PREPARATION AND CHARACTERIZATION OF TRIPLY-
BRIDGED DINUCLEAR COPPER(II) COMPLEXES CONTAINING
THE \([\text{Cu}_2(\mu-OH)(\mu-X)(\mu-OAc)]^+\) CORE \((X = \text{Cl}, \text{Br})\), AND THE
CRYSTAL STRUCTURE OF \([\text{Cu}_2(\text{OH})\text{Cl}(\text{OAc})(\text{bpy})_2](\text{ClO}_4)\cdot\text{H}_2\text{O}\)

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Abstract—Synthetic procedures are described that allow access to complexes containing the
cation \([\text{Cu}_2(\mu-OH)(\mu-X)(\mu-O,CMe)(\text{bpy})_2]^+(X = \text{Cl}, \text{Br})\). Reaction mixtures consisting of
\(\text{CuX}_2\), \(\text{bpy}\), \(\text{OH}^-\), \(\text{MeC0}_2^-\) and \(\text{ClO}_4^-\) \((X = \text{Cl}^-)\) in \(\text{MeOH}/\text{H}_2\text{O}\) give blue solutions from
which the products \([\text{Cu}_2(\text{OH})\text{Cl}(\text{O,CMe})(\text{bpy})_2](\text{ClO}_4)\cdot\text{H}_2\text{O}\) (1) and \([\text{Cu}_2(\text{OH})\text{Br}(\text{O,CMe})(\text{bpy})_2]\text{Br}\cdot\text{H}_2\text{O}\) (4) can be obtained in good yield. Complex 1 may also be prepared
from the known complexes \([\text{Cu}_2(\text{OH})(\text{H}_2\text{O})(\text{O,CMe})(\text{bpy})_2](\text{ClO}_4)_2\) (2) and \(\text{Cu}_2(\text{OH})(\text{bpy})_2\)
\((\text{ClO}_4)_2\) (3). Complex 1 crystallizes in monoclinic space group \(P2_1/n\) with \((a = 8.434(1), b = 16.074(2), c = 9.430(1) \text{ Å, } \beta = 98.09(1)^\circ, Z = 2 and V = 1265.83 \text{ Å}^3\). The
structure was solved by direct methods (MULTAN) and refined to values of conventional
indices \(R(R_w)\) of 3.38 (3.54)% using 1499 unique reflections with \(F > 2.33\sigma(F)\). The structure
of the cation consists of a triply-bridged pair of five-coordinate copper(II) atoms. One of
the bridging ligands is a \(\text{sym,sym}^1: \eta^1\):\(\mu_2\) acetate group, the others being the \(\text{Cl}^-\) and \(\text{OH}^-\)
ions; a terminal bpy molecule completes five-ordination at each metal. The Cu···Cu
separation is 2.957(1) Å. The metal coordination geometry is best described as distorted
square-pyramidal with the \(\text{Cl}^-\) ligand occupying the apical site for each metal. The oxygen
atom of the water molecule is hydrogen-bonded to the \(\text{OH}^-\) hydrogen. Recrystallization
of 1 from warm water yields 3 in 20% yield; addition of \(\text{NaClO}_4\) to the solution increases
the yield to 40%. Complex 1 in warm water containing one equiv. of \(\text{NaClO}_4\) and one
equiv. of \(\text{NaOH}\) also gives 3 (yield 73%). The thermal decomposition, room temperature
\(\mu_{\text{eff}}\) values, and electronic and IR spectra of 1 and 4 are discussed in terms of the nature of
bonding and structure of 1.

The bridged dinuclear structure \(\text{M}_2(\text{O}_2\text{CR})_4\text{L}_2\), first
documented in 1953 for copper(II) acetate mono-
hydrate,\(^1\) is ubiquitous in modern coordination
chemistry. It is found not only for carboxylates of
many transition elements,\(^2\) but also for dimers containing a wide variety of other triatomic bridg-
ing ligands.\(^3\) This structural type is associated with
a spectrum of metal–metal interactions\(^4\) ranging
from no interactions, weak spin-pairing in the copper(II)
carboxylates, various orders of metal–metal bonding, to the “super-short” metal–metal

