# Synthetic, Structural and Magnetic Studies of Asymmetric Trinuclear Copper(II) Compounds $[CuX_2(Hae)_2][Cu_2(ae)_2X_2]$ (X = Cl or Br; Hae = 2-aminoethanol)†

**Sari Myllyviita,**[a] **Reijo Sillanpää,**[a] **Jeroen J. A. Kolnaar**[b] **and Jan Reedijk**[b]

[a] *University of Turku, Department of Chemistry, FIN-20500 Turku, Finland*

[b] *Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, PO Box 9502, 2300 RA Leiden, The Netherlands*

The structure of a novel complex $[Cu^{II}Br_2(Hae)_2][Cu^{II}_2(ae)_2Br_2]$ **1** (Hae = 2-aminoethanol) containing a neutral mononuclear copper unit bridged by a $\mu_4$-bromide ion and hydrogen bonds to a dinuclear copper(II) unit has been determined: orthorhombic, space group *Pbca*, $a = 15.726(2)$, $b = 20.984(3)$, $c = 12.637(1)$ Å, $R = 0.049$ ($R' = 0.047$), 1477 observed [$I > 3.00\sigma(I)$] reflections. The bridging bromide ion is unique; it links two copper(II) ions in the dinuclear unit and a mononuclear and two dinuclear units, thereby forming a chain-type structure. Hydrogen bonding additionally extensively stabilizes the formation of the chains along the *c* axis and links the chains together along the *b* axis. A very short O···O contact [2.61(2) Å] is present between a co-ordinated alcohol and an alcoholate of a different trinuclear unit. The resulting layers are connected only by van der Waals contacts. The synthesis, spectroscopic and magnetic properties of the complex are compared with those of the isomorphous chloride. The magnetic behaviour can be understood on the basis of the structure, and corresponds to that of a weakly antiferromagnetically coupled dinuclear unit and a mononuclear paramagnetic unit. The small value of the antiferromagnetic coupling can be explained by the roof-shaped $CuO_2Cu$ unit, which prevents the magnetic orbitals from undergoing significant overlap.

Copper(II) complexes of aminoalcohols are usually oligo- or poly-meric and often have interesting magnetic and conducting properties. In earlier studies we concentrated on 1,3-aminoalcohols as ligands.[1] The present report describes a reaction product of CuBr and copper(II) trifluoromethanesulfonate with 2-aminoethanol (Hae) (a 1,2-aminoalcohol).

A large number of complexes of copper(II) with 2-aminoethanol and its derivatives has been studied.[2,3] Some of these studies have concentrated on potentiometric and conductometric titrations,[4,5] polarographic[6] and spectrophotometric measurements[7] in solution and magnetic susceptibility measurements in the solid state.[8] It was shown that 2-aminoethanol co-ordinates to copper(II) ion through the amine rather than the hydroxyl group, but an alkoxo group is easily formed, which is highly active in the co-ordination process. Also, derivatives of 2-aminoethanol generally form di- or poly-nuclear units, while 2-aminoethanol itself favours mononuclear units.

The first structural study of $Cu^{II}$–Hae complexes showed that there exists a dinuclear cation $[\{Cu^{II}(ae)(Hae)\}_2]^{2+}$ in which each copper(II) shows square-planar co-ordination, and two $[Cu^{II}(ae)(Hae)]^+$ ions are hydrogen bonded to each other.[9] In the alkoxide-bridged dinuclear complex $[\{Cu^{II}_2(ae)_2(NCS)_2\}_\infty]$ the alkoxo ion bridges two copper(II) ions to give a dimer.[10] The dimeric units are centrosymmetric and the copper co-ordination is best described as distorted tetragonal pyramidal (4 + 1). We now report the first crystal structure of a copper(II)-monoaminoethanol complex, which contains both mono- and di-nuclear units. The so-formed trinuclear units are linked in chains by a weakly co-ordinating $\mu_4$-bromide ligand. There are also hydrogen-bonding affects. The roof shape of the bis(alkoxo) bridge in their dinuclear unit explains the low antiferromagnetism.

## Experimental

*Materials.*—All chemicals were of reagent grade and used as received.

