1)
O(6)	0.3373(2)	0.1442(3)	0.7608(2)	8.5(1)
O(7)	0.3073(3)	0.2860(3)	0.7883(2)	6.9(1)
O(8)	0.0301(2)	0.3537(3)	0.5726(2)	5.2(1)
O(9)	−0.0747(2)	0.4239(3)	0.4931(2)	6.1(1)
O(10)	−0.0038(2)	0.4880(3)	0.6089(2)	7.5(1)
N(1)	0.3108(2)	−0.0616(2)	0.8611(2)	3.22(7)
N(2)	0.3552(2)	−0.1148(3)	0.7504(2)	4.27(9)
N(3)	−0.0140(2)	0.2715(3)	0.3986(2)	4.72(9)
N(4)	−0.0969(2)	0.1953(3)	0.4697(2)	4.07(9)
N(5)	0.2952(2)	0.2181(3)	0.7401(2)	4.3(1)
N(6)	−0.0167(2)	0.4228(3)	0.5582(2)	4.2(1)
C(1)	0.1686(2)	0.0766(4)	0.7849(2)	4.1(1)
C(2)	0.2358(2)	0.0774(4)	0.8682(2)	4.1(1)
C(3)	0.2661(2)	−0.0279(3)	0.8966(2)	3.7(1)
C(4)	0.2610(2)	−0.0060(3)	0.5892(2)	3.4(1)
C(5)	0.3160(2)	−0.0939(4)	0.6083(2)	4.3(1)
C(6)	0.3802(2)	−0.0919(4)	0.6928(2)	5.0(1)
C(7)	0.1489(2)	0.1865(4)	0.4836(2)	4.2(1)
C(8)	0.1141(3)	0.2778(4)	0.4295(3)	5.5(1)
C(9)	0.0361(3)	0.2670(5)	0.3660(2)	5.8(1)
C(10)	0.0073(2)	0.0884(4)	0.6322(3)	5.3(1)
C(11)	−0.0748(2)	0.0853(5)	0.5809(3)	5.6(1)
C(12)	−0.1093(2)	0.1814(4)	0.5370(3)	4.6(1)
H(N11)	0.352(3)	−0.039(4)	0.887(3)	5.0
H(N12)	0.313(3)	−0.127(4)	0.865(3)	5.0
H(N21)	0.339(3)	−0.175(4)	0.744(3)	5.0
H(N22)	0.389(3)	−0.120(4)	0.796(3)	5.0
H(N31)	−0.012(3)	0.344(4)	0.416(3)	5.0
H(N32)	−0.051(3)	0.258(4)	0.364(3)	5.0
H(N41)	−0.124(3)	0.160(4)	0.426(3)	5.0
H(N42)	−0.116(3)	0.263(4)	0.449(3)	5.0
H(11)	0.136(3)	0.027(4)	0.785(3)	5.0
H(12)	0.150(3)	0.144(4)	0.772(3)	5.0
H(21)	0.220(3)	0.106(4)	0.906(3)	5.0
H(22)	0.270(3)	0.112(4)	0.870(3)	5.0
H(31)	0.293(3)	−0.031(4)	0.951(3)	5.0
H(32)	0.225(3)	−0.076(4)	0.879(3)	5.0
H(41)	0.285(3)	0.058(4)	0.604(3)	5.0
H(42)	0.230(3)	−0.001(4)	0.533(3)	5.0
H(51)	0.335(3)	−0.090(4)	0.574(3)	5.0
H(52)	0.288(3)	−0.163(4)	0.601(3)	5.0
H(61)	0.417(3)	−0.147(4)	0.699(3)	5.0
H(62)	0.397(3)	−0.023(4)	0.700(3)	5.0
H(71)	0.156(3)	0.130(4)	0.453(3)	5.0
H(72)	0.200(3)	0.197(4)	0.522(3)	5.0
H(81)	0.142(3)	0.287(4)	0.401(3)	5.0
H(82)	0.113(3)	0.350(4)	0.467(3)	5.0
H(91)	0.024(2)	0.323(4)	0.328(3)	5.0
H(92)	0.048(2)	0.191(4)	0.351(3)	5.0
H(101)	0.018(3)	0.156(4)	0.661(3)	5.0
H(102)	0.025(3)	0.024(4)	0.662(3)	5.0
H(111)	−0.099(3)	0.055(4)	0.616(3)	5.0
H(112)	−0.085(3)	0.025(4)	0.540(3)	5.0
H(121)	−0.160(3)	0.181(4)	0.525(3)	5.0
H(122)	−0.086(3)	0.254(5)	0.576(3)	5.0