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reactions between 3d metal carboxylates and N,N- and O,N-bidentate ligands. Most of our efforts have been concentrated in manganese but we recently extended our efforts to copper and have found that the reactions of \( \text{Cu}_2(O_2CMe)_4(H_2O)_2 \) with chelating 2,2'-bipyridine (bpy) lead to a wide variety of products with bridging units not previously observed in \( \text{Cu}^{++} \) chemistry. In extending the above work, attempts have been made to prepare a trinuclear complex with the \([\text{Cu}_3(\mu_3-\text{OR})(\mu-O_2C\text{CR})_3]^{++}\) core, as this structural unit has not yet been identified in copper(II) chemistry. Initial attempts have instead led to interesting dinuclear complexes containing three bridging ligands; the properties of these species are described in this report.

**EXPERIMENTAL**

**Starting materials**

All manipulations were performed under aerobic conditions using materials as received; water was distilled in-house. The complex \( [\text{Cu}_2(OH)(H_2O)(O_2CMe)(bpy)]_3(\text{ClO}_4)_2 \) (2) was available from previous work. \( \text{Cu}_2(OH)(bpy)_2(\text{ClO}_4)_2 \) was prepared as described. Caution: Perchlorate salts are potentially explosive. Although no detonation tendencies have been observed in our work, caution is advised and handling of only small quantities is recommended.

**Compound preparation**

1. **Preparation of [Cu_2(OH)Cl(O_2CMe)(bpy)]_2 (ClO_4)_2 \cdot H_2O (1).** Method A. To a stirred pale green solution of CuCl_2 (0.67 g, 5.0 mmol) in MeOH (25 cm³) was added bpy (0.78 g, 5.0 mmol) in small portions to give a green precipitate of the known compound CuCl_2(bpy). This was collected by filtration and dissolved in H_2O (70 cm³). The resulting blue solution was stirred while an aqueous solution (10 cm³) containing NaOH (0.07 g, 1.7 mmol), NaO_2CMe (0.41 g, 5.0 mmol) and NaClO_4 (0.41 g, 3.3 mmol) was added. The solution soon began to deposit violet–blue microcrystals. The flask was stored at ambient temperature overnight, and the precipitate was collected by filtration, washed with H_2O and Et_2O and dried in vacuo; yield, 0.82 g (49% based on available copper). Found: C, 39.4; H, 3.2; N, 8.1; Cl, 10.5. Calcd. for C_{22}H_{22}N_{4}O_{8}Cl_2Cu_4: C, 39.5; H, 3.3; N, 8.4; Cl, 10.6%. IR spectrum (Nujol mull, cm⁻¹): 3450mb, 3365mb, 1601s, 1576m, 1551sb, 1445sh, 1319m, 1252m, 1171m, 1157m, 1082vsb, 1055m, 1019m, 978w, 932w, 918w, 891w, 810w, 768vs, 731s, 663m, 650sh, 623s, 545w, 488m, 459m, 417m. Magnetic moment per copper(II) (Faraday method): 2.03 \( \mu_B \) at 26°C. Solid-state (diffuse reflectance) electronic spectrum: \( \lambda_{\text{max}} \) nm; 3200, 3500, 2900, 2500, 2200, 1800, 1500. Electronic spectrum in MeCN: \( \lambda_{\text{max}} \) nm (ε_M/Cu₂, L mol⁻¹ cm⁻¹); 685 (165). Using 0.67 g (5.0 mmol) of CuCl_2, 0.78 g (5.0 mmol) of bpy, 0.10 g (2.5 mmol) of NaOH, 0.21 g (2.5 mmol) of NaO_2CMe and 0.31 g (2.5 mmol) of NaClO_4, the above synthetic procedure again yielded complex 1; yield, 1.05 g (63%).

**Method B.** A slurry of [Cu_2(OH)(H_2O)(O_2CMe)(bpy)]_3(\text{ClO}_4)_2 (2) (0.25 g, 0.34 mmol) in H_2O (10 cm³) was treated with solid NaCl (0.04 g, 0.68 mmol). No noticeable colour change occurred. The reaction mixture was stirred for 1 h at 50°C. After cooling to room temperature, the blue solid was collected by filtration, washed with H_2O and Et_2O, and dried in vacuo; yield, 0.16 g (70%). The product had IR and electronic spectra identical with those detailed under method A.

