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PREPARATION AND CHARACTERIZATION OF DINUCLEAR COPPER(II) COMPLEXES CONTAINING THE $[Cu_2(\mu\text{-}OAc)_2]^{2+}$ CORE

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Abstract—Treatment of an aqueous slurry of known $Cu_2(OH)_2(bpy)_2(ClO_4)_2$ (**1**) with an excess of MeCOOH led to rapid formation of the blue complex $[Cu_2(O_2CMe)_2(H_2O)_2(bpy)_2](ClO_4)_2 \cdot H_2O$ (**3**). Complex **3** has also been prepared by slow crystallization from an H_2O/MeCOOH reaction mixture containing the polymeric compound $[Cu_4(O_2CMe)_8(bpy)_2]_n$ (**5**), bpy and $NaClO_4$. A similar reaction system containing a lesser amount of H_2O led to fast precipitation of the anhydrous compound $[Cu_2(O_2CMe)_2(OClO_3)_2(bpy)_2]$ (**4**). The transformation of **1** to **3** is reversible; treatment of **3** with neat H_2O led to high-yield isolation of **1**. Using a significantly shorter reaction time and a smaller volume of H_2O, the procedure yielded the known complex $[Cu_2(OH)(H_2O)(O_2CMe)(bpy)_2](ClO_4)_2$ (**2**). Similarly, complex **4** can be transformed to **2** in good yield. Complex **3** crystallizes in the monoclinic space group $P2_1/a$ with (at −172°C) $a = 17.037(3)$, $b = 9.743(2)$, $c = 18.357(4)$ Å, $\beta = 98.19(5)°$, $Z = 4$ and $V = 3016.05$ Å^3. A total of 3651 unique data with $F > 2.33\sigma(F)$ were refined to values of conventional indices R (R_w) of 7.89 (8.74)%. Complex **4** crystallizes in the monoclinic space group $C2/c$ with (at −172°C) $a = 11.555(4)$, $b = 15.231(5)$, $c = 15.885(6)$ Å, $\beta = 100.27(2)°$, $Z = 4$ and $V = 2750.76$ Å^3. A total of 1456 unique data with $F > 2.33\sigma(F)$ were refined to values of R and R_w of 3.23 and 3.63%, respectively. The structure of **3** consists of the doubly-bridged $[Cu_2(O_2CMe)_2(H_2O)_2(bpy)_2]^{2+}$ cation, two considerably disordered ClO_4^- anions and the disordered H_2O solvate molecule. The two acetates are in the familiar $\eta^1:\eta^1:\mu_2$ bridging mode; a terminal bpy molecule and one aqua ligand complete five-coordination at each metal atom. The molecule of **4** is very similar to the cation of **3**; the aqua ligands of **3** are replaced by two terminal, axial monodentate perchlorato groups. In both **3** and **4**, the dimers are stabilized by bpy–bpy stacking interactions, and the precise structural effects of these interactions are described.

A unifying theme in some of our recent work has been the desire to establish the products from the reaction of 2,2′-bipyridine (bpy) with metal carboxylates. With the 3*d* metals Mn,[1] Fe[2] and Cu,[3,4] a number of products of different nuclearity have been obtained, none of which have had significant structural similarity to the starting material. In contrast, with the 4*d* metal carboxylates $Mo_2(O_2CCF_3)_4$ and $Rh_2(O_2CMe)_4(MeOH)_2$ metal–metal bonding has helped ensure retention of the $[M_2]^{4+}$ unit in the products $Rh_2(O_2CMe)_4(bpy)$,[5] $Mo_2(O_2CCF_3)_4(bpy)_2$[6] and $[Mo_2(O_2CCF_3)_2(bpy)_2](O_2CCF_3)_2$.[6] The latter pair have been of particular interest because they are isomers, and it has been discovered that the ion-pair form can be thermally and photochemically converted to the neutral molecule. In probing the driving force for this isomerization, it is becoming clear that many factors are involved in this still-evolving story, including M—M bonding considerations and bpy–bpy π-stacking interactions.[7] In attempting to delineate the relative importance of these and other factors, we have realized the importance of accessing a structurally-analogous