diffractometer using Mo $K\alpha$ radiation. The data obtained were corrected for Lorentz and polarization effects. The crystal data and experimental details are presented in Table 1.

The lattice parameters were calculated by least-squares refinements of 25 reflections. The structure was solved by direct methods (MULTAN 11/82)[20] and refined by least-squares techniques to an R-value of 0.028 ($R_w = 0.039$) for 2603 independent reflections having $I > 3\sigma(I)$. Hydrogen atoms were refined with an isotropic temperature parameter $B = 5.00$ Å^2. All calculations were performed on a VAX II microcomputer using SDP-PLUS software.[21] Figures were drawn with the PLUTO[22] and ORTEP[23] programs. The final atomic positional coordinates and equivalent isotropic temperature factors are listed in Table 2. Tables of the anisotropic thermal parameters and observed and calculated structural factors can be obtained from the authors upon request.

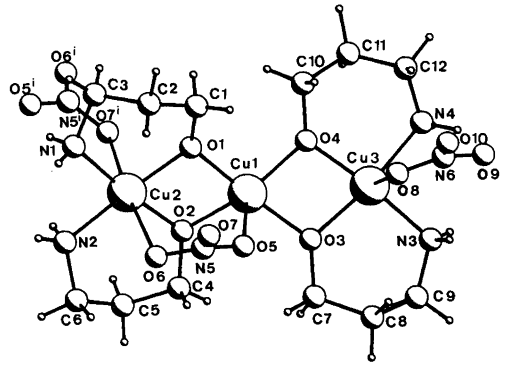

Fig. 1. Perspective view of $Cu_3(ap)_4(NO_3)_2$ showing an extra nitrate group generated by symmetry.

Results and discussion

Syntheses. The crystallization of certain 3-aminopropanolatonitrate complexes of the copper(II) ion in ethanol–THF solutions (30 % THF) was found to be dependent on the ap-to-$Cu(NO_3)_2$ ratio. (The Cu concentration was 1–2 mol l^{-1}.) If the ap:Cu ratio is below 1.8, pure $Cu(ap)NO_3$ is formed. If this ratio is greater than 2.4, $Cu(ap)(Hap)NO_3$ is obtained quantitatively. If the ratio is between 1.8 and 2.4 a trimer is generally obtained as the main component. Pure $Cu_3(ap)_4(NO_3)_2$ crystals are most likely to be formed if the

Table 3. Bond distances (pm) and angles (°) with estimated standard deviations in parentheses for $Cu_3(ap)_4(NO_3)_2$.[a]