**Method C.** To a slurry of Cu_2(OH)_2(bpy)_2(\text{ClO}_4)_2 (3) (0.67 g, 1.0 mmol) in H_2O (10 cm³) was added glacial MeCOOH (0.06 cm³, 1.0 mmol). A noticeable colour change from lavender to blue occurred. To this were added solid NaCl (0.08 g, 1.4 mmol) and MeOH (3 cm³). The reaction mixture was stirred for 1 h at 40°C. The resulting blue solid was collected by filtration, washed with H_2O and Et_2O, and dried in vacuo; yield, 0.56 g (84%). The product was identical on spectroscopic examination with 1 prepared by method A.

2. **Preparation of [Cu_2(OH)Br(O_2CMe)(bpy)]_2 Br \cdot H_2O (4).** To a stirred dark brown solution of CuBr_2 (1.12 g, 5.0 mmol) in MeOH (25 cm³) was slowly added solid bpy (0.78 g, 5.0 mmol) in small portions to give a pale brown precipitate of CuBr_2(bpy). This was collected by filtration and dissolved in H_2O (105 cm³). The resulting blue solution was stirred while an aqueous solution (10 cm³) containing NaOH (0.10 g, 2.5 mmol) and NaO_2CMe \cdot 3H_2O (0.34 g, 2.5 mmol) was added. The dark blue solution was left at ambient temperature. The pale blue, microcrystalline powder that formed was collected by filtration, washed with H_2O and Et_2O (not added to the filtrate) and dried in vacuo over silica gel; yield, 0.65 g (38%). Overnight storage of the filtrate at 4°C yielded a second crop of microcrystals of 4, which were isolated as above; overall yield ca 60%. Found: Cu, 18.6; Br, 23.3; H_2O, 2.5. Calcd. for C_{22}H_{22}N_{4}O_{8}Br_2Cu_2: Cu, 18.3; Br, 23.0; H_2O, 2.6%. IR spectrum (KBr pellet, cm⁻¹): 3440mb, 2265sb, 1607m, 1597vs, 1558m, 1487m, 1467m, 1438s, 1430sh, 1319m, 1312m, 1250m, 1169m, 1153m, 1098m, 1069w, 1057w.
1041 w, 1022 s, 1010 s, 942 w, 907 sh, 890 m, 802 w, 764 vs, 728 s, 652 w, 575 mb, 484 mb, 460 m, 413 m.

Magnetic moment per copper(I) (Faraday method): 2.16 \( \mu_B \) at 23°C. Solid-state (diffuse reflectance) electronic spectrum: \( \lambda_{\text{max}} \) nm: 342, 375, 665, 705 sh. Attempts to isolate the ClO$_4^-$ or PF$_6^-$ salt of \([\text{Cu}_2(\text{OH})\text{Br(O,CMe)(bpy)_2}][\text{Br} \cdot \text{H}_2\text{O} \quad (Y = \text{ClO}_4 \text{ or PF}_6)\) as deduced from analytical data and IR spectroscopy.

(3) Conversion of complex 1 to complex 3

(i) A slurry of complex 1 (0.30 g, 0.45 mmol) in H$_2$O (20 cm$^3$) was stirred at 50°C for 45 min. A colour change from blue to lavender occurred. After cooling the mixture to room temperature, the solid was collected by filtration, washed with H$_2$O and Et$_2$O, and dried in vacuo; yield, 0.06 g (20% based on copper). The identity of the product was deduced by IR spectral comparison with authentic material. An identical procedure but with added NaClO$_4$ (0.06 g, 0.50 mmol) leads to an increased yield of 3, 0.12 g (40%).

(ii) To a slurry of complex 1 (0.30 g, 0.45 mmol) in H$_2$O (20 cm$^3$) was added solid NaClO$_4$ (0.06 g, 0.50 mmol) and solid NaOH (0.18 g, 0.45 mmol) in H$_2$O (10 cm$^3$). An immediate colour change from blue to lavender occurred. The reaction mixture was stirred for 15 min at 50–60°C and the resulting solid was collected by filtration, washed with H$_2$O and Et$_2$O, and dried in vacuo; yield, 0.22 g (73%). The product had an IR spectrum identical with that of compound 3.

