

Copper(II) Complexes of 3-Aminopropanols. Synthesis and Crystal Structure of a Compound Containing a Trinuclear Copper(II) Cation and a Novel Hexanuclear Iodocuprate(I) Anion

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The reaction of the copper(II) ion with 3-aminopropanol and iodide ion in a DMF–methanol mixture gave a mixed-valence Cu(I)/Cu(II) compound $[\text{Cu}_3(\text{ap})_4\text{DMF}]_2[\text{Cu}_6\text{I}_{10}]$, which crystallises in the triclinic space group $P\bar{1}$, with $a = 1029.4(2)$, $b = 1132.4(2)$, $c = 1561.2(3)$ pm; $\alpha = 77.89(2)$, $\beta = 76.60(2)$, $\gamma = 82.22(2)^\circ$; $Z = 1$. The Cu(II) ions form trinuclear alkoxobridged cations with the 3-aminopropanolato ligand, while the Cu(I) ions form hexanuclear iodobridged anions. The DMF molecule is weakly coordinated to the copper(II) ion, with a Cu–O bond length of 260.1(7) pm.

The Cu...Cu distances in the trinuclear $[\text{Cu}_3(\text{ap})_4\text{DMF}]_2^{2+}$ cation are 291.4(1) and 294.5(1) pm. The bridging Cu–O(alkoxy) bond lengths are from 191.0(7) to 193.7(6) pm. The hexanuclear $[\text{Cu}_6\text{I}_{10}]^{4-}$ anion has a crystallographic symmetry C_2 and contains an eight-membered ring and two six-membered rings. The Cu...Cu distances in the hexamer vary from 253.7(2) to 273.0(2) pm and the Cu–I bond lengths from 249.3(2) to 290.9(2) pm.

Earlier studies on the reactions of the copper(II) ion with 3-aminopropanol have revealed the existence of cationic copper(II) dimers and trimers.^{1–3} The complexes were assigned the formulas $[\{\text{Cu}(\text{ap})\text{X}\}_2]$, $[\{\text{Cu}(\text{ap})(\text{Hap})\}_2]\text{X}_2$ and $[\text{Cu}_3(\text{ap})_4(\text{NO}_3)_2]$, where Hap is 3-aminopropanol, ap is the 3-aminopropanolato ion and X is an anion. The anions X in the compounds have been halides (chloride, bromide and iodide), nitrate and formate. The $[\{\text{Cu}(\text{ap})\text{I}\}_2]$ compound has proved difficult to obtain. We have explored several synthetic routes in the hope of preparing the pure crystals, so far without success.

One system we studied was the reaction of copper(II) trifluoromethanesulfonate and 3-aminopropanol in a DMF–methanol mixture in the presence of iodide ion and triethylamine in a molar ratio 1:1:1:1. From this solution we isolated dark blue crystals which were characterized by UV–VIS and IR spectra. The spectra suggested that a new compound had formed. X-Ray structure analysis of the crystals showed the compound to be a mixed-valence Cu(I)/Cu(II) complex formed of trinuclear Cu(II) cations and hexanuclear Cu(I) anions. The compound can be formulated as $[\text{Cu}_3(\text{ap})_4\text{DMF}]_2[\text{Cu}_6\text{I}_{10}]$ and is made up of trinuclear $[\text{Cu}_3(\text{ap})_4\text{DMF}]_2^{2+}$ cations and hexanuclear $[\text{Cu}_6\text{I}_{10}]^{4-}$

anions. The compound has formal similarities with $[\text{Cu}(\text{LH})_2][\text{Cu}_2\text{I}_4]$ (LH = 1,1-di-2-pyridylethanol),⁴ $[\text{Co}(\text{cp})_2]_3[\text{Cu}_3\text{I}_6]$ and $[\text{Co}(\text{cp})_2]_4[\text{Cu}_4\text{I}_8]$.⁵