Cu(1)–O(1)	191.9(2)	Cu(2)–O(1)	192.6(3)	Cu(2)–O(7^i)	269.1(4)	Cu(3)–O(8)	253.8(3)
Cu(1)–O(2)	196.2(3)	Cu(2)–O(2)	195.2(2)	Cu(3)–O(3)	193.7(3)	Cu(1)···Cu(2)	295.16(5)
Cu(1)–O(3)	193.8(3)	Cu(2)–N(1)	200.1(3)	Cu(3)–O(4)	191.5(3)	Cu(2)···Cu(2^i)	660.07(7)
Cu(1)–O(4)	192.6(3)	Cu(2)–N(2)	199.6(4)	Cu(3)–N(3)	198.1(4)	Cu(1)···Cu(3)	301.06(5)
Cu(1)–O(5)	248.0(4)	Cu(2)–O(6)	270.3(4)	Cu(3)–N(4)	201.8(4)		
O(1)–Cu(1)–O(2)	79.7(1)	O(1)–Cu(2)–N(1)	95.8(1)	N(2)–Cu(2)–O(6)	92.2(1)	N(3)–Cu(3)–O(8)	89.3(1)
O(1)–Cu(1)–O(3)	169.6(1)	O(1)–Cu(2)–N(2)	174.7(1)	N(2)–Cu(2)–O(7^i)	89.7(2)	N(4)–Cu(3)–O(8)	87.1(1)
O(1)–Cu(1)–O(4)	100.4(1)	O(1)–Cu(2)–O(6)	88.7(1)	O(6)–Cu(2)–O(7^i)	174.0(1)	Cu(1)–O(1)–Cu(2)	100.3(1)
O(1)–Cu(1)–O(5)	87.6(1)	O(1)–Cu(2)–O(7)	88.9(1)	O(3)–Cu(3)–O(4)	77.5(1)	Cu(1)–O(2)–Cu(2)	97.9(1)
O(2)–Cu(1)–O(3)	107.4(1)	O(2)–Cu(2)–N(1)	174.5(1)	O(3)–Cu(3)–N(3)	95.9(2)	Cu(1)–O(3)–Cu(2)	102.0(1)
O(2)–Cu(1)–O(4)	150.8(1)	O(2)–Cu(2)–N(2)	95.1(1)	O(3)–Cu(3)–N(4)	167.9(1)	Cu(1)–O(4)–Cu(2)	103.2(2)
O(2)–Cu(1)–O(5)	92.0(1)	O(2)–Cu(2)–O(6)	87.7(1)	O(3)–Cu(3)–O(8)	102.3(1)	Cu(2)–Cu(1)–Cu(3)	175.04(2)
O(3)–Cu(1)–O(4)	77.2(1)	O(2)–Cu(2)–O(7^i)	86.5(1)	O(4)–Cu(3)–N(3)	172.7(1)	Cu(1)–O(5)–N(5)	124.3(3)
O(3)–Cu(1)–O(5)	84.6(1)	N(1)–Cu(2)–N(2)	89.3(1)	O(4)–Cu(3)–N(4)	95.3(1)	Cu(2)–O(6)–N(5)	114.1(3)
O(4)–Cu(1)–O(5)	117.2(1)	N(1)–Cu(2)–O(6)	95.6(1)	O(4)–Cu(3)–O(8)	89.0(1)	Cu(2^i)–O(7)–N(5)	124.8(3)
O(1)–Cu(2)–O(2)	79.7(1)	N(1)–Cu(2)–O(7^i)	90.2(1)	N(3)–Cu(3)–N(4)	91.7(2)	Cu(3)–O(8)–N(6)	126.4(3)
3-Amino-1-propanolato ligands:							
C(1)–O(1)	139.1(6)	C(7)–O(3)	140.1(6)	C(3)–N(1)	147.2(6)	C(9)–N(3)	146.4(8)
C(1)–C(2)	151.8(4)	C(7)–C(8)	151.2(6)	C(2)–C(3)	149.9(6)	C(8)–C(9)	147.7(6)
C(4)–O(2)	141.2(6)	C(10)–O(4)	139.4(7)	C(6)–N(2)	147.8(7)	C(12)–N(4)	145.9(7)
C(4)–C(5)	153.2(6)	C(10)–C(11)	148.9(5)	C(5)–C(6)	151.1(5)	C(11)–C(12)	148.6(7)
O(1)–C(1)–C(2)	113.5(3)	C(5)–C(6)–N(2)	110.9(4)	O(4)–C(10)–C(11)	114.1(3)	C(4)–C(5)–C(6)	113.6(4)
C(2)–C(3)–N(1)	110.6(4)	O(3)–C(7)–C(8)	113.3(4)	C(11)–C(12)–N(4)	111.4(5)	C(7)–C(8)–C(9)	116.7(4)
O(2)–C(4)–C(5)	112.0(3)	C(8)–C(9)–N(3)	111.3(4)	C(1)–C(2)–C(3)	112.4(4)	C(10)–C(11)–C(12)	115.2(5)
Nitrate ions:							
N(5)–O(5)	123,3(4)	N(6)–O(8)	125.3(5)	O(5)–N(5)–O(6)	122.7(4)	O(8)–N(6)–O(9)	119.5(3)
N(5)–O(6)	123.0(5)	N(6)–O(9)	123.7(4)	O(5)–N(5)–O(7)	118.2(4)	O(8)–N(6)–O(10)	119.2(3)
N(5)–O(7)	121.8(5)	N(6)–O(10)	124.4(5)	O(6)–N(5)–O(7)	118.8(4)	O(9)–N(6)–O(10)	121.4(4)