*Physical Measurements.*—Elemental analyses were performed by standard titrimetric methods (for Cu, Br and Cl) and with a Perkin-Elmer 2400 Series II CHNS/O Analyzer (for C, H and N). Fourier-transform IR measurements were made in Nujol mulls on Mattson 6030 (MIR 4000–400 $cm^{-1}$) and 4060 (FIR 500–80 $cm^{-1}$) Galaxy series spectrometers. The magnetic susceptibility of the compounds in the 4–300 K region was obtained using a fully automated Manics DSM-8 susceptometer, equipped with a TBT continuous-flow cryostat and a Drusch EAF 16NC electromagnet operating at 1.4 T. Data were corrected for diamagnetic contributions (calculated from Pascal constants) and for magnetization of the sample holder.

*Preparation of Complexes.*—$[Cu^{II}Br_2(Hae)_2][Cu^{II}_2(ae)_2Br_2]$ **1**. A 0.1 mol $dm^{-3}$ solution of $[Cu^I_2Br_6]^{2-}$ was prepared from CuBr (2.5 mmol) and $NBu_4Br$ (5.0 mmol) in MeCN (25 $cm^3$). A sample (5 $cm^3$) of this solution (0.5 mmol $Cu^I$) was added with stirring to a solution containing copper(II) trifluoromethanesulfonate (0.5 mmol) and Hae (1.5 mmol) in a 1:3 molar ratio in MeCN, total volume 15 $cm^3$. A light blue powder precipitated immediately, but it dissolved during 1 d and green needles were formed (266 mg, yield 70% based on $Cu^{II}$). The crystals were separated by decantation and washed with MeCN and diethyl ether (Found: C, 13.2; H, 3.3; Br, 42.6; Cu, 25.1; N, 7.4. Calc. for $C_8H_{26}Br_4Cu_3N_4O_4$: C, 12.8; H, 3.5; Br, 42.5; Cu, 25.3; N, 7.4%), m.p. 175 °C.

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† *Supplementary data available:* (No. SUP 57087, 4 pp.): plots of $\chi T$ *vs.* *T* for compounds **1** and **2**. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

$[Cu^{II}Cl_2(Hae)_2][Cu^{II}_2(ae)_2Cl_2]$ **2**. A 0.1 mol dm$^{-3}$ solution of $[Cu^I_2Cl_4]^{2-}$ was prepared from CuCl (5 mmol) and $NBu_4Cl$ (5 mmol) in MeCN (25 cm$^3$). A sample (2 cm$^3$) of this solution (0.2 mmol $Cu^I$) was added with stirring to a solution containing copper(II) trifluoromethanesulfonate (0.25 mmol) and Hae (0.75 mmol) in a 1:3 molar ratio in MeCN, total volume 10 cm$^3$. A bluish green powder precipitated immediately, but dissolved during 1 d giving turquoise needles (83 mg, yield 67% based on $Cu^{II}$). The crystals were separated by decantation and washed with MeCN and ether (Found: C, 16.9; H, 4.6; Cl, 24.8; Cu, 33.4; N, 9.8. Calc. for $C_8H_{26}Cl_4Cu_3N_4O_4$: C, 16.7; H, 4.6; Cl, 24.7; Cu, 33.2; N, 9.8%), m.p. 160 °C.

The complex $[Cu^{II}Br_2(Hae)_2][Cu^{II}_2(ae)_2Br_2]$ decomposes in water to a blue solution and green powder, and $[Cu^{II}Cl_2(Hae)_2][Cu^{II}_2(ae)_2Cl_2]$ dissolves in water to give a turquoise solution. Both compounds are slightly soluble in dimethylformamide (dmf) giving green and blue solutions, respectively, and are insoluble in MeOH, EtOH, MeCN, tetrahydrofuran, trifluoroethanol and $CH_2Cl_2$.

*Crystallography.*—Single-crystal X-ray studies of compound **1** mounted on a glass fibre were carried out on a Rigaku AFC5S diffractometer with graphite-monochromated Mo-K$\alpha$ ($\lambda$ = 0.710 69 Å) radiation. Crystal data and experimental details are listed in Table 1.

Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 20 carefully centred reflections in the range $10.1 < 2\theta < 22.3°$. The data were collected using the $\omega$–$2\theta$ scan technique to a maximum $2\theta$ value of 50.0°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.15° with a take-off angle of 6.0°. Scans of $(0.84 + 0.30 \tan \theta)°$ were made at speed of 4.0° min$^{-1}$ (in $\omega$). The weak reflections $[I < 10.0\sigma(I)]$ were rescanned (maximum of two rescans) and the counts were accumulated to assure good counting statistics. The intensities of three representative reflections decayed by −4.0%; a linear correction factor was applied. An empirical absorption correction, based on azimuthal scans of three reflections, was applied which resulted in transmission factors ranging from 0.76 to 1.00. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods [12,13] followed by successive Fourier syntheses and least-squares refinements. Cromer and Waber's values [14] of neutral atom scattering factors were used. The structure was refined with 1477 observed reflections $[I > 3.00\sigma(I)]$ and 211 variable parameters and converged to a final $R$ value of 0.049 ($R'$ = 0.047). The non-hydrogen atoms were refined anisotropically. The CH and NH hydrogen atoms were included in calculated positions with fixed thermal parameters 1.2 times that of the host atom. The two OH hydrogens were found from the Fourier map, but only one was refined with a fixed thermal parameter, the other was kept in the found position with a fixed thermal parameter.

All calculations were performed using the TEXSAN [15] crystallographic software. The figures were drawn with the ORTEP [16] program. Atomic coordinates are listed in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

## Results and Discussion

*Syntheses.*—An intriguing, unanswered question is why compound **1** is formed only in the presence of $Cu^I$. If the $[Cu^I_2Br_6]^{2-}$ solution is replaced by a bromide-ion solution, blue, prismatic crystals precipitate from the bright-blue solution. These crystals have also been analysed by X-ray diffractometry and confirmed to be a new dinuclear compound, $[Cu(ae)(Hae)]_2Br_2$.[17] The structure is formed of dinuclear linear alkoxide-bridged copper(II) units, where the neutral Hae molecule bonds to copper through N in the equatorial plane and through O in the apical position. It is similar to that of $[Cu(ap)(Hap)]_2I_2$ (ap = 3-aminopropanolate),[18] but in the Cu–Hae compound the neutral Hae molecule is co-ordinated as a chelate ligand, whereas in the Cu–Hap compound the neutral Hap molecule bridges two dinuclear units.

The crystal-structure determination of compound **1** was performed on the crystals formed from a solution in which the molar ratio of Cu:Hae was 1:4 and which contained EtOH (2 cm$^3$), total volume 10 cm$^3$. The yield had decreased to 61%, but the size of the crystals was suitable for X-ray analysis. The bromide complex can be synthesized without the formation of the blue powder when the molar ratio of Cu:Hae is 1:2, but then the yield is lowered to 50%. Dilution also decreased the yield.

The synthesis of the corresponding chloride compound **2** was performed similarly, but using $[Cu^I_2Cl_4]^{2-}$. However, no crystals suitable for X-ray diffraction analysis were obtained.

*Fourier-transform IR Spectroscopic Studies.*—The Fourier-transform IR spectra of complexes **1** and **2** in the range 4000–300 cm$^{-1}$ are quite similar and show all the characteristic ligand peaks, with many bands due to O–H and N–H stretching. Complex **1** shows four $\nu$(NH) vibrations, at 3287, 3216, 3127 and 3071 cm$^{-1}$, while five are resolved for the chloride **2**, at 3295, 3233, 3212, 3130 and 3069 cm$^{-1}$. The frequencies are in good agreement with those of related ethylenediamine complexes.[19–21] The bands due to $\nu$(OH) vibrations are found around 3530, 2600 and 3530, 2600 cm$^{-1}$ for the bromide and chloride compounds, respectively. The higher is due to a weak hydrogen bond from H(2) to Br(3) in the bromide and the band at 2600 cm$^{-1}$ is related to a strong hydrogen bond $[H(1)\cdots O(2^{II})]$.

In the region 1600–542 cm$^{-1}$ the spectra show only a few minor differences. A change of intensity in bands at 1260, 1155 and 542 cm$^{-1}$ and an extra band at 812 cm$^{-1}$ in the spectrum of the bromide complex are the main ones. The bands at 1580, 1060, 720, 673 and 656 cm$^{-1}$ in the spectrum of the bromide have shifted to higher frequency and have to be tentatively assigned totally or partly to $\nu$(NH).