Experimental

Preparation of $[\text{Cu}_3(\text{ap})_4\text{DMF}]_2[\text{Cu}_6\text{I}_{10}]$. To a 1.6 mmol sample of $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ dissolved in 2 ml of DMF was added 1 ml methanol containing 1.9 mmol Hap (3-amino-1-propanol). To this solution were added 2 mmol $\text{N}(\text{Et})_3$ in 2 ml of methanol and 1.7 mmol $\text{N}(\text{Bu})_4\text{I}$ in 2 ml of DMF and methanol (1:1). Finally 6 ml of diethyl ether were added, and the blue solution was kept overnight in a freezer at 255 K. The blue crystals (167 mg, 45%) were separated by filtration and washed with ethanol and ether. Found: C 13.46; H 2.87. Calc. for $\text{C}_{15}\text{H}_{39}\text{Cu}_6\text{I}_5\text{N}_5\text{O}_5$: C 13.01, H 2.84.

Spectral measurements. The solid-state UV–VIS spectrum of the compound was recorded on a Cary 17D spectrometer using the nujol mull technique. Above 300 nm there is a strong band at 350 nm ($28\,600\text{ cm}^{-1}$) and a very broad band with much lower intensity at 590 nm ($16\,900\text{ cm}^{-1}$).

The solid-state IR spectrum was recorded on a Perkin Elmer 180 grating infrared spectrophotometer using the

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Table 1. Crystal data and experimental details of structure determination of $[\text{Cu}_3(\text{ap})_4\text{DMF}]_2[\text{Cu}_6\text{I}_{10}]$.

Formula	$[\text{Cu}_3\text{C}_{15}\text{H}_{39}\text{N}_5\text{O}_5]_2[\text{Cu}_6\text{I}_{10}]$
M_r	2770.60
Space group	$P\bar{1}$
Cell parameters at 296 K	
a/pm	1029.4(2)
b/pm	1132.4(2)
c/pm	1561.2(3)
$\alpha/^\circ$	77.89(2)
$\beta/^\circ$	76.60(2)
$\gamma/^\circ$	82.22(2)
V/nm^3	1.723(2)
Calculated density/ g cm^{-3}	2.669
Z	1
$\mu(\text{MoK}\alpha)/\text{cm}^{-1}$	81.1
Crystal description	blue, prismatic
Crystal dimensions/mm	0.12×0.15×0.10
Instrument	Enraf-Nonius CAD4
Data collection	$\omega/2\theta$
Corrections	Lorentz-polarization, absorption
Maximum $2\theta/^\circ$	60
No. of reflections measured	10 002 unique
No. of observations [$I > 3\sigma(I)$]	5388
Solution	Multan11/82
Hydrogen atoms	Not included
Parameters refined	325
$R = \sum(F_o - F_c) / \sum F_o $	0.038
$R_w = [\sum w(F_o - F_c)^2 / \sum w F_o ^2]^{1/2}$	0.039
E.S.D. of obs. of unit weight	2.66
Least-squares weights	$w = [\sigma^2(F_o) + (0.032F_o)^2]^{-1}$
Highest peak in diff. map/ $e \text{ \AA}^{-3}$	1.17
Lowest peak in diff. map/ $e \text{ \AA}^{-3}$	-1.18

nujol mull technique. In the IR spectrum the N–H stretchings are at 3280s, 3250s, 3230s, 3210s, 3150m and 3130m; NH_2 scissorings are the broad band with peaks at 1596s, 1585s, 1577s, 1568s; and the C=O stretching of DMF is at 1635vs cm^{-1} .

X-Ray measurements. Single-crystal X-ray measurements were made on an Enraf-Nonius CAD4 diffractometer using $\text{MoK}\alpha$ radiation. The data obtained were corrected for Lorentz and polarisation effects. Also, an absorption correction was made (DIFABS).⁶ The crystal data and experimental details are presented in Table 1. The structure was solved by direct methods (MULTAN11/82)⁷ and refined to an R -value of 0.038 ($R_w = 0.039$) for 5388 independent reflections having $I > 3\sigma(I)$. Hydrogen atoms were not included in the refinement. All calculations were performed on a VAX II microcomputer using SDP-PLUS software.⁸ Figures were drawn with the PLUTO software.⁹ 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 one of the authors (J. V.) upon request.