[a]Symmetry code: (i) $0.5 - x$, $y - 0.5$, $1.5 - z$.

ratio is between 2.0 and 2.3 and 10% trifluoroethanol is added, since Cu(ap)(Hap)NO_3 is very soluble in this solvent.

Structure and spectra of $Cu_3(ap)_4(NO_3)_2$. The structure of the trimeric $Cu_3(ap)_4(NO_3)_2$ unit and atom numbering are shown in Fig. 1. The bond distances and angles are presented in Table 3. Cu(1) has a square-pyramidal coordination (4 + 1) with a CuO_5 chromophore, Cu(2) has a tetragonally distorted octahedral (4 + 2) coordination with a $CuN_2O_2O_2$ chromophore, and Cu(3) has a square-pyramidal coordination (4 + 1) with a CuN_2O_2O chromophore.

Four alkoxy oxygens are bound to Cu(1) in a plane and the fifth coordination site of Cu(1) is occupied by a nitrate oxygen atom, O(5). The short bonds around Cu(2) are made of two alkoxide ions and two amine nitrogens. The fifth and sixth coordination sites are occupied by nitrate oxygens O(6) and O(7^i). Around Cu(3) there are also two alkoxy oxygens and two amine nitrogens at equatorial positions. Here the axial ligand is O(8) of the nitrate ion.

In the UV-VIS spectrum of the compound there is a broad band with a maximum at 16300 cm^{-1}, indicating distorted five- and six-coordinated Cu(II) ions with oxygen and nitrogen ligand atoms. There is also a charge-transfer band at 28300 cm^{-1}. A similar band in dimers Cu(ap)NO_3 and Cu(ap)(Hap)I is at 29000 and 28600 cm^{-1}, respectively.[3] Thus it is seems impossible to distinguish alkoxo-bridged dimers and trimers from each other by their UV spectra.

The N–O bond lengths of the nitrate ions [N(5)–O(5) = 123.3(4), N(5)–O(6) = 123.0(5), N(5)–O(7) = 121.8(5), N(6)–O(8) = 125.3(5), N(6)–O(9) = 123.7(4) and N(6)–O(10) = 122.4(5) pm] are very similar, and this indicates that nitrate ions are only weakly bonded to copper(II) ions.[24] Nitrate-1 is rather unusual, since it acts as a tridentate ligand, bonding to three different copper(II) ions. A similar case was found earlier in $[Cu_3(OH)(pz)_3(Hpz)_2(NO_3)] \cdot H_2O$.[25] In the IR spectrum of $Cu_3(ap)_4(NO_3)_2$ there is a broad band at 1340 cm^{-1}, which might contain several bands. This, together with the combination bands at 1746 and 1753 cm^{-1}, indicates the presence of essentially ionic NO_3 groups.[26,27]

Table 4. Distances (in pm) and angles (in °) associated with the possible hydrogen bonds of $Cu_3(ap)_4(NO_3)_2$.[a]