The interpretation of the FIR part of the spectra is difficult due to the similar masses of O and N atoms and the fact that M–L vibrations are highly dependent on the co-ordination number of the metal ion and are also coupled to ring deformation vibrations. The assignments are complicated also by the different bonding natures of Cu–O (alcoholate) and Cu–O (alcohol). The $\nu$(Cu–Cl) bands lie at 298, 258 and 230 cm$^{-1}$ and the corresponding $\nu$(Cu–Br) bands are at 183, 166 and 152 cm$^{-1}$.[22] The ratio $\nu$(Cu–Br):$\nu$(Cu–Cl) is 0.64–0.66:1 for the above stretching bands and the values are in good agreement with the literature.[23]

*Crystal Structure of Compound* **1**.—Compound **1** consists of neutral, mononuclear $[Cu^{II}Br_2(Hae)_2]$ molecules and neutral, dinuclear $[Cu^{II}_2(ae)_2Br_2]$ molecules. The asymmetric unit is shown in Fig. 1. The mono- and di-nuclear units are polymerized *via* the $\mu_4$-bromide ion and further contributions from hydrogen bonds as shown in Fig. 2. Important bonding parameters are given in Table 3. In the mononuclear units the copper(II) [Cu(3)] ion is bound to two oxygen atoms and to two nitrogen atoms of the chelated neutral 2-amino ethanol molecules and to two bromide ions forming a 4 + 2 co-ordination sphere. The long bonds are from O(4) and Br(4).

In the alkoxide-bridged dinuclear unit each of the two copper atoms is bound to a bromide ion and to two oxygens and a nitrogen atom. These are the four strong bonds. In addition, Cu(1) has two bromides at distances of 3.287(3) and 3.167(3) Å (symmetry code: I $x, -\frac{1}{2} - y, \frac{1}{2} + z$); one of these is bridging to Cu(2) at 2.945(3) Å, which implies that Cu(1) has a 4 + 2 and Cu(2) a 4 + 1 co-ordination. In the dinuclear unit the atoms O(1), N(1), O(2), Br(1) and O(2), N(2), O(1), Br(2) form four

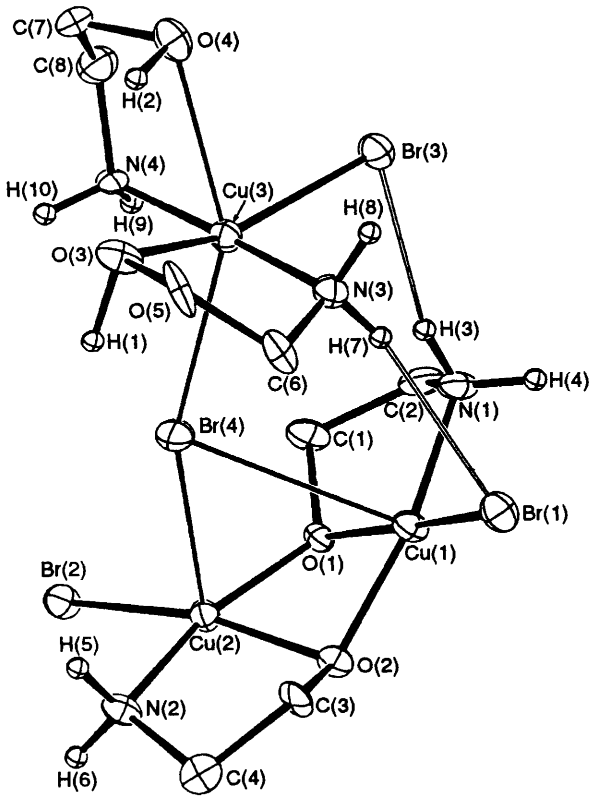

**Fig. 1** The asymmetric unit of $[Cu^{II}Br_2(Hea)_2][Cu^{II}_2(ea)_2Br_2]$. The thermal ellipsoids are drawn at the 30% probability level