Results

The title compound is formed of trinuclear $[\text{Cu}_3(\text{ap})_4\text{DMF}]_2$

Table 2. Atomic positional parameters and equivalent isotropic temperature factors for $[\text{Cu}_3(\text{ap})_4\text{DMF}]_2[\text{Cu}_6\text{I}_{10}]$.^a

Atom	x	y	z	B_{eq}
I(1)	0.69108(6)	0.49753(6)	0.06166(4)	3.81(1)
I(2)	0.75615(7)	0.15272(6)	0.29624(5)	4.77(2)
I(3)	0.31984(7)	0.69574(5)	0.14963(4)	3.92(1)
I(4)	0.52703(7)	0.48526(6)	0.36334(4)	4.12(1)
I(5)	0.36739(6)	0.29473(6)	0.20122(4)	4.08(1)
Cu(1)	0.9503(1)	-0.14590(9)	0.22112(7)	3.16(2)
Cu(2)	0.8410(1)	0.06013(9)	0.10429(7)	3.36(2)
Cu(3)	1.0640(1)	-0.35047(9)	0.34046(7)	3.18(2)
Cu(4)	0.5018(2)	0.5355(1)	0.20235(9)	5.82(4)
Cu(5)	0.5659(2)	0.3092(1)	0.2740(1)	5.58(3)
Cu(6)	0.4042(2)	0.4958(1)	0.07713(9)	5.82(3)
O(1)	0.8062(6)	-0.1052(5)	0.1586(1)	3.8(1)
O(2)	1.0113(6)	-0.0062(5)	0.1350(4)	3.8(1)
O(3)	1.0496(6)	-0.1752(5)	0.3140(4)	3.8(1)
O(4)	0.9395(6)	-0.3164(5)	0.2622(4)	3.5(1)
O(5)	0.8633(6)	-0.3663(6)	0.4774(4)	4.6(2)
N(1)	0.6572(7)	0.1138(7)	0.0808(5)	4.1(2)
N(2)	0.9177(8)	0.2058(8)	0.0197(6)	4.9(2)
N(3)	1.1839(7)	-0.3685(7)	0.4274(5)	3.8(2)
N(4)	1.0922(8)	-0.5292(6)	0.3411(5)	3.8(2)
N(5)	0.6900(8)	-0.2175(7)	0.4746(5)	4.3(2)
C(1)	0.6805(9)	-0.1564(9)	0.1879(7)	4.3(2)
C(2)	0.5627(9)	-0.0605(9)	0.1901(7)	4.6(2)
C(3)	0.5617(9)	0.0187(9)	0.0983(7)	4.6(2)
C(4)	1.1144(9)	0.0633(8)	0.1406(7)	4.3(2)
C(5)	1.143(1)	0.1640(8)	0.0585(7)	4.4(2)
C(6)	1.025(1)	0.2562(8)	0.0482(7)	4.8(2)
C(7)	1.092(1)	-0.0941(9)	0.3557(7)	5.5(2)
C(8)	1.187(2)	-0.150(1)	0.4137(9)	12.9(4)
C(9)	1.205(1)	-0.260(1)	0.4588(8)	7.9(3)
C(10)	0.8909(9)	-0.3929(8)	0.2185(6)	4.0(2)
C(11)	0.975(1)	-0.5149(9)	0.2173(7)	4.7(2)
C(12)	0.990(1)	-0.5820(9)	0.3089(7)	4.8(2)
C(13)	0.757(1)	-0.3192(9)	0.4541(6)	4.2(2)
C(14)	0.735(1)	-0.149(1)	0.5291(9)	7.3(4)
C(15)	0.562(1)	-0.174(1)	0.4478(8)	6.0(3)

^aThe equivalent isotropic temperature factors are of the form $B_{\text{eq}} = 4/3 \sum_i \beta_{ij} a_i \cdot a_j$.