X–H···Y[b]	X–H	H···Y	X···Y	X–H···Y
N(1)–H(N11)···O(9^{ii})	81(5)	239(5)	306.3(4)	143(6)
N(1)–H(N12)···O(5^{iii})	86(6)	219(5)	296.6(5)	150(4)
N(2)–H(N22)···O(8^{iii})	82(4)	226(4)	307.3(4)	170(6)
N(3)–H(N31)···O(10^{iii})	100(6)	231(6)	317.5(6)	145(5)
N(3)–H(N32)···O(6^{iv})	75(4)	253(4)	311.2(4)	137(6)
N(4)–H(N41)···O(7^{iv})	88(4)	241(4)	306.1(5)	131(5)
N(4)–H(N42)···O(9)	98(5)	227(5)	302.2(5)	134(3)

[a] Estimated standard deviations in parentheses. [b] Symmetry codes: (ii) 0.5 + *x*, 0.5 – *y*, 0.5 + *z*; (iii) 0.5 – *x*, *y* – 0.5, 1.5 – *z*; (iv) *x* – 0.5, 0.5 – *y*, 1 – *z*.

The bond distances and angles of the 3-amino-1-propanolato ligands are given in Table 3. The C–H bond distances are between 83(6) and 120(6) pm. Upon coordination all four 3-amino-1-propanolato groups adopt a chelated conformation with O–C–C–C and C–C–C–N torsion angles of −54.7(5) to −70.1(5) and 68.6(6) to 78.8(5)°, respectively.

The trimeric $Cu_3(ap)_4(NO_3)_2$ units are joined together by a CuONOCu bridge and probably by NH···O hydrogen bonds (Table 4), forming layers along the (10$\bar{1}$) plane (Fig. 2). The CuONOCu bridge binds the trimers along the *b*-axis via copper atoms, and the amine nitrogen hydrogens form a net of hydrogen bonds to the nitrate oxygen atoms in different directions of the (10$\bar{1}$) plane.

The remaining interactions between the $Cu_3(ap)_4(NO_3)_2$ trimer layers are weak van der Waals type CH···CH contacts.

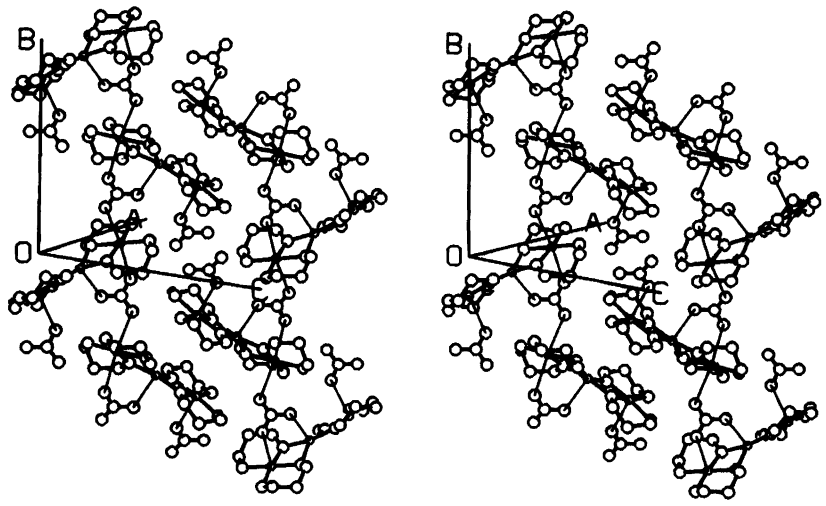

Fig. 2. Structure of one polymeric layer of $Cu_3(ap)_4(NO_3)_2$. Hydrogen atoms are omitted for clarity.

Conclusion

In ethanolic solutions of the copper(II) ion and 3-amino-1-propanol both dimeric and trimeric cationic species seem to be present. The precipitation of a particular type of complex depends on the ratio of copper(II) ion to aminoalcohol and on the choice of anions and solvents used.