X-ray crystallographic studies

Crystals suitable for crystallography were grown by careful layering of a green solution of 1 (0.2 g) in DMF (15 cm$^3$) with Et$_2$O (25 cm$^3$) at room temperature. Data were collected on a Picker four-circle diffractometer at −175°C; details of the diffractometry, low-temperature facilities and computational procedures employed by the Molecular Structure Centre are available elsewhere.$^{20}$ Data collection parameters are summarized in Table 1.

The structure was solved by a combination of direct methods (MULTAN) and Fourier techniques and refined by full-matrix least-squares. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with symmetry and systematic absences corresponding to a

<table>
<thead>
<tr>
<th>Formula</th>
<th>C$<em>2$H$</em>{32}$N$_4$O$_5$Cl$_2$Cu$_2$</th>
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<tbody>
<tr>
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<td>P2$_1$/n</td>
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<tr>
<td>( a ) (Å)</td>
<td>8.434(1)</td>
</tr>
<tr>
<td>( b ) (Å)</td>
<td>16.074(2)</td>
</tr>
<tr>
<td>( c ) (Å)</td>
<td>9.430(1)</td>
</tr>
<tr>
<td>( \beta ) (°)</td>
<td>98.09(1)</td>
</tr>
<tr>
<td>( V ) (Å$^3$)</td>
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<tr>
<td>( Z )</td>
<td>2</td>
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<tr>
<td>( \rho_{calc} ) (g cm$^{-3}$)</td>
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<td>Absorption coefficient (cm$^{-1}$)</td>
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<td>Scan speed (deg min$^{-1}$)</td>
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<tr>
<td>Scan width (°)</td>
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<tr>
<td>Take-off angle (°)</td>
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<td>Data collected</td>
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<td>Unique data</td>
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<tr>
<td>Data with ( F &gt; 2.33\sigma(F) )</td>
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<tr>
<td>( R_e )</td>
<td>0.0354</td>
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<tr>
<td>Goodness of fit for last cycle</td>
<td>1.063</td>
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</table>
monoclinic space group, \( P2_1 \) or \( P2_1/m \). Subsequent solution and refinement of the structure confirmed the centrosymmetric choice, \( P2_1/m \). All non-hydrogen atoms were readily located and refined with anisotropic thermal parameters. All hydrogen atoms were clearly visible in a subsequent difference Fourier map; these atoms were included in the final cycles and refined isotropically. The final difference Fourier map was essentially featureless, the largest peak being 0.45 e Å\(^{-3} \). The two largest peaks were located in the vicinity of the perchlorate ion. No absorption correction was deemed necessary. Final discrepancy indices \( R \) and \( R_w \) are included in Table 1.

**Physical measurements**

IR spectra were recorded as Nujol mulls between CsI plates or KBr discs using a Nicolet 510P Fourier transform spectrometer or a Perkin Elmer Model 283 spectrophotometer. Solid-state (diffuse reflectance, 890–330 nm) and solution (800–350 nm) electronic spectra were recorded on Varian 634 and Hewlett-Packard 4450A instruments, respectively. Magnetic susceptibilities were measured at room temperature by the Faraday method with a Cahn–Ventron RM-2 balance standardized with HgCo (SCN). The molar susceptibilities were corrected for the diamagnetism of the constituent atoms using Pascal’s constants. 1G/10G data were obtained with a DuPont R90 instrument equipped with a 951 thermogravimetric analyser in a nitrogen gas flow for the diamagnetism of the constituent atoms using Pascal’s constants. 1G/10G data were obtained with a DuPont R90 instrument equipped with a 951 thermogravimetric analyser in a nitrogen gas flow (50 cm\(^3\) min\(^{-1} \)); sample weights of 5–10 mg and heating rates of 1 and 5°C min\(^{-1} \) were used.