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compound with no metal–metal bonding to better establish the precise effect of the bpy–bpy interactions alone on the structure. Unfortunately, parallel studies of $Cu_2(O_2CMe)_4(H_2O)_2$ reactions with bpy had not resulted in the desired type of unit, namely $[Cu_2(\mu\text{-}O_2CMe)_2(bpy)_2]^{2+}$, although other interesting dinuclear products had been obtained.[3,4] However, we are pleased to now be able to report that conditions have been developed that allow access to these types of compounds.

In a recent report,[3] the known[8] compound $Cu_2(OH)_2(bpy)_2(ClO_4)_2$ (**1**) was converted to the triply-bridged complex $[Cu_2(OH)(H_2O)(O_2CMe)(bpy)_2](ClO_4)_2$ (**2**) by treatment with one equiv. of acetic acid [eq. (1)].

$$Cu_2(OH)_2(bpy)_2(ClO_4)_2\,(\mathbf{1}) + MeCO_2H \xrightarrow{H_2O} [Cu_2(OH)(H_2O)(O_2CMe)(bpy)_2](ClO_4)_2\,(\mathbf{2}) \quad (1)$$

It was mentioned that an excess of acetic acid led to a different product that had yet to be identified. We herein report the characterization of this product, $[Cu_2(O_2CMe)_2(H_2O)_2(bpy)_2](ClO_4)_2 \cdot H_2O$ (**3**), and the anhydrous analogue $[Cu_2(O_2CMe)_2(OClO_3)_2(bpy)_2]$ (**4**). A detailed structural analysis of $[M_2(O_2CMe)_2(bpy)_2]^{2+}$ species that do not possess metal–metal bonds is now possible, and is described.

EXPERIMENTAL

Starting materials

All manipulations were performed under aerobic conditions using materials as received; water was distilled in-house. The complexes $[Cu_2(OH)(H_2O)(O_2CMe)(bpy)_2](ClO_4)_2$ (**2**) and $[Cu_4(O_2CMe)_8(bpy)_2]_n$ (**5**) were available from previous work.[3,4] $Cu_2(OH)_2(bpy)_2(ClO_4)_2$ was prepared as described.[8]

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.

Reaction procedures

(a) *Preparation of* $[Cu_2(O_2CMe)_2(H_2O)_2(bpy)_2](ClO_4)_2 \cdot H_2O$ (**3**). *Method A*. A slurry of lavender **1** (0.78 g, 1.2 mmol) in H_2O (15 cm^3) was treated with glacial MeCOOH (0.15 cm^3, 2.5 mmol). The lavender solid rapidly dissolved, and an intense blue solution was obtained. An excess of MeCOOH (total volume added: 0.45 cm^3, 7.50 mmol) was then added to begin precipitation of a blue solid. The reaction mixture was stirred for 10 min at room temperature and cooled to 5°C in a refrigerator for 3 h. The precipitate was collected by filtration, washed with EtOH and Et_2O and dried *in vacuo*; yield, 0.65 g (69%). Found: C, 36.3; H, 3.5; N, 6.9; Cu, 16.4; Cl, 8.7. Calc. for $C_{24}H_{28}N_4O_{15}Cl_2Cu_2$: C, 35.6; H, 3.5; N, 6.9; Cu, 15.7; Cl, 8.7%. Selected IR data (Nujol mull, cm^{-1}): 3580m, 3450mb, 1609sh, 1603s, 1580vsb, 1495m, 1455mb, 772vs, 748w, 731s, 681m, 671m, 650m, 621sb. Magnetic moment per Cu^{II}(Faraday method): 1.77 μ_B at 19°C. Solid-state (diffuse reflectance) electronic spectrum; λ_{max}, nm: 365, 660, 885 sh. *d–d* electronic spectrum in MeCN (400–800 nm); λ_{max}, nm (ε_m per Cu_2, L mol^{-1} cm^{-1}): 626 (205). The above procedure, employing PhCOOH instead of MeCOOH and a little EtOH to aid dissolution, yielded the known[5] complex $[Cu_2(O_2CPh)_3(bpy)_2](ClO_4)$.

