

PREPARATION AND CHARACTERIZATION OF TRIPLY-BRIDGED DINUCLEAR COPPER(II) COMPLEXES CONTAINING THE $[\text{Cu}_2(\mu\text{-OH})(\mu\text{-X})(\mu\text{-OAc})]^+$ CORE (X = Cl, 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 $[\text{Cu}_2(\mu\text{-OH})(\mu\text{-X})(\mu\text{-O}_2\text{CMe})(\text{bpy})_2]^+$ (X = Cl, Br). Reaction mixtures consisting of CuX_2 , bpy, OH^- , MeCO_2^- and ClO_4^- (X = Cl^-) in $\text{MeOH}/\text{H}_2\text{O}$ give blue solutions from which the products $[\text{Cu}_2(\text{OH})\text{Cl}(\text{O}_2\text{CMe})(\text{bpy})_2](\text{ClO}_4) \cdot \text{H}_2\text{O}$ (**1**) and $[\text{Cu}_2(\text{OH})\text{Br}(\text{O}_2\text{CMe})(\text{bpy})_2]\text{Br} \cdot \text{H}_2\text{O}$ (**4**) can be obtained in good yield. Complex **1** may also be prepared from the known complexes $[\text{Cu}_2(\text{OH})(\text{H}_2\text{O})(\text{O}_2\text{CMe})(\text{bpy})_2](\text{ClO}_4)_2$ (**2**) and $\text{Cu}_2(\text{OH})_2(\text{bpy})_2(\text{ClO}_4)_2$ (**3**). Complex **1** crystallizes in monoclinic space group $P2_1/n$ with (at -175°C) $a = 8.434(1)$, $b = 16.074(2)$, $c = 9.430(1)$ Å, $\beta = 98.09(1)^\circ$, $Z = 2$ and $V = 1265.83$ Å³. 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 *syn, syn* $\eta^1 : \eta^1 : \mu_2$ acetate group, the others being the Cl^- and OH^- ions; a terminal bpy molecule completes five-coordination at each metal. The $\text{Cu} \cdots \text{Cu}$ separation is 2.957(1) Å. The metal coordination geometry is best described as distorted square-pyramidal with the Cl^- ligand occupying the apical site for each metal. The oxygen atom of the water molecule is hydrogen-bonded to the OH^- hydrogen. Recrystallization of **1** from warm water yields **3** in 20% yield; addition of NaClO_4 to the solution increases the yield to 40%. Complex **1** in warm water containing one equiv. of NaClO_4 and one equiv. of NaOH also gives **3** (yield 73%). The thermal decomposition, room temperature μ_{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 monohydrate,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 bridging ligands.³ This structural type is associated with a spectrum of metal–metal interactions⁴ ranging from no interactions, weak spin-pairing in the copper(II) carboxylates, various orders of metal–metal bonding, to the “super-short” metal–metal

bonds. The axial groups are normally monodentate ligands but they may represent inter-dimer association into a polymeric structure⁵ or may be absent.⁶

Only a few attempts have been made to incorporate chelating ligands (mainly tridentate), instead of monodentate ones into the $\text{Cu}_2(\text{O}_2\text{CMe})_4$ structural unit.^{7–14} In all cases, dimeric^{7–11,13} or polymeric^{12,14} complexes with a smaller number of acetate ligands and interesting structural and magnetic characteristics have been obtained. A matter of interest is how much versatility there is in the type of bridging found in copper(II) acetate and whether other small bridging ligands can be incorporated together with acetate bridges in the same complex.

In recent years, we have been investigating the

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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 manganese¹⁵ and iron,¹⁶ but we recently extended our efforts to copper and have found that the reactions of $\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{H}_2\text{O})_2$ with chelating 2,2'-bipyridine (bpy) lead to a wide variety of products¹⁷ with bridging units not previously observed in Cu_2^{4+} chemistry. In extending the above work, attempts have been made to prepare a trinuclear complex with the $[\text{Cu}_3(\mu_3\text{-OR})(\mu\text{-O}_2\text{CR}')_3]^{2+}$ core, as this structural unit has not yet been identified in copper(II) chemistry.¹⁸ 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 $[\text{Cu}_2(\text{OH})(\text{H}_2\text{O})(\text{O}_2\text{CMe})(\text{bpy})_2](\text{ClO}_4)_2$ (**2**) was available from previous work.¹⁷ $\text{Cu}_2(\text{OH})_2(\text{bpy})_2(\text{ClO}_4)_2$ was prepared as described.^{19a} *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* $[\text{Cu}_2(\text{OH})\text{Cl}(\text{O}_2\text{CMe})(\text{bpy})_2](\text{ClO}_4) \cdot \text{H}_2\text{O}$ (**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 $\text{CuCl}_2(\text{bpy})$.^{19b} 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. Calc. for $\text{C}_{22}\text{H}_{22}\text{N}_4\text{O}_8\text{Cl}_2\text{Cu}_2$: 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, 1312m, 1252m, 1171m, 1157m, 1082vsb, 1055m, 1019m,