**Analytical procedures**

Elemental analyses for 1 were performed at the Microanalytical Laboratory, Department of Chemistry, Manchester University, England. For the bromide determination, samples of 4 were decomposed in 2 M HNO\(_3 \); the total bromides were determined potentiometrically with a standard 0.1 M AgNO\(_3 \) solution, using a Corning–Eel Model 12 potentiometer with calomel and sulphide-selective electrodes.\(^{21} \) Copper(II) was estimated gravimetrically as copper(I1) quinaldate.\(^{22} \) The amount of water in 4 was determined from the TG pattern.

**RESULTS AND DISCUSSION**

**Syntheses**

In our development of Cu\(^{II}/\text{RCO}_2^-/\text{bpy} \) chemistry,\(^{17} \) we had employed Cu\(_2\)(O\(_2\)CMe)\(_4\) (H\(_2\)O)\(_2\) and Cu:bpy ratios of 1:1 (a 1:2 ratio is known to produce mononuclear [Cu(O\(_2\)CMe)\(_2\)(bpy)]\(^2+ \) complexes);\(^{23} \) all the synthetic methods used led to dinuclear complexes.\(^{17} \) In extending this chemistry, we considered it of interest to try to prepare trinuclear complexes. These are far less common than are dinuclear copper(II) systems and limited to two structural types,\(^{24} \) i.e. linear and triangular; they also present interesting structural and magnetic features.\(^{24–30} \) Recently, we tried to prepare a linear trimmer of the formula Cu\(_2\)(O\(_2\)CMe)\(_5\)(bpy)\(_2\), like the Mn\(^{II} \) analogue,\(^{28} \) employing a Cu\(^{II} \) bpy ratio of 1.5:1; however, the reaction instead led to [Cu\(_2\)(O\(_2\)CMe)\(_4\)(bpy)]\(_2\)·2H\(_2\)O and [Cu\(_4\)(O\(_2\)CMe)\(_3\)(bpy)]\(_4\).\(^{17} \) In this work, the influence of added OH\(^-\) (C\(_\text{u}^+:\text{OH}^- = 3 : 1 \) was investigated, wondering whether a product with a [Cu\(_3\)(\mu\(_3\)-OH)(\mu\(-\text{O}_2\text{CMe})\(_3\)]\(^2+ \) core might be attainable. An MeOH/H\(_2\)O (ca 1:3) reaction mixture containing CuCl\(_2\), bpy, NaOH, NaO\(_2\)CMe and NaClO\(_4\) in a 3:3:1:3:2 molar ratio gave a blue solution from which the dinuclear complex 1 was isolated in good yield. The crystal structure of 1 identified the complex to be triply-bridged [Cu\(_2\)(O\(_2\)CMe)\(_5\)(bpy)]\(_2\)(ClO\(_4\))\(_2\)·H\(_2\)O. Whether Cu\(_3\) species are present in the reaction solution is unclear and difficult to ascertain given the presence of paramagnetism. Nevertheless, as 1 is the first triply-bridged dinuclear copper(II) complex containing three different anionic bridging ligands, we decided to pursue the study of this new family of complexes further and a higher yield of 1 was subsequently obtained by changing the Cu:OH\(^-\) ratio from 3:1 to 2:1 [eq. (1)].

\[
2\text{CuCl}_2 + 2\text{bpy} + \text{OH}^- + \text{MeCO}_2^- + \text{ClO}_4^- \xrightarrow{\text{MeOH/H}_2\text{O}} [\text{Cu}_2(\text{OH})\text{Cl}(\text{O}_2\text{CMe})(\text{bpy})_2]\text{(ClO}_4\text{)}_2\cdot\text{H}_2\text{O} + 3\text{Cl}^- \\
\text{(1)}
\]

Complex 1 may also be prepared from the complexes [Cu\(_2\)(OH)(H\(_2\)O)(O\(_2\)CMe)(bpy)\(_2\)]\(_2\) (2) and Cu\(_3\)(OH)(2(bpy))\(_2\)(ClO\(_4\))\(_2\) (3). Reaction of 2 with an excess of NaCl in H\(_2\)O at 50°C gave a clean and high-yield conversion to 1, emphasizing the lability to substitution of the weakly-bound, bridging aqua group.\(^{17} \) This reaction is summarized in eq. (2).