Method B. To a stirred, blue solution of complex **5** (0.31 g, 0.30 mmol) in H_2O (8 cm^3) was added a solution of bpy (0.094 g, 0.60 mmol) in glacial MeCOOH (2.5 cm^3). To the resulting royal blue solution was added an aqueous solution (5 cm^3) of $NaClO_4$ (0.15 g, 1.22 mmol). The solution was stirred for a further 5 min and the flask stored in a refrigerator (5°C) overnight. The large, dark blue crystals thus obtained were collected by filtration, washed with $EtOH/Et_2O$ (1 : 1) and dried in air; yield, 0.27 g (55%). The product had IR and electronic spectra identical with those detailed under Method A.

(b) *Preparation of* $[Cu_2(O_2CMe)_2(OClO_3)_2(bpy)_2]$ (**4**). To a blue solution of complex **5** (0.31 g, 0.3 mmol) in H_2O (3.5 cm^3) was added a solution of bpy (0.094 g, 0.60 mmol) in glacial MeCOOH (1.5 cm^3). The resulting royal blue solution was treated with solid $NaClO_4$ (0.15 g, 1.2 mmol). A royal blue, microcrystalline powder formed almost immediately. After 10 min stirring, this was collected by filtration, washed with H_2O (2 × 0.5 cm^3), EtOH and Et_2O, and dried *in vacuo*; yield, 0.18 g (40%). Found: C, 38.2; H, 2.9; N, 7.1; Cl, 9.1; Cu, 16.5. Calc. for $C_{24}H_{22}N_4O_{12}Cl_2Cu_2$: C, 38.1; H, 2.9; N, 7.4; Cl, 9.4; Cu, 16.8%. Selected IR data (Nujol mull, cm^{-1}): 1613sh, 1603s, 1576vsb, 1495m, 1455sb, 768vs, 748w, 729s, 675m, 667m, 652w, 619s. Magnetic moment per Cu^{II} (Faraday method): 1.83 μ_B at 23°C. Solid-state (diffuse reflectance) electronic spectrum; λ_{max}, nm: 355, 645, 875 sh. *d–d* electronic spectrum in MeCN (400–800 nm); λ_{max}, nm (ε_m per Cu_2, L mol^{-1} cm^{-1}): 626 (195).

(c) *Conversion of complex* **3** *to complex* **1**. A slurry of complex **3** (0.23 g, 0.28 mmol) in H_2O (15 cm^3) was stirred at room temperature for 1 h. A colour change from blue to lavender occurred. The solid was collected by filtration, washed with H_2O, EtOH and Et_2O, and dried *in vacuo*; yield, 0.13 g (69%). The identity of the product was deduced by IR spectral comparison with authentic material.

(d) *Conversion of complex* **3** *to complex* **2**. A slurry of complex **3** (0.23 g, 0.28 mmol) in H_2O (5 cm^3) was stirred at room temperature for 3 min. No noticeable colour change occurred. The solid was collected by filtration, washed with H_2O, THF and Et_2O, and dried in air; yield, 0.13 g (63%). The product was identical on spectroscopic examination with **2**.[3]

(e) *Conversion of complex* **4** *to compound* **2**. Employing complex **4** (0.21 g, 0.28 mmol) and 5 cm^3 of H_2O, the above procedure again yielded complex **2**, yield, 0.11 g (54%).