978w, 932w, 918w, 897w, 810w, 768vs, 731s, 663m, 650sh, 623s, 545w, 488m, 459m, 417m. Magnetic moment per copper(II) (Faraday method): 2.03 μ_{B} at 26°C. Solid-state (diffuse reflectance) electronic spectrum: λ_{max} , nm; 340sh, 370, 670, 710sh. Electronic spectrum in MeCN: λ_{max} , nm ($\epsilon_{\text{M}}/\text{Cu}_2$, 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 $[\text{Cu}_2(\text{OH})(\text{H}_2\text{O})(\text{O}_2\text{CMe})(\text{bpy})_2](\text{ClO}_4)_2$ (**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 $\text{Cu}_2(\text{OH})_2(\text{bpy})_2(\text{ClO}_4)_2$ (**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* $[\text{Cu}_2(\text{OH})\text{Br}(\text{O}_2\text{CMe})(\text{bpy})_2]\text{Br} \cdot \text{H}_2\text{O}$ (**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 $\text{CuBr}_2(\text{bpy})$. 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 $\text{NaO}_2\text{CMe} \cdot 3\text{H}_2\text{O}$ (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. Calc. for $\text{C}_{22}\text{H}_{22}\text{N}_4\text{O}_4\text{Br}_2\text{Cu}_2$: 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,

1041w, 1022s, 1010s, 942w, 907sh, 890m, 802w, 764vs, 728s, 652w, 575mb, 484mb, 460m, 413m. Magnetic moment per copper(II) (Faraday method): $2.16 \mu_{\text{B}}$ at 23°C . Solid-state (diffuse reflectance) electronic spectrum: λ_{max} , nm: 342, 375, 665, 705sh. Attempts to isolate the ClO_4^- or PF_6^- salt of $[\text{Cu}_2(\text{OH})\text{Br}(\text{O}_2\text{CMe})(\text{bpy})_2]^+$ led to mixtures of $[\text{Cu}_2(\text{OH})\text{Br}(\text{O}_2\text{CMe})(\text{bpy})_2]\text{Br} \cdot \text{H}_2\text{O}$ and $[\text{Cu}_2(\text{OH})\text{Br}(\text{O}_2\text{CMe})(\text{bpy})_2]\text{Y} \cdot \text{H}_2\text{O}$ ($\text{Y} = \text{ClO}_4$ 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_2O (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_2O and Et_2O , 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_2O (20 cm^3) was added solid NaClO_4 (0.06 g,

0.50 mmol), followed by addition of a solution of NaOH (0.18 g, 0.45 mmol) in H_2O (10 cm^3). An immediate colour change from blue to lavender occurred. The reaction mixture was stirred for 15 min at $50\text{--}60^\circ\text{C}$ and the resulting solid was collected by filtration, washed with H_2O and Et_2O , 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_2O (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 1. Crystallographic data collection and refinement parameters for $[\text{Cu}_2(\text{OH})\text{Cl}(\text{O}_2\text{CMe})(\text{bpy})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (1)

Formula	$\text{C}_{22}\text{H}_{22}\text{N}_4\text{O}_8\text{Cl}_2\text{Cu}_2$
Formula weight	668.46
Space group	$P2_1/n$
Temperature ($^\circ\text{C}$)	-175
a (\AA)	8.434(1)
b (\AA)	16.074(2)
c (\AA)	9.430(1)
β ($^\circ$)	98.09(1)
V (\AA^3)	1265.83
Z	2
ρ_{calc} (g cm^{-3})	1.754
Crystal dimensions (mm)	$0.25 \times 0.25 \times 0.25$
Radiation (λ , \AA)	$\text{Mo-K}\alpha$ (0.71069)
Absorption coefficient (cm^{-1})	19.512
2θ range ($^\circ$)	6.00–45.00
Scan speed (deg min^{-1})	4.0
Scan width ($^\circ$)	2.0 + dispersion
Take-off angle ($^\circ$)	2.0
Data collected	3354
Unique data	1710
Data with $F > 2.33\sigma(F)$	1499
Averaging R	0.025
R	0.0338
R_w	0.0354
Goodness of fit for last cycle	1.063