\[
[\text{Cu}_3(\text{OH})(\text{H}_2\text{O})(\text{O}_2\text{CMe})(\text{bpy})_2]\text{(ClO}_4\text{)}_2 + \text{Cl}^- \xrightarrow{\text{H}_2\text{O}} [\text{Cu}_3(\text{OH})(\text{Cl}(\text{O}_2\text{CMe})(\text{bpy})_2)]\text{(ClO}_4\text{)}_2\cdot\text{H}_2\text{O} + \text{ClO}_4^- \\
\text{(2)}
\]

In addition, treatment of 3 with one equiv. of acetic acid in H\(_2\)O at 40°C, followed by addition of a slight excess of NaCl led to clean, high-yield
Copper(I) complexes containing $[\text{Cu}_2(\mu-\text{OH})(\mu-X)(\mu-\text{OAc})]^+$

isolation of 1 [eq. (3)], presumably by protonation

$$\text{Cu}_2(\text{OH})_2(bpy)_2(\text{ClO}_4)_2 + \text{MeCO}_2\text{H} + \text{Cl}^- \rightarrow \text{H}_2\text{O/MeOH}$$

$$[\text{Cu}_2(\text{OH})\text{Cl}(@\text{O,CMe})(bpy)_2](\text{ClO}_4) \cdot \text{H}_2\text{O}$$

of an OH⁻ bridge followed by binding of the generated MeCO₂⁻ and substitution of the bridging aqua ligand by the chloro group. This transformation of 3 to 1 is reversible. Recrystallization of 1 from warm water (~50°C) yielded 3 in 20% yield based on copper; the yield is ClO₄⁻ limited, however, and addition of NaClO₄ to the mixture [eq. (4)] increases the yield of isolated 3

$$2[\text{Cu}_2(\text{OH})\text{Cl}(\text{O,CMe})(bpy)_2](\text{ClO}_4) \cdot \text{H}_2\text{O}$$

$$+ 2\text{NaClO}_4 \rightarrow 2\text{Cu}_2(\text{OH})_2(bpy)_2(\text{ClO}_4)_2$$

$$+ 2\text{MeCO}_2\text{H} + 2\text{NaCl}$$

(4)

to 40%. Complex 1 in H₂O containing NaClO₄ (one equiv.) and NaOH (one equiv.) also gives 3 (73% isolated yield) at 50–60°C.

The access to $[\text{Cu}_2(\mu-\text{OH})(\mu-\text{Cl})(\mu-\text{O,CMe})]^+$ species from CuCl₂ suggested that the reaction system might be capable of extension to other CuₙX₂ salts ($X =$ halide). The above procedure but with CuBr₂ was found to successfully yield the $[\text{Cu}_2(\mu-\text{OH})(\mu-\text{Br})(\mu-\text{O,CMe})]^+$ species in good overall yield [eq. (5)].

$$2\text{CuBr}_2 + 2\text{bpy} + \text{OH}^- + \text{MeCO}_2^- \rightarrow \text{MeOH/H}_2\text{O}$$

$$[\text{Cu}_2(\text{OH})\text{Br}(\text{O,CMe})(bpy)_2]\cdot \text{H}_2\text{O} + 2\text{Br}^-$$

(5)

Efforts to isolate the ClO₄⁻ or PF₆⁻ salt of $[\text{Cu}_2(\text{OH})\text{Br}(\text{O,CMe})(bpy)_2]^+$ led to mixtures of 4 and $[\text{Cu}_2(\text{OH})\text{Br}(\text{O,CMe})(bpy)_2]\text{Y} \cdot \text{H}_2\text{O}$ ($Y =$ ClO₄⁻ or PF₆⁻), due to the low solubility of the bromide salt.

**Description of structure**

An ORTEP projection of the cation of complex 1 is given in Fig. 1. An ORTEP plot of the inner coordination sphere about the Cu₂ core for the same complex is depicted in Fig. 2. The important structural parameters are listed in Table 2.