$\text{DMF}]^{2+}$ cations and hexanuclear $[\text{Cu}_6\text{I}_{10}]^{4-}$ anions. The trinuclear $[\text{Cu}_3(\text{ap})_4\text{DMF}]^{2+}$ cation with its atom numbering is shown in Fig. 1, and selected bond parameters are given in Table 3. The body of the $[\text{Cu}_3(\text{ap})_4\text{DMF}]^{2+}$ ion is identi-

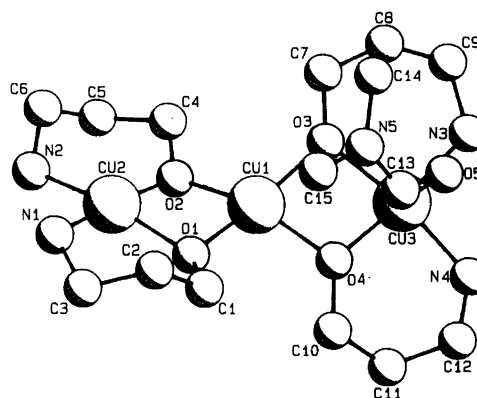


Fig. 1. Structure of the $[\text{Cu}_3(\text{ap})_4\text{DMF}]^{2+}$ cation.

Table 3. Bond distances (in pm) and angles (in °) with estimated standard deviations in parentheses for $[\text{Cu}_3(\text{ap})_4\text{DMF}]_2[\text{Cu}_6\text{I}_{10}]$.

Distances around Cu(I) ions			
Cu(4)–I(1)	264.5(1)	Cu(6)–I(1)	290.9(2)
Cu(4)–I(3)	257.8(2)	Cu(6)–I(3)	269.3(2)
Cu(4)–I(4)	252.4(2)	Cu(6)–I(5)	266.9(1)
Cu(5)–I(2)	249.3(2)	Cu(6)–I(1')	256.1(2)
Cu(5)–I(4)	260.2(2)	Cu(4)⋯Cu(5)	263.3(2)
Cu(5)–I(5)	259.6(2)	Cu(4)⋯Cu(6)	253.7(2)
		Cu(6)⋯Cu(6')	273.0(2)
Angles			
I(1)–Cu(4)–I(3)	108.98(5)	I(3)–Cu(6)–I(5)	111.14(5)
I(1)–Cu(4)–I(4)	125.70(6)	I(1')–Cu(6)–I(3)	111.85(6)
I(3)–Cu(4)–I(4)	122.18(6)	I(1')–Cu(6)–I(5)	115.01(5)
I(2)–Cu(5)–I(4)	117.35(7)	Cu(4)–I(1)–Cu(6)	54.10(5)
I(2)–Cu(5)–I(5)	127.37(7)	Cu(4)–I(1)–Cu(6')	112.33(5)
I(4)–Cu(5)–I(5)	113.71(6)	Cu(6)–I(1)–Cu(6')	59.48(4)
I(1)–Cu(6)–I(1')	120.52(5)	Cu(4)–I(3)–Cu(6)	57.49(5)
I(1)–Cu(6)–I(3)	98.67(6)	Cu(4)–I(4)–Cu(5)	61.79(5)
I(1)–Cu(6)–I(5)	97.91(5)	Cu(5)–I(5)–Cu(6)	96.27(5)
Distances around Cu(II) ions			
Cu(1)–O(1)	191.4(7)	Cu(3)–O(3)	193.3(6)
Cu(1)–O(2)	192.1(6)	Cu(3)–O(4)	191.8(7)
Cu(1)–O(3)	191.0(7)	Cu(3)–N(3)	200.0(8)
Cu(1)–O(4)	191.2(5)	Cu(3)–N(4)	200.4(7)
Cu(2)–O(1)	193.0(6)	Cu(3)–O(5)	260.1(7)
Cu(2)–O(2)	193.7(6)	Cu(1)⋯Cu(2)	291.4(1)
Cu(2)–N(1)	200.0(8)	Cu(1)⋯Cu(3)	294.5(1)
Cu(2)–N(2)	201.1(8)		
Angles			
O(1)–Cu(1)–O(2)	79.1(3)	O(3)–Cu(3)–O(4)	78.6(3)
O(1)–Cu(1)–O(3)	161.9(2)	O(3)–Cu(3)–N(3)	95.9(3)
O(1)–Cu(1)–O(4)	101.2(3)	O(3)–Cu(3)–N(4)	168.4(3)
O(2)–Cu(1)–O(3)	108.6(3)	O(3)–Cu(3)–O(5)	95.2(3)
O(2)–Cu(1)–O(4)	153.6(3)	O(4)–Cu(3)–N(3)	173.2(3)
O(3)–Cu(1)–O(4)	79.3(3)	O(4)–Cu(3)–N(4)	95.4(3)
O(1)–Cu(2)–O(2)	78.3(3)	O(4)–Cu(3)–O(5)	89.3(3)
O(1)–Cu(2)–N(1)	96.1(3)	N(3)–Cu(3)–N(4)	90.6(3)
O(1)–Cu(2)–N(2)	162.1(3)	N(3)–Cu(3)–O(5)	87.4(3)
O(2)–Cu(2)–N(1)	174.2(3)	N(4)–Cu(3)–O(5)	94.7(3)
O(2)–Cu(2)–N(2)	93.7(3)		
N(1)–Cu(2)–N(2)	92.1(3)		
Cu(1)–O(1)–Cu(2)	98.6(3)	Cu(1)–O(3)–Cu(3)	100.1(3)
Cu(1)–O(2)–Cu(2)	98.1(3)	Cu(1)–O(4)–Cu(3)	100.5(3)
Cu(2)–Cu(1)–Cu(3)	178.73(6)		
Distances in 3-amino-1-propanolato ligands			
C(1)–O(1)	143(1)	C(7)–O(3)	140(1)
C(1)–C(2)	151(1)	C(7)–C(8)	147(2)
C(3)–N(1)	150(1)	C(9)–N(3)	148(1)
C(2)–C(3)	152(1)	C(8)–C(9)	131(2)
C(4)–O(2)	143(1)	C(10)–O(4)	141(1)
C(4)–C(5)	153(1)	C(10)–C(11)	153(1)
C(6)–N(2)	150(2)	C(12)–N(4)	150(2)
C(5)–C(6)	150(1)	C(11)–C(12)	151(2)
Angles			
O(1)–C(1)–C(2)	112.3(8)	O(3)–C(7)–C(8)	114.3(9)
C(1)–C(2)–C(3)	112.2(8)	C(7)–C(8)–C(9)	132(2)
C(2)–C(3)–N(1)	109.6(9)	C(8)–C(9)–N(3)	123(1)
O(2)–C(4)–C(5)	111.2(9)	O(4)–C(10)–C(11)	112.8(8)
C(4)–C(5)–C(6)	113.7(8)	C(10)–C(11)–C(12)	113.5(8)
C(5)–C(6)–N(2)	111.9(8)	C(11)–C(12)–N(4)	110.8(8)
Distances in DMF molecules			
C(13)–O(5)	125(1)	C(13)–N(5)	132(1)
C(14)–N(5)	145(2)	C(15)–N(5)	146(1)
Angles			
O(5)–C(13)–N(5)	125.6(9)	C(13)–N(5)–C(14)	121.5(9)
C(13)–N(5)–C(15)	120.8(8)	C(14)–N(5)–C(15)	117.6(8)
Symmetry code: $i = 1-x, 1-y, -z$.			

cal to the body of the trinuclear unit in $[\text{Cu}_3(\text{ap})_4(\text{NO}_3)_2]$.³ Only the ligands coordinating weakly to copper(II) are different.

The copper(II) ion in the middle of the trimer has a tetrahedrally distorted square-planar coordination. The four alkoxy oxygen atoms form a CuO_4 chromophore with the copper atom. Since the Cu(1)–I(2) distance is 327.1(1) pm, there may be some attractive interaction between these atoms. Cu(2) has a square-planar and Cu(3) has a square-pyramidal (4 + 1) coordination geometry. The two alkoxy oxygens and two amine nitrogens coordinated with Cu(2) form with it a CuN_2O_2 chromophore, while the two alkoxy oxygens and two amine nitrogens at equatorial positions and the O(5) atom of the DMF molecule in the axial position of the coordination sphere of Cu(3) form a $\text{CuN}_2\text{O}_2\text{O}'$ chromophore. Coordination of the DMF molecule is thus through its oxygen atom.

The Cu⋯Cu distances in the trinuclear cation are 291.4 (1) and 294.5(1) pm. The Cu–O(alkoxy) bond lengths range from 191.0(7) to 193.7(6) pm, and the Cu–N bond lengths from 200.0(8) to 201.1(8) pm. The Cu(3)–O(5) distance is 260.1(7) pm. All these values are normal for copper(II) aminoalcohol complexes.

The hexanuclear $[\text{Cu}_6\text{I}_{10}]^{4-}$ anions have a crystallographic symmetry of C_3 and are thus composed of two Cu_3I_5 trimer units as shown in Fig. 2. Selected distances and angles of the anion are given in Table 3. The anion contains an eight-membered ring and two six-membered rings. The Cu⋯Cu distances vary from 253.7(2) to 273.0(2) pm and the Cu–I bond lengths from 249.3(2) to 290.9(2) pm. Two of the three copper(I) ions in the trimer units have a nearly planar trigonal coordination. The third copper(I) ion, Cu(6), has a coordination sphere that is intermediate between planar trigonal and tetrahedral. In Fig. 2 only three bonds are drawn to the Cu(6) atom. Several iodicuprates(I) are reported in the literature,¹⁰ but the ion $[\text{Cu}_6\text{I}_{11}]^{5-}$, which has the closest stoichiometric ratio to $[\text{Cu}_6\text{I}_{10}]^{4-}$, has a completely different structure.¹¹

The UV–VIS spectrum of $[\text{Cu}_3(\text{ap})_4\text{DMF}]_2[\text{Cu}_6\text{I}_{10}]$ has a broad d–d band with an unresolved peak at 16900 cm^{-1} . The CT band is at 28600 cm^{-1} . The ligand field energies of

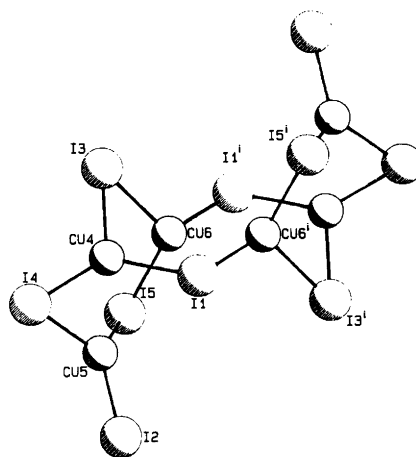


Fig. 2. Structure of the $[\text{Cu}_6\text{I}_{10}]^{4-}$ anion.

CuO_4 , CuN_2O_2 and $\text{CuN}_2\text{O}_2\text{O}'$ chromophores with distorted square-planar and square-pyramidal structure around the Cu(II) ion are almost equal.¹² Thus the expected broad d-d band is seen. The energy values for the d-d and CT bands are near to those found in $[\text{Cu}_3(\text{ap})_4(\text{NO}_3)_2]$.³

The IR spectrum of the compound contains many more bands than those mentioned in the experimental section, but the assignment of these additional bands is difficult. The reported bands may help in identifying the compound.

Some iodocuprates(I) and argentates(I) are ionic conductors, and their conductivity is strongly dependent on the structure of the cluster.¹³ When the cation is the alkylammonium ion the formation of a certain aggregate in the solid state seems mainly to depend on the properties of the cation (size, charge and shape) and concentration of the halide.^{5,10}

However, when the cation is a complex ion, other of its properties (whether it is inert or labile, coordinatively saturated or not) may be important in the formation of a certain compound. Thus solvent and reaction temperature may play an important role in the synthesis of new compounds.

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