Preparation of single crystals of **3** *and* **4**

Suitable crystals of **3** were prepared by recrystallization of the microcrystalline solid from aqueous acetic acid. For the preparation of single crystals of **4**, the powder (0.20 g) was dissolved in 10 cm^3 of freshly-distilled MeCN. The homogeneous blue solution was layered with double the volume of a 1 : 1 mixture of hexane and Et_2O. Slow mixing yielded a crystalline material, which was collected by filtration, washed with Et_2O and dried in air. Microscopic examination showed both dark blue crystals and blue needles to be present in a visual ratio of 1 : 2, respectively; the two products were readily separated manually. The unit cell dimensions and IR spectrum of the hand-picked needles confirmed this product to be complex **2**, on the basis of comparison with those of an authentic material. The dark blue crystals were found to be good diffractors of X-rays and proved to be unchanged complex **4**.

X-Ray crystallographic studies

Data were collected on a Picker four-circle diffractometer at −172°C for both complexes **3** and **4**; details of the diffractometry, low-temperature facilities, and computational procedures employed by the Molecular Structure Center are available elsewhere.[9] Data collection parameters are summarized in Table 1. For both complexes, crystals were attached to glass fibres using a little silicone grease, and then transferred to a goniostat and placed in a cold stream. The structures were solved by the usual combination of direct methods

Table 1. Crystal data and data collection parameters for $[Cu_2(O_2CMe)_2(H_2O)_2(bpy)_2](ClO_4)_2 \cdot H_2O$ (**3**) and $[Cu_2(O_2CMe)_2(OClO_3)_2(bpy)_2]$ (**4**)

	3	**4**
Formula	$C_{24}H_{28}N_4O_{15}Cl_2Cu_2$	$C_{24}H_{22}N_4O_{12}Cl_2Cu_2$
Formula weight	810.52	756.49
Space group	$P2_1/a$	$C2/c$
a (Å)	17.037(3)	11.555(4)
b (Å)	9.743(2)	15.231(5)
c (Å)	18.357(4)	15.885(6)
β (°)	98.19(5)	100.27(2)
V (Å^3)	3016.05	2750.76
Z	4	4
ρ_{calc} (g cm^{-3})	1.785	1.827
Crystal dimensions (mm)	0.25 × 0.25 × 0.25	0.25 × 0.25 × 0.25
Radiation (λ, Å)	Mo-K_α (0.71069)	Mo-K_α (0.71069)
Linear absorption coefficient (cm^{-1})	16.694	18.166
2θ range (°)	6.00–45.00	6.00–45.00
Scan speed (° min^{-1})	8.0	4.0
Scan width (°)	2.0 + dispersion	2.0 + dispersion
Take-off angle (°)	2.0	2.0
Data collected	5117	2405
Unique data	3940	1789
Data with $F > 2.33\sigma(F)$	3651	1456
Averaging R	0.018	0.021
R	0.0789	0.0323
R_w	0.0874	0.0363
Goodness of fit for last cycle	2.384	0.935

(MULTAN) and Fourier techniques and refined by full-matrix least squares.

For **3**, a systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with symmetry and systematic absences corresponding to the unique monoclinic space group $P2_1/a$. Subsequent solution and refinement of the structure confirmed this choice. A rotational disorder was observed for both perchlorate groups. Several different models were examined, and the final refinement used a $\frac{1}{3}:\frac{2}{3}$ ratio for three oxygens on one Cl, and for all four on the other. In addition to this disorder, there is a water of hydration that also suffers from a $\frac{1}{3}:\frac{2}{3}$ disorder; its O-atom is labelled O(37). Hydrogen atoms were placed in fixed idealized positions for the organic ligands, based on observed peaks. No attempt was made to include the hydrogen atoms associated with the water molecules. The final difference Fourier map was essentially featureless, with the largest peaks being associated with the perchlorate groups.

For complex **4**, a systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with symmetry and systematic absences corresponding to a centred monoclinic space group, either $C2/c$ or Cc. Subsequent solution and refinement of the structure confirmed the centrosymmetric choice, $C2/c$. 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, and were included in the final cycles and refined with isotropic thermal parameters. A final difference Fourier map was essentially featureless, with the largest peak being 0.56 e $Å^{-3}$. Final discrepancy indices R and R_w for **3** and **4** are included in Table 1.

Other measurements

Elemental analyses were performed at the Microanalytical Laboratory, Department of Chemistry, Manchester University, U.K. IR spectra were recorded as Nujol mulls between CsI plates using a Nicolet 510P Fourier transform spectrometer or a Perkin–Elmer Model 283 spectrophotometer. Solid-state (diffuse reflectance) and solution 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 $HgCo(NCS)_4$. The molar susceptibilities were corrected for the diamagnetism of the constituent atoms using Pascal's constants.

RESULTS AND DISCUSSION

Synthesis and reactivity studies

Treatment of an aqueous slurry of **1** with an excess of MeCOOH leads to dissolution of the solid and then formation of a blue precipitate in good yield. It was obvious from the IR spectrum and analytical data that a ClO_4^- salt with bpy, bridging $MeCO_2^-$ and two types of H_2O groups had been obtained, and our initial suspicion had been that the compound $[Cu_2(\mu\text{-}H_2O)(\mu\text{-}O_2CMe)_2(bpy)_2](ClO_4)_2\cdot 2H_2O$ was the product, facilitated by protonation of the bridging OH^- group in **2** under acidic conditions. However, the X-ray crystal structure of **3** showed the complex to be the related but doubly-bridged complex $[Cu_2(\mu\text{-}O_2CMe)_2(H_2O)_2(bpy)_2](ClO_4)_2\cdot H_2O$ rather than the triply-bridged dimer. The formation of **3** is summarized in eq. (2).

$$Cu_2(OH)_2(bpy)_2(ClO_4)_2\,(\mathbf{1}) + 2MeCO_2H + H_2O \xrightarrow{H_2O/MeCO_2H} [Cu_2(O_2CMe)_2(H_2O)_2(bpy)_2](ClO_4)_2\cdot H_2O\,(\mathbf{3}) \qquad (2)$$

Discrete Cu^{II} dimers containing the $[Cu_2(\mu\text{-}O_2CR)_2]^{2+}$ core are rare,[10–13] and none have contained bpy, so it was decided to pursue further synthetic methods to this new family. Subsequently, an additional route to **3** has been developed, employing the polymeric compound $(Cu_4(O_2CMe)_8(bpy)_2]_n$[4] (**5**). Thus, treatment of **5** with bpy and $NaClO_4$ in aqueous MeCOOH gives a blue solution from which pure, highly crystalline **3** is slowly obtained in good yield [eq. (3)].

$$[Cu_4(O_2CMe)_8(bpy)_2]_n\,(\mathbf{5}) + 2n\text{bpy} + 4nClO_4^- + 6nH_2O \xrightarrow[\text{slow pptn}]{H_2O/MeCOOH} 2n[Cu_2(O_2CMe)_2(H_2O)_2(bpy)_2](ClO_4)_2\cdot H_2O\,(\mathbf{3}) + 4nMeCO_2^- \qquad (3)$$

In parallel experiments employing complex **5** and a decreased $H_2O:MeCOOH$ ratio, the product was found not to be **3** but the anhydrous product $[Cu_2(O_2CMe)_2(OClO_3)_2(bpy)_2]$ (**4**) [eq. (4)].

$$[Cu_4(O_2CMe)_8(bpy)_2]_n\,(\mathbf{5}) + 2n\text{bpy} + 4nClO_4^- \xrightarrow[H_2O/MeCOOH]{\text{fast pptn}} 2n[Cu_2(O_2CMe)_2(OClO_3)_2(bpy)_2]\,(\mathbf{4}) + 4nMeCO_2^- \qquad (4)$$

Crystallographic characterization showed that the structure of **4** is similar to that of the cation of **3**; the aqua ligands in **3** have been replaced by terminal monodentate perchlorates (*vide infra*).

The transformation of **1** to **3** is reversible; treatment of solid **3** with H_2O for 1 h led to high-yield isolation of **1**. The carboxylate groups of **3** are presumably acting as H^+ acceptors to facilitate formation of OH^- ions and complex **1**. Using a significantly shorter reaction time, however, the above procedure instead yielded complex **2** [eq. (5)].

$$[Cu_2(O_2CMe)_2(H_2O)_2(bpy)_2](ClO_4)_2 \cdot H_2O\,(\mathbf{4}) \xrightarrow{H_2O} [Cu_2(OH)(H_2O)(O_2CMe)(bpy)_2](ClO_4)_2\,(\mathbf{2}) + MeCOOH + H_2O \quad (5)$$

Similarly, complex **4** can be transformed to **2** in good yield (54%). That complex **2** should be the product of the heterogeneous reaction at short reactions times is reasonable, for it represents an intermediate stage in the carboxylate loss/OH^- incorporation process that represents the conversion of **3** to **1** [eq. (6)].

$$\underset{\mathbf{3}}{[Cu_2(\mu\text{-}O_2CMe)_2]^{2+}} \longrightarrow \underset{\mathbf{2}}{[Cu_2(\mu\text{-}OH^-)(\mu\text{-}O_2CMe)]^{2+}} \longrightarrow \underset{\mathbf{1}}{[Cu_2(\mu\text{-}OH^-)_2]^{2+}} \quad (6)$$

Description of structures

ORTEP projections of the cations of complex **3** and compound **4** are given in Figs 1 and 2. The important structural parameters are listed in Tables 2 and 3.

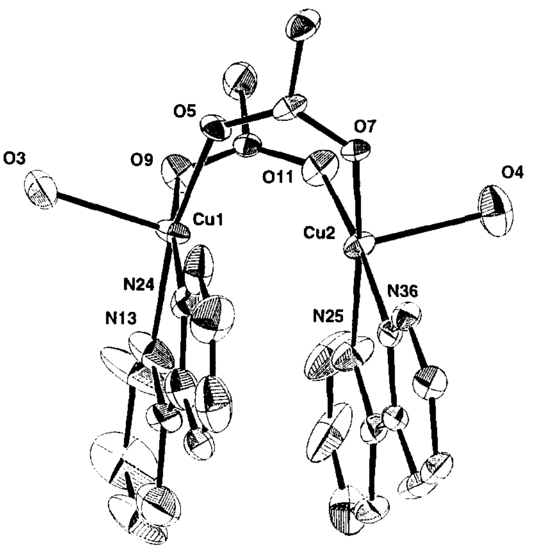

Fig. 1. ORTEP representation of the cation of complex 3 at the 50% probability level. Bipyridine carbon atoms are labelled consecutively from N(13) and N(25). The acetate methyl carbon atoms are C(8) and C(12).

The structure of **3** consists of the dinuclear, doubly-bridged $[Cu_2(O_2CMe)_2(H_2O)_2(bpy)_2]^{2+}$ cation, two disordered ClO_4^- anions and one disordered H_2O solvate molecule. The latter two will not be further discussed; disorder problems also preclude consideration of possible hydrogen bonds between the H_2O, cation and anions. The two acetates are in the familiar bidentate $\eta^1:\eta^1:\mu_2$ bridging mode; a terminal bpy molecule and one aqua ligand com-