The structure of 1 consists of a dinuclear triply-bridged cation lying on a crystallographic mirror plane, a molecule of water of crystallization and a well-separated perchlorate anion; the latter will not be further discussed. The cations are well separated from each other. The acetate group is in the familiar bidentate syn,syn $\eta^1: \eta^1$ : $\mu$-, bridging mode; a terminal bpy molecule completes five-coordination at each metal atom. The Cu····Cu separation in 1 is noticeably shorter than in dinuclear triply-bridged copper(II) complexes containing three or two acetato bridges (2.96 vs 3.15–3.40 Å), presumably due to the greater number of mono-atomic bridges.

The metal coordination geometry may be described as distorted square-pyramidal with the chloro ligand occupying the apical position at each metal; this is particularly emphasized by Fig. 2. Analysis of the shape-determining angles using the approach of Addison et al., 31 yields a value for trigonality index, $\tau$, of 0.40 for the copper ($\tau = 0$ and 1.09 for square-pyramidal and trigonal bipyramidal geometry, respectively). Thus, the geometry about Cu(1) and Cu(1') is significantly distorted,
Table 2. Selected bond distances (Å) and angles (deg) for complex 1

<table>
<thead>
<tr>
<th>Distances</th>
<th>Angles</th>
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<td>2.957(1)</td>
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<td>Cu(1)−Cl(2)</td>
<td>Cu(1)−O(4)</td>
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<td>2.557(1)</td>
<td>1.971(3)</td>
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<td>Cu(1)−N(7)</td>
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<td>2.012(3)</td>
<td>0.817(7)</td>
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<td>O(23)···H(1)</td>
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<tr>
<td>1.998(4)</td>
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<td>Cu(1)−Cl(2)−Cu(1')</td>
<td>N(18)−Cu(1)−O(4)</td>
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<td>70.6(1)</td>
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<td>100.7(2)</td>
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<tr>
<td>Cl(2)−Cu(1)−N(7)</td>
<td>O(4)−Cu(1)−O(3)</td>
</tr>
<tr>
<td>102.8(1)</td>
<td>94.2(2)</td>
</tr>
<tr>
<td>Cl(2)−Cu(1)−N(18)</td>
<td>Cu(1)−O(4)−Cl(2)</td>
</tr>
<tr>
<td>96.4(1)</td>
<td>54.7(1)</td>
</tr>
<tr>
<td>Cl(2)−Cu(1)−O(4)</td>
<td>Cu(1)−Cu(1')−N(18)</td>
</tr>
<tr>
<td>105.0(1)</td>
<td>144.0(1)</td>
</tr>
<tr>
<td>Cl(2)−Cu(1)−O(3)</td>
<td>Cu(1)−Cu(1)−N(7)</td>
</tr>
<tr>
<td>85.0(1)</td>
<td>123.0(1)</td>
</tr>
<tr>
<td>N(7)−Cu(1)−N(18)</td>
<td>Cu(1)−Cu(1)−O(4)</td>
</tr>
<tr>
<td>80.6(2)</td>
<td>79.7(1)</td>
</tr>
<tr>
<td>N(7)−Cu(1)−O(4)</td>
<td>O(23)···H(1)−O(3)</td>
</tr>
<tr>
<td>151.4(1)</td>
<td>171.0(6)</td>
</tr>
<tr>
<td>N(7)−Cu(1)−O(3)</td>
<td>94.9(2)</td>
</tr>
</tbody>
</table>

and the four atoms N(7), N(18), O(4) and O(3) defining the basal plane deviate from that plane by an average of 0.22 Å [maximum deviation by N(18), 0.233 Å]; Cu(1) lies 0.245 Å out of the least-squares basal plane towards Cl(2). The dihedral angle between the two CuN₂O₃ planes is 60.6°.

The bond lengths to the bridging hydroxo and acetate oxygens and to the two bpy nitrogen atoms are typical. The distance Cu(1)−Cl(2) [2.557(1) Å] and the acute angle Cu(1)−Cl(2)−Cu(1') [70.6(1)°] are very similar to those observed in other dinuclear, square-pyramidal copper(I) complexes sharing a common p₂-C₃- apex; the bond from the copper to the bridging apical chloro ligand is longer than that to bridging basal chloro ligands (~2.3 Å).

The oxygen atom O(23) of the water molecule hydrogen-bonds to the OH⁻ hydrogen H(1) [O(3)−H(1), 0.817(7) Å; H(1)···O(23), 2.027(7) Å; O(23)···H(1)−O(3), 171.6°]. No evidence of inter-cation hydrogen bonds was found.