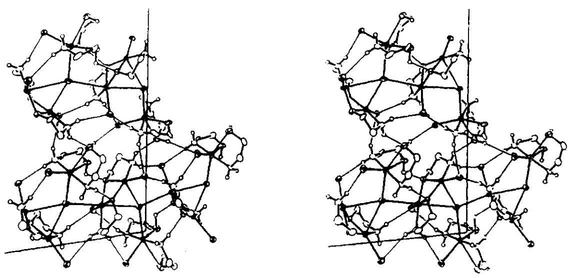

**Fig. 2** Packing diagram showing chain character and hydrogen bonding for $[Cu^{II}Br_2(Hea)_2][Cu^{II}_2(ea)_2Br_2]$. Copper(II) cations are shown as principal ellipses and axes (dashed), bromide ions as ellipsoids with octant shading and oxygen atoms as principal and enveloping ellipses

short bonds to copper. These co-ordination planes are at an angle of 143.7° and are tilted toward Br(4), resulting in a roof-shape conformation with a $CuO_2BrCu$ bridge. The dihedral angle between the planes Cu(1), O(1), O(2) and Cu(2), O(1), O(2) is 139.7°. A somewhat similar roof-shape structure has been reported for the hydroxide-bridged dinuclear compound $[\{Cu(C_6H_{11}NH_2)_2(OH)\}_2][ClO_4]_2$ ($C_6H_{11}NH_2$ = cyclohexylamine).[24] The roof angle [between Cu(1), O(2), O(3) and Cu(2), O(2), O(3) planes] in that compound is 147.5°. The origin for the tilting in **1** clearly is the $\mu_4$-Br ligand, bridging also Cu(1) and Cu(2). Additional stabilization of the lattice structure results from the hydrogen bonding of O(1) to H(9) and the very short O(2) to O(3) contact [2.61(2) Å].

The Cu(1) ··· Cu(2) distance is quite short [2.856(3) Å], as expected for such a roof shape. The other short Cu ··· Cu distances in the trimer are Cu(1) ··· Cu(3) 4.766(3) and Cu(2) ··· Cu(3) 5.551(3) Å. In the chain the following Cu ··· Cu distances are found: Cu(1) ··· Cu(2$^{I}$) 4.873(3), Cu(1) ··· Cu(3$^{I}$) 4.489(3) and Cu(2) ··· Cu(3$^{I}$) 4.843(3) Å.

**Table 1** Crystal data and experimental details for $[Cu^{II}Br_2(Hae)_2]$-$[Cu^{II}_2(ae)_2Br_2]$ **1**

| | |
|---|---|
| Formula | $C_8H_{26}Br_4Cu_3N_4O_4$ |
| *M* | 752.57 |
| Crystal size/mm | 0.050 × 0.050 × 0.150 |
| Crystal description | Green, needle |
| Crystal system | Orthorhombic |
| Space group (no.) | *Pbca* (61) |
| *a*/Å | 15.726(2) |
| *b*/Å | 20.984(3) |
| *c*/Å | 12.637(1) |
| *U*/Å$^3$ | 4169.9(8) |
| *Z* | 8 |
| $D_c$/g cm$^{-3}$ | 2.397 |
| μ(Mo-Kα)/cm$^{-1}$ | 106.56 |
| *F*(000) | 2888 |
| Reflections measured | 4118 |
| Observed reflections [$I > 3.00\sigma(I)$] | 1477 |
| Secondary extinction coefficient* | 9(3) × 10$^{-9}$ |
| *R* | 0.049 |
| *R'* | 0.047 |
| *w* | $1/\sigma^2(F_o)$ |
| Goodness of fit, *S* | 1.23 |
| Maximum, minimum in final difference map/e Å$^{-3}$ | 0.88, −0.82 |

* Ref. 11.