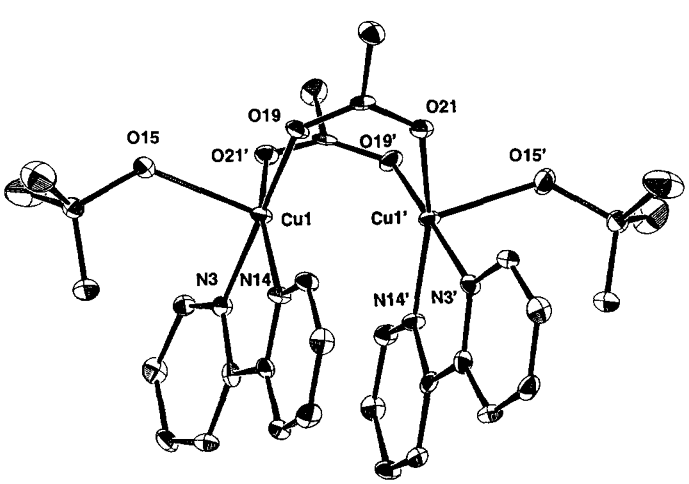

Fig. 2. ORTEP representation of 4 at the 50% probability level. Bipyridine carbon atoms are labelled consecutively from N(3). The acetate methyl carbon atom and perchlorate oxygens are C(22) and O(16), O(17) and O(18), respectively. The symmetry-related atoms are primed.

Table 2. Selected bond distances (Å) and angles (°) for $[Cu_2(O_2CMe)_2(H_2O)_2(bpy)_2](ClO_4)_2\cdot H_2O$ (3)

	Distances		
Cu(1)···Cu(2)	3.002(1)		
Cu(1)—O(3)	2.187(7)	Cu(2)—O(4)	2.265(7)
Cu(1)—O(5)	1.922(6)	Cu(2)—O(7)	1.954(6)
Cu(1)—O(9)	1.976(6)	Cu(2)—O(11)	1.933(6)
Cu(1)—N(13)	2.015(9)	Cu(2)—N(25)	2.002(8)
Cu(1)—N(24)	2.001(8)	Cu(2)—N(36)	1.978(8)
	Angles		
O(3)—Cu(1)—O(5)	91.5(3)	O(4)—Cu(2)—O(7)	90.8(2)
O(3)—Cu(1)—O(9)	92.9(3)	O(4)—Cu(2)—O(11)	89.5(3)
O(3)—Cu(1)—N(13)	99.7(3)	O(4)—Cu(2)—N(25)	96.1(3)
O(3)—Cu(1)—N(24)	96.9(3)	O(4)—Cu(2)—N(36)	95.2(3)
O(5)—Cu(1)—O(9)	90.6(3)	O(7)—Cu(2)—O(11)	91.1(3)
O(5)—Cu(1)—N(13)	166.8(4)	O(7)—Cu(2)—N(25)	171.2(3)
O(5)—Cu(1)—N(24)	92.1(3)	O(7)—Cu(2)—N(36)	92.8(3)
O(9)—Cu(1)—N(13)	95.8(3)	O(11)—Cu(2)—N(25)	94.5(3)
O(9)—Cu(1)—N(24)	169.8(3)	O(11)—Cu(2)—N(36)	173.9(3)
N(13)—Cu(1)—N(24)	79.7(4)	N(25)—Cu(2)—N(36)	81.2(3)
Cu(1)—O(5)—C(6)	129.7(6)	Cu(2)—O(7)—C(6)	125.6(6)
Cu(1)—O(9)—C(10)	123.3(6)	Cu(2)—O(11)—C(10)	131.9(6)
O(5)—C(6)—O(7)	125.8(8)	O(9)—C(10)—O(11)	125.3(8)

plete five-coordination at each metal atom. The metal coordination geometries are well described as square-pyramidal with the water oxygens O(3) and O(4) occupying the apical positions for Cu(1) and Cu(2), respectively. Analysis of the shape-determining angles using the approach of Reedijk and co-workers[14] yields τ values of 0.05 for both Cu(1) and Cu(2) ($\tau = 0$ and 1 for perfect *sp* and *tbp* geometries, respectively). As expected, the axial bonds are the longest. Cu(1) lies 0.177 Å and Cu(2) lies 0.096 Å out of their respective least-squares basal planes towards O(3) and O(4), respectively [max. deviation from the least-squares basal plane of Cu(1) and Cu(2) is 0.012 Å by N(24) and 0.020 Å by N(36), respectively]. The dihedral angle between the two basal CuO_2N_2 planes is 22.6°, and the angle between the two bpy planes is 8.24°. The Cu(1)···Cu(2) distance is 3.002(1) Å.

The structure of $[Cu_2(O_2CMe)_2(OClO_3)_2(bpy)_2]$ (**4**) shows great similarity to that of the cation of **3** with replacement of the aqua ligands of the latter by two terminal, axial monodentate perchlorato groups; this results in little structural perturbation. In **4** there is a two-fold crystallographic axis per-

Table 3. Selected bond distances (Å) and angles (°) for $[Cu_2(O_2CMe)_2(OClO_3)_2(bpy)_2]$ (4)

	Distances		
Cu(1)···Cu(1′)	3.035(1)	Cu(1)—O(21′)	1.957(3)
Cu(1)—O(15)	2.268(3)	Cu(1)—N(3)	1.974(3)
Cu(1)—O(19)	1.936(3)	Cu(1)—N(14)	1.997(3)
	Angles		
O(15)—Cu(1)—O(19)	84.9(1)	O(19)—Cu(1)—N(14)	93.9(1)
O(15)—Cu(1)—O(21′)	92.4(1)	O(21′)—Cu(1)—N(3)	91.4(1)
O(15)—Cu(1)—N(3)	94.0(1)	O(21′)—Cu(1)—N(14)	162.6(1)
O(15)—Cu(1)—N(14)	104.0(1)	N(3)—Cu(1)—N(14)	81.7(1)
O(19)—Cu(1)—O(21′)	93.4(2)	Cu(1)—O(19)—C(20)	130.6(3)
O(19)—Cu(1)—N(3)	175.1(1)	Cu(1)—O(21′)—C(20′)	127.4(3)
Cl(2)—O(15)—Cu(1)	130.5(2)	O(19)—C(20)—O(21)	125.4(4)

Table 4. Comparative structural data (Å, °) for complexes containing the $[Cu_2(syn,syn\text{-}\eta^1:\eta^1:\mu_2\text{-}O_2CR)_2]^{2+}$ core

Complex[a]	Cu···Cu	$Cu—O_{ax}$	O—C—O	Cu—O—C	Ref.
$[Cu_2(O_2CCH_2CH_2C_6H_5)_2(H_2O)_2(phen)_2]^{2+}$	3.054(1)	2.201(3)	126.3(4)	127.5	10
$[Cu_2(O_2CH)_2(H_2O)_2(phen)_2]^{2+}$	3.103(2)	2.151(5)	127.7(5)	128.7	11
$[Cu_2(O_2CMe)_2(H_2O)_2(phen)_2]^{2+}$	3.063(3)	2.201(7)	126.1(8)	129.3	11
$[Cu_2(O_2CMe)_2(H_2O)_2(bpy)_2]^{2+}$	3.002(1)	2.187(7), 2.265(7)	125.8(8), 125.3(8)	127.6	[b]
$[Cu_2(O_2CMe)_2(OClO_3)_2(bpy)_2]$	3.035(1)	2.268(3)	125.4(4)	129.0	[b]
$[Cu_2(O_2CC_2H_5)_2L_2]_n$[c]	3.122(1)	2.371(3), 2.519(3)	126.2(4), 126.2(3)	129.0	12
$[Cu_2(O_2CC_2H_5)_4L_2]_n$[d]	3.197(4)	2.318(13), 2.465(14)	122.6(23), 123.9(24)	129.9	13

[a] phen = 1,10-phenanthroline: L = *N*-*p*-tolylsalicylideneaminato (−1); L′ = *p*-toluidine.

[b] This work.

[c] The axial ligand at each Cu^{II} is provided by the phenolic oxygen atom of one L belonging to a neighbouring dimer.

[d] Only two of the four independent carboxylate groups function as *syn,syn* bidentate bridging ligands within each dimeric unit; the remaining two propionate groups form monoatomic oxygen bridges from a basal site of one copper atom to the apical site of its centrosymmetric equivalent belonging to a neighboring dimer.

pendicular to the mid-point of the Cu–Cu axis. The τ value is