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 $0.45 \text{ e } \text{\AA}^{-3}$. 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 $\text{HgCo}(\text{SCN})_4$. The molar susceptibilities were corrected for the diamagnetism of the constituent atoms using Pascal's constants. TG/DTG data were obtained with a DuPont R90 instrument equipped with a 951 thermogravimetric analyser in a nitrogen gas flow ($50 \text{ cm}^3 \text{ min}^{-1}$); sample weights of 5–10 mg and heating rates of 1 and 5°C min^{-1} were used.

Analytical procedures

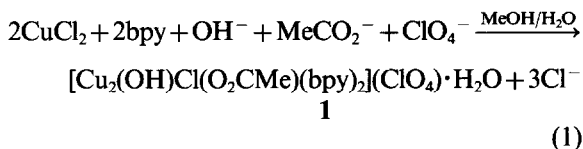
Elemental analyses for **1** were performed at the Microanalytical Laboratory, Department of Chemistry, Manchester University, England. For the bromide determination, samples of **4** were decomposed in 2 M HNO_3 ; the total bromides were determined potentiometrically with a standard 0.1 M AgNO_3 solution, using a Corning-Eel Model 12 potentiometer with calomel and sulphide-selective electrodes.²¹ Copper(II) was estimated gravimetrically as copper(II) quinaldate.²² The amount of water in **4** was determined from the TG pattern.

RESULTS AND DISCUSSION

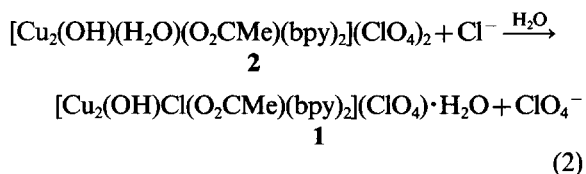
Syntheses

In our development of $\text{Cu}^{\text{II}}/\text{RCO}_2^-/\text{bpy}$ chemistry,¹⁷ we had employed $\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{H}_2\text{O})_2$ and Cu:bpy ratios of 1:1 (a 1:2 ratio is

known to produce mononuclear $[\text{Cu}(\text{O}_2\text{CMe})(\text{bpy})_2]^+$ 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 trimer of the formula $\text{Cu}_3(\text{O}_2\text{CMe})_6(\text{bpy})_2$, like the Mn^{II} analogue,²⁸ employing a Cu^{II} :bpy ratio of 1.5:1; however, the reaction instead led to $[\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{bpy})_2] \cdot 2\text{H}_2\text{O}$ and $[\text{Cu}_4(\text{O}_2\text{CMe})_4(\text{bpy})_2]_n$.¹⁷ In this work, the influence of added OH^- ($\text{Cu}:\text{OH}^- = 3:1$) was investigated, wondering whether a product with a $[\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-O}_2\text{CMe})_3]^{2+}$ core might be attainable. An $\text{MeOH}/\text{H}_2\text{O}$ (*ca* 1:3) reaction mixture containing CuCl_2 , bpy, NaOH, NaO_2CMe 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 $[\text{Cu}_2(\text{OH})\text{Cl}(\text{O}_2\text{CMe})(\text{bpy})_2](\text{ClO}_4) \cdot \text{H}_2\text{O}$. 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 $\text{Cu}:\text{OH}^-$ ratio from 3:1 to 2:1 [eq. (1)].

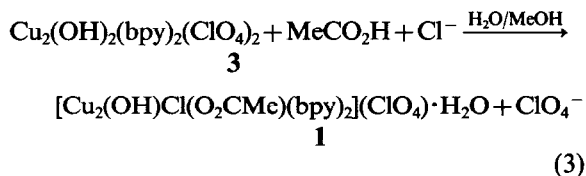


Complex **1** may also be prepared from the complexes $[\text{Cu}_2(\text{OH})(\text{H}_2\text{O})(\text{O}_2\text{CMe})(\text{bpy})_2](\text{ClO}_4)_2$ (**2**) and $\text{Cu}_2(\text{OH})_2(\text{bpy})_2(\text{ClO}_4)_2$ (**3**). Reaction of **2** with an excess of NaCl in H_2O at 50°C gave a clean 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).

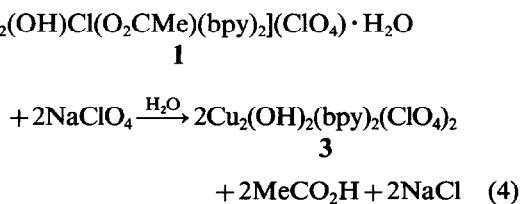


In addition, treatment of **3** with one equiv. of acetic acid in H_2O at 40°C , followed by addition of a slight excess of NaCl led to clean, high-yield

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

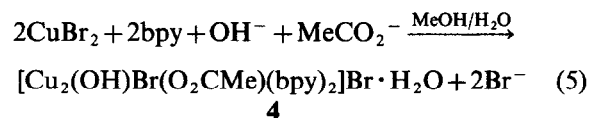


of an OH^- bridge followed by binding of the generated MeCO_2^- and substitution of the bridging aqua ligand by the chloro group. This transformation of **3** to **1** is reversible. Recrystallization of **1** from warm water ($\sim 50^\circ\text{C}$) yielded **3** in 20% yield based on copper; the yield is ClO_4^- -limited, however, and addition of NaClO_4 to the mixture [eq. (4)] increases the yield of isolated **3**



to 40%. Complex **1** in H_2O containing NaClO_4 (one equiv.) and NaOH (one equiv.) also gives **3** (73% isolated yield) at $50\text{--}60^\circ\text{C}$.

The access to $[\text{Cu}_2(\mu\text{-OH})(\mu\text{-Cl})(\mu\text{-O}_2\text{CMe})]^+$ species from CuCl_2 suggested that the reaction system might be capable of extension to other CuX_2 salts ($\text{X} = \text{halide}$). The above procedure but with CuBr_2 was found to successfully yield the $[\text{Cu}_2(\mu\text{-OH})(\mu\text{-Br})(\mu\text{-O}_2\text{CMe})]^+$ species in good overall yield [eq. (5)].



Efforts to isolate the ClO_4^- or PF_6^- salt of $[\text{Cu}_2(\text{OH})\text{Br}(\text{O}_2\text{CMe})(\text{bpy})_2]^+$ led to mixtures of **4** and $[\text{Cu}_2(\text{OH})\text{Br}(\text{O}_2\text{CMe})(\text{bpy})_2]\text{Y} \cdot \text{H}_2\text{O}$ ($\text{Y} = \text{ClO}_4$ or PF_6), 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 Cu_2 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

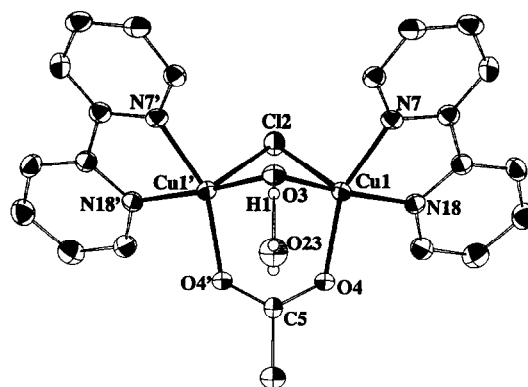


Fig. 1. ORTEP representation of the cation of complex **1** at the 50% probability level. Bipyridine carbon atoms are labelled consecutively from N7. The unlabelled acetate carbon atom is C6. OH^- and H_2O hydrogen atoms are included as spheres of arbitrary size.

from each other. The acetate group is in the familiar bidentate *syn,syn* $\eta^1:\eta^1:\mu_2$ -bridging mode; a terminal bpy molecule completes five-coordination at each metal atom. The $\text{Cu}\cdots\text{Cu}$ separation in **1** is noticeably shorter than in dinuclear triply-bridged copper(II) complexes containing three or two acetate 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, τ , of 0.40 for the copper ($\tau = 0$ and 1.09 for square-pyramidal and trigonal bipyramidal geometry, respectively). Thus, the geometry about $\text{Cu}(1)$ and $\text{Cu}(1')$ is significantly distorted,

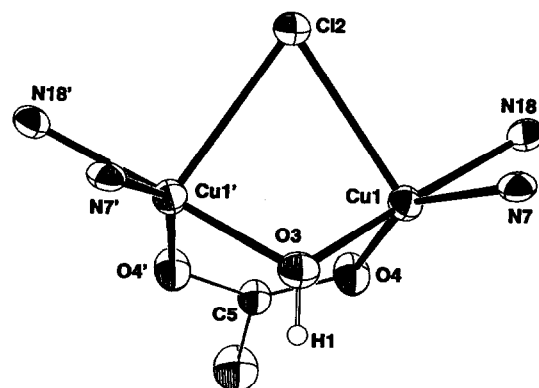


Fig. 2. ORTEP representation of the inner coordination sphere of the Cu_2 core for complex **1**.

Table 2. Selected bond distances (Å) and angles (deg) for complex 1

Distances			
Cu(1)···Cu(2)	2.957(1)	Cu(1)—O(3)	1.920(3)
Cu(1)—Cl(2)	2.557(1)	Cu(1)—O(4)	1.971(3)
Cu(1)—N(7)	2.012(3)	O(3)—H(1)	0.81(7)
Cu(1)—N(18)	1.998(4)	O(23)···H(1)	2.02(7)
Angles			
Cu(1)—Cl(2)—Cu(1')	70.6(1)	N(18)—Cu(1)—O(4)	89.7(1)
Cu(1)—O(3)—Cu(1')	100.7(2)	N(18)—Cu(1)—O(3)	175.4(2)
Cl(2)—Cu(1)—N(7)	102.8(1)	O(4)—Cu(1)—O(3)	94.2(2)
Cl(2)—Cu(1)—N(18)	96.4(1)	Cu(1)—O(4)—C(5)	127.1(3)
Cl(2)—Cu(1)—O(4)	105.0(1)	Cu(1')—Cu(1)—Cl(2)	54.7(1)
Cl(2)—Cu(1)—O(3)	85.0(1)	Cu(1')—Cu(1)—N(18)	144.0(1)
N(7)—Cu(1)—N(18)	80.6(2)	Cu(1')—Cu(1)—N(7)	123.0(1)
N(7)—Cu(1)—O(4)	151.4(1)	Cu(1)—Cu(1)—O(4)	79.7(1)
N(7)—Cu(1)—O(3)	94.9(2)	O(23)···H(1)—O(3)	171.0(6)

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 CuN₂O₂ planes is 60.6°.

The bond lengths to the bridging hydroxo and acetate oxygens and to the two bpy nitrogen atoms are typical.^{17,32} The distance Cu(1)—Cl(2) [2.557(1) Å] and the acute angle Cu(1)—Cl(2)—Cu(1') [70.6(1)°] are both very similar to those observed in other dinuclear, square-pyramidal copper(II) complexes sharing a common μ_2 -Cl⁻ apex;³³ the bond from the copper to the bridging apical chloro ligand is longer than that to bridging basal chloro ligands (~2.3 Å).³⁴

The oxygen atom O(23) of the water molecule hydrogen-bonds to the OH⁻ hydrogen H(1) [O(3)—H(1), 0.81(7) Å; H(1)···O(23), 2.02(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(II) 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 aryloxy 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)LX₂] [X = Cl, Br; L = bi-

nucleating phthalazine or pyridazine ligands³⁶ and 2,7-bis(2-pyridyl)-1,8-naphthyridine]³³ 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 · MeOH³⁷ (L—L = a binucleating tetradentate hexaimidazole ligand) and complex 2¹⁷ 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 μ_2 -H₂O by μ_2 -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 μ_{eff} 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"^{38,39} of MeCO_2^- and OH^- orbitals with $d_{x^2-y^2}$ magnetic orbitals. It is interesting to note that all Cu_2^{II} systems bridged by one $\text{R}'\text{CO}_2^-$ and one RO^- ($\text{R} = \text{H}$, 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 transitions⁴⁰ 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 ~ 3450 and 3365 cm^{-1} , assigned to $\nu(\text{OH}^-)$ and $\nu(\text{H}_2\text{O})$, respectively;⁴¹ their broadness and low frequency are both indicative of hydrogen bonding. The $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ bands of **1** and **4** are at $1558\text{--}1551$ and $1445\text{--}1438 \text{ cm}^{-1}$, respectively; the difference Δ [$\Delta = \nu_{\text{as}}(\text{COO}) - \nu_{\text{s}}(\text{COO})$]; 106 cm^{-1} for **1**, 120 cm^{-1} for **2**] is less than that for NaO_2CMe (164 cm^{-1}), as expected for the bidentate bridging mode of carboxylate ligation.⁴²

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