**Table 2** Atomic positional parameters for $[Cu^{II}Br_2(Hae)_2][Cu^{II}_2(ae)_2Br_2]$

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Br(1) | 0.405 1(1) | −0.326 3(1) | 0.428 5(2) |
| Br(2) | 0.134 6(1) | −0.100 1(1) | 0.178 1(2) |
| Br(3) | 0.165 3(1) | −0.451 4(1) | 0.285 8(2) |
| Br(4) | 0.267 4(1) | −0.278 17(8) | 0.152 9(2) |
| Cu(1) | 0.283 3(1) | −0.256 4(1) | 0.409 7(2) |
| Cu(2) | 0.249 1(1) | −0.155 6(1) | 0.264 1(2) |
| Cu(3) | 0.247 0(1) | −0.408 0(1) | 0.132 5(2) |
| O(1) | 0.186 5(7) | −0.198 0(5) | 0.374 7(9) |
| O(2) | 0.344 4(7) | −0.181 0(5) | 0.361(1) |
| O(3) | 0.327 6(8) | −0.411 5(6) | −0.002(1) |
| O(4) | 0.209 8(8) | −0.514 5(6) | 0.022(1) |
| N(1) | 0.193 3(9) | −0.319 5(7) | 0.444(1) |
| N(2) | 0.340 1(9) | −0.118 1(6) | 0.176(1) |
| N(3) | 0.354(1) | −0.428 1(6) | 0.203(1) |
| N(4) | 0.143(1) | −0.387 3(6) | 0.053(1) |
| C(1) | 0.112(1) | −0.235 0(8) | 0.360(2) |
| C(2) | 0.111(1) | −0.285(1) | 0.449(2) |
| C(3) | 0.421(1) | −0.181(1) | 0.300(1) |
| C(4) | 0.421(1) | −0.119 2(9) | 0.238(2) |
| C(5) | 0.409(1) | −0.431(1) | 0.027(2) |
| C(6) | 0.428(1) | −0.411(1) | 0.140(2) |
| C(7) | 0.144(1) | −0.488(1) | −0.048(2) |
| C(8) | 0.093(1) | −0.442(1) | 0.017(2) |

The packing of the structure in compound **1** is stabilized in two dimensions by extensive hydrogen bonding (Table 4). The polymerized chain (along the *c* axis) contains alternately mono- and di-nuclear units, which are held together by bromide ions and hydrogen bonds, and these chains are joined together by hydrogen bonds in the direction of the *b*-axis to form layers. A piece of such a layer is shown in Fig. 2. The layers are held together through van der Waals type forces. Hydrogen bonding of this type is also known to link two $[Cu^{II}(ae)(Hae)]^+$ ions to a dimer in $[Cu^{II}(ae)(Hae)]_2[NO_3]_2$ [9] (two of such bonds). On the other hand a linear hydrogen-bonded trinuclear unit is formed in the compound $[Cu_3(RS\text{-pa})_2(RS\text{-Hpa})_6][CF_3SO_3]_4$ (*RS*-Hpa = *R*,*S*-2-aminopropan-1-ol).[25]

These examples illustrate again that hydrogen bonding plays a crucial role in the solid-state structures of complexes of 1,2-aminoalcohols. The roof shape of the dinuclear unit and the

**Table 3** Bond distances (in Å) and angles (°) with estimated standard deviations in parentheses for [$\mathrm{Cu^{II}Br_2(Hae)_2}$][$\mathrm{Cu^{II}{}_2(ae)_2Br_2}$]

| | | | | | |
|---|---|---|---|---|---|
| Cu(1)–Br(1) | 2.424(3) | Cu(2)–Br(2) | 2.404(3) | Cu(3)–Br(3) | 2.497(3) |
| Cu(1)–Br(4) | 3.287(3) | Cu(2)–Br(4) | 2.945(3) | Cu(3)–Br(4) | 2.754(3) |
| Cu(1)–Br(4$^{I}$) | 3.167(3) | Cu(2)–O(1) | 1.929(11) | Cu(3)–O(3) | 2.126(12) |
| Cu(1)–O(1) | 2.005(11) | Cu(2)–O(2) | 2.009(11) | Cu(3)–O(4) | 2.702(14) |
| Cu(1)–O(2) | 1.950(11) | Cu(2)–N(2) | 1.974(14) | Cu(3)–N(3) | 1.948(15) |
| Cu(1)–N(1) | 1.986(14) | Cu(1) ··· Cu(2) | 2.856(3) | Cu(3)–N(4) | 1.966(14) |
| O(1)–C(1) | 1.42(2) | N(1)–C(2) | 1.50(2) | C(1)–C(2) | 1.54(3) |
| O(2)–C(3) | 1.43(2) | N(2)–C(4) | 1.49(2) | C(3)–C(4) | 1.52(2) |
| O(3)–C(5) | 1.40(2) | N(3)–C(6) | 1.45(2) | C(5)–C(6) | 1.52(3) |
| O(4)–C(7) | 1.47(2) | N(4)–C(8) | 1.46(2) | C(7)–C(8) | 1.49(3) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Cu(2)–Br(4)–Cu(3) | 153.7(1) | Br(1)–Cu(1)–O(2) | 97.6(3) | O(1)–Cu(1)–Br(4) | 79.0(3) | O(2)–Cu(1)–Br(4$^{I}$) | 99.1(4) |
| Br(1)–Cu(1)–Br(4) | 94.2(1) | Br(1)–Cu(1)–N(1) | 98.0(4) | O(1)–Cu(1)–Br(4$^{I}$) | 90.8(3) | N(1)–Cu(1)–Br(4) | 98.0(4) |
| Br(1)–Cu(1)–Br(4$^{I}$) | 96.1(1) | O(1)–Cu(1)–O(2) | 79.0(4) | O(2)–Cu(1)–N(1) | 163.8(5) | N(1)–Cu(1)–Br(4$^{I}$) | 83.4(5) |
| Br(1)–Cu(1)–O(1) | 172.8(3) | O(1)–Cu(1)–N(1) | 85.1(5) | O(2)–Cu(1)–Br(4) | 80.8(4) | Br(4)–Cu(1)–Br(4$^{I}$) | 169.7(1) |
| Br(2)–Cu(2)–Br(4) | 106.3(1) | Br(2)–Cu(2)–N(2) | 95.6(4) | Br(4)–Cu(2)–O(2) | 89.3(3) | O(1)–Cu(2)–N(2) | 164.1(6) |
| Br(2)–Cu(2)–O(1) | 99.7(3) | Br(4)–Cu(2)–O(1) | 89.6(3) | Br(4)–Cu(2)–N(2) | 90.5(4) | O(2)–Cu(2)–N(2) | 84.8(5) |
| Br(2)–Cu(2)–O(2) | 164.4(3) | | | O(1)–Cu(2)–O(2) | 79.3(5) | | |
| Br(3)–Cu(3)–Br(4) | 110.4(1) | Br(3)–Cu(3)–N(4) | 92.8(4) | Br(4)–Cu(3)–N(4) | 85.8(4) | N(3)–Cu(3)–N(4) | 176.4(6) |
| Br(3)–Cu(3)–O(3) | 156.4(3) | Br(4)–Cu(3)–O(3) | 92.3(3) | O(3)–Cu(3)–O(4) | 71.6(4) | O(4)–Cu(3)–N(3) | 104.1(5) |
| Br(3)–Cu(3)–O(4) | 89.3(3) | Br(4)–Cu(3)–O(4) | 153.1(3) | O(3)–Cu(3)–N(3) | 80.9(6) | O(4)–Cu(3)–N(4) | 74.8(5) |
| Br(3)–Cu(3)–N(3) | 90.7(5) | Br(4)–Cu(3)–N(3) | 94.1(4) | O(3)–Cu(3)–N(4) | 95.4(5) | | |
| Cu(1)–O(1)–Cu(2) | 93.1(5) | Cu(3)–O(3)–C(5) | 110(1) | O(1)–C(1)–C(2) | 107(1) | O(3)–C(5)–C(6) | 110(2) |
| Cu(1)–O(2)–Cu(2) | 92.3(4) | Cu(3)–O(4)–C(7) | 98(1) | N(1)–C(2)–C(1) | 107(2) | N(3)–C(6)–C(5) | 106(2) |
| Cu(1)–O(1)–C(1) | 108.7(9) | Cu(1)–N(1)–C(2) | 108(1) | O(2)–C(3)–C(4) | 106(1) | O(4)–C(7)–C(8) | 107(2) |
| Cu(2)–O(1)–C(1) | 125(1) | Cu(2)–N(2)–C(4) | 109(1) | N(2)–C(4)–C(3) | 106(1) | N(4)–C(8)–C(7) | 113(2) |
| Cu(1)–O(2)–C(3) | 126(1) | Cu(3)–N(3)–C(6) | 113(1) | | | | |
| Cu(2)–O(2)–C(3) | 107(1) | Cu(3)–N(4)–C(8) | 116(1) | | | | |

Symmetry relation: I $x, -\frac{1}{2} - y, \frac{1}{2} + z$.

**Table 4** Distances (Å) and angles (°) related to hydrogen-bond formation (standard deviations in parentheses)

| | X–H | H ··· Y | N ··· Y | X–H ··· Y |
|---|---|---|---|---|
| O(3)–H(1) ··· O(2$^{II}$)* | 1.15 | 1.92 | 2.61(2) | 113 |
| O(4)–H(2) ··· Br(3$^{III}$) | 1.2(2) | 2.7(2) | 3.64(1) | 138(10) |
| N(1)–H(3) ··· Br(3) | 0.95 | 2.52 | 3.44(2) | 165 |
| N(1)–H(4) ··· Br(2$^{I}$) | 0.95 | 2.71 | 3.53(2) | 144 |
| N(2)–H(5) ··· Br(1$^{II}$) | 0.95 | 2.59 | 3.49(1) | 158 |
| N(2)–H(6) ··· O(4$^{IV}$) | 0.95 | 2.22 | 3.03(2) | 142 |
| N(3)–H(7) ··· Br(1) | 0.95 | 2.74 | 3.65(1) | 163 |
| N(3)–H(8) ··· Br(2$^{V}$) | 0.95 | 2.72 | 3.63(1) | 160 |
| N(4)–H(9) ··· O(Br) | 0.95 | > 3.14 | | |
| N(4)–H(10) ··· O(1$^{II}$) | 0.95 | 2.01 | 2.96(2) | 172 |

Symmetry relations: I $x, -\frac{1}{2} - y, \frac{1}{2} + z$; II $x, -\frac{1}{2} - y, -\frac{1}{2} + z$; III $\frac{1}{2} - x, -1 - y, -\frac{1}{2} + z$; IV $\frac{1}{2} - x, \frac{1}{2} + y, z$; V $\frac{1}{2} - x, -\frac{1}{2} + y, z$. * Hydrogen atom could not be refined.

general tendency of 1,2-aminoalcohols to form mononuclear structural units with copper(II) ions is clearly related to a tension, which is caused by a five-membered chelate ring to a bis(μ-alkoxo) bridge.

*Magnetic Measurements.*—The magnetic susceptibility for complex **1** recorded between 4 and 300 K shows a Curie–Weiss behaviour, and antiferromagnetic behaviour becomes visible only below 50 K. The obtained magnetic data were fitted to Bleaney–Bowers equation (1), using the Hamiltonian $H = -2J(\hat{S}_A \cdot \hat{S}_B)$.

$$\chi_m = \frac{1}{3}\frac{N\beta^2 g^2}{3kT} S(S+1) + \frac{2}{3}\frac{2N\beta^2 g^2}{kT}\frac{1}{3+\exp(-2J/kT)} + N\alpha \quad (1)$$

In this equation interactions over the bromide and chloride bridges were neglected as were those over the hydrogen-bond network. The first term accounts for the paramagnetic mononuclear Cu, the second for the dinuclear unit. The fractions $\frac{1}{3}$ and $\frac{2}{3}$ are introduced to average the susceptibility. The data was fitted by this formula using the sum of least squares, *R*, as a measure of the goodness of fit. The best fit for the chloride compound was obtained for $J = -6.0$ cm$^{-1}$ and $g = 2.14$ with $R = 4.04 \times 10^{-4}$, and for the bromide $J = -5.3$ cm$^{-1}$ and $g = 2.10$ with $R = 4.58 \times 10^{-4}$.

The small antiferromagnetic interaction can be explained by the roof shape of the dinuclear unit.[26] The sharp dihedral angle prevents any significant overlap of the magnetic orbitals.

Unlike hydroxide-bridged dinuclear copper(II) compounds, no clear correlation has been obtained yet between the dihedral angle of a dinuclear alkoxide-bridged unit and the magnetic exchange in this unit.[27–29] This fact can be attributed to the rather small number of compounds with such a bridge, and to the variety of origins for the bridging oxygen. There is, however, the possibility that a correlation between the dihedral angle and the magnetic exchange, if ever found, does not apply to this system due to the additional halide bridge.

## Conclusion

The magnetic behaviour of an unusual, novel trinuclear copper(II) compound has been correlated with the crystal structure, which incorporates mono- and di-meric magnetic units. The structure appears to be largely determined by hydrogen-bonding effects, both intra- and inter-molecularly.

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