Complex 1 represents the first structurally characterized example of a triply-bridged, dinuclear copper(I) complex containing three different anionic bridging ligands. Another triply-bridged Cu₂ complex is somewhat structurally related to compound 1 in that it has three different anionic bridging ligands: [Cu₂(OH)(ClO₄)L]⁺[35] [L = the monoanion of 2,6-bis(N-(2-pyridylmethyl)formidoyl)-4-methylphenol]; in this complex, however, the third bridging ligand is provided by the aryloxide oxygen of the pentadentate binucleating L.

Some other triply-bridged Cu₂ complexes with three different bridging ligands (two anionic, one neutral) should be mentioned at this point: (i) [Cu₂(μ-OH)(μ-X)LX₃] [X = Cl, Br; L = bi-nucleating phthiazuline or pyridazine ligands[36] and 2,7-bis(2-pyridyl)-1,8-naphthyridine[32] are also the only other examples of dinuclear copper(II) complexes bridged by both equatorial OH⁻ and apical X⁻. (ii) The MeOH inclusion compound [Cu₂(μ-OH)(μ-O₂CMe)(L−L)](ClO₄)₂·MeOH,[37] (L−L = a binucleating tetradeinate hexaimidazole ligand) and complex 2 are also the only other examples of Cu₂ complexes bridged by one OH⁻ and one MeCO₂⁻.

The structure of the cation of 1 shows some similarity to that of [Cu₂(OH)(H₂O)(O₂CMe)(bpy)]²⁺,[17] (2); obviously, the replacement of p₂-H₂O by p₂-Cl⁻ at the common apical position has little structural effect. However, the cations of 2 form infinite chains as a result of hydrogen-bonding interactions with the ClO₄⁻ counter-ions,[17] while 1 is an isolated dinuclear species with only an intramolecular hydrogen bond.

**Thermal decomposition of 1 and 4, IR and electronic spectroscopy**

The thermal decomposition of 1 and 4 was studied using TG/DTG techniques. We first comment on the dehydration process. The TG curve of 1 shows a one-step, first mass loss between 75 and 100°C, which corresponds exactly to the release of the water content (Found: 2.7. Calc.: 2.7%). The low temperature of H₂O loss shows that this is not coordinated. A TG plateau is present from 105 to 202°C. The anhydrous complex decomposes in four steps, as revealed by the appearance of four DTG maxima, between 205 and 280°C and in a slower process between 280 and 670°C. The absence of TG plateaux during decomposition indicates that stable intermediates are not formed. The final, thermally-
stable residue is CuO (Found 23.4. Calc. 23.8%). The thermal decomposition of 4 is completely analogous.

The room temperature $\mu_{ee}$ values of 1 and 4 would appear to exclude strong antiferromagnetic coupling, but it is difficult to rule out weak antiferromagnetic interactions. In fact, both complexes are likely either weakly antiferromagnetically- or ferromagnetically-coupled, due to the "non-complementarity" of MeCO$_2$- and OH$^-$ orbitals with $d_{x^2-y^2}$ magnetic orbitals. It is interesting to note that all Cu$^{II}$ systems bridged by one RCO$_2^-$ and one RO$^-$ (R = H, alkyl) are known to be weakly antiferromagnetic or ferromagnetic.$^{17,37-39}$

Complexes 1 and 4 possess very similar solid-state electronic spectra, supporting similar structures for their cations. Both exhibit two LMCT transitions$^{40}$ in the 375–340 nm range and d-d transitions at lower energies. The d-d frequencies are fairly typical of distorted square-pyramidal structures. $^{34,40}$ The d-d spectrum of 1 in dry MeCN is different from the solid-state spectrum, indicating structural changes upon dissolution and/or cation-solvent interactions.

In the IR spectra, complexes 1 and 4 exhibit bands at $\sim$3450 and 3365 cm$^{-1}$, assigned to $\nu$(OH$^-$) and $\nu$(H$_2$O), respectively; their broadness is different from the solid-state spectrum, indicating structural changes upon dissolution and/or cation-solvent interactions.

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REFERENCES