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References

1. Sillanpää, R., Lindgren, T. and Hiltunen, L. *Inorg. Chim. Acta 131* (1987) 85.
2. Sillanpää, R., Lindgren, T. and Rissanen, K. *Inorg. Chim. Acta 134* (1987) 233.
3. Lindgren, T., Sillanpää, R., Rissanen, K., Thompson, L. K., O'Connor, C. J., van Albada, G. A. and Reedijk, J. *Inorg. Chim. Acta 171* (1990) 95.
4. Henkel, G., Tremel, W. and Krebs, B. *Angew. Chem., Int. Ed. Engl. 20* (1981) 1033.
5. Bertrand, J. A., Kelley, J. A. and Vassian, E. G. *J. Am. Chem. Soc. 23* (1969) 2394.
6. Busch, D. H. and Jicha, D. C. *Inorg. Chem. 1* (1962) 884.
7. Suades, J., Solans, X., Font-Altaba, M. and Aguilo, M. *Inorg. Chim. Acta 99* (1985) 1.
8. Nicholson, J. R., Wang, R.-J., Huffman, J. C., Christou, J. C., Chang, H.-R. and Hendrickson, D. N. *J. Chem. Soc., Chem. Commun.* (1985) 1781.
9. Barrera, H., Suades, J., Perucaud, M. C. and Brianso, J. L. *Polyhedron 3* (1984) 839.
10. Tremel, W., Kriege, M., Krebs, B. and Henkel, G. *Inorg. Chem. 27* (1988) 3886.
11. Pulla Rao, Ch., Dorfman, J. R. and Holm, R. H. *Inorg. Chem. 25* (1986) 428.
12. Baker, W. A., Jr. and Helm, F. T. *J. Am. Chem. Soc. 97* (1975) 2295.
13. Ferguson, G., Langrick, C. R., Parker, D. and Matthes, K. *J. Chem. Soc., Chem. Commun.* (1985) 1609.
14. Curtis, N. F., Gainsford, G. J. and Morgan, K. R. *Aust. J. Chem. 41* (1988) 1545.
15. Epstein, J. M., Figgis, B. N., White, A. H. and Willis, A. C. *J. Chem. Soc., Dalton Trans.* (1975) 1954.
16. Matsumoto, N., Nishida, Y., Kida, S. and Ueda, I. *Bull. Chem. Soc. Jpn. 49* (1976) 117.
17. Muhonen, H., Pajunen, A. and Hämäläinen, R. *Acta Crystallogr., Sect. B. 36* (1980) 2790.
18. Chiari, B., Piovesana, O., Tarantelli, T. and Zanazzi, P. F. *Inorg. Chem. 24* (1985) 4615.
19. Haase, W. and Gehring, S. *J. Chem. Soc., Dalton Trans.* (1985) 2609.
20. Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declerq, J. P. and Woolfson, M. M. *MULTAN 82: A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data,* Universities of York, England and Louvain, Belgium 1982.
21. Frenz, B. A. In: Schenck, H., Olthof-Hazelkamp, R. van Koningsveld, H. and Bassi, G. C., Eds., *The Enraf-Nonius CAD4-SDP. – A Real-Time System for Concurrent X-Ray Data Collection and Crystal Structure Determination, Computing in Crystallography,* Delft University Press, Delft, Holland 1978, pp. 64–71.
22. Motherwell, W. D. S. and Clegg, W. *PLUTO 78: A Program for Plotting Crystal and Molecular Structures,* University of Cambridge, England 1978.
23. Johnson, C. K. *ORTEP-II: A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations. Report ORNL-5138,* Oak Ridge National Laboratory, Oak Ridge, TN 1976.
24. Addison, C. C., Logan, N., Wallwork, S. C. and Carner, C. D. *Quart. Rev. 25* (1971) 289.
25. Hulsbergen, F. B., ten Hoedt, R. W. M., Verschoor, G. C., Reedijk, J. and Spek, A. J. *J. Chem. Soc., Dalton Trans.* (1983) 539.
26. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds,* 4th ed., Wiley-Interscience, New York 1986.
27. Lever, A. B. P., Montovani, E. and Ramaswamy, B. S. *Can. J. Chem. 49* (1971) 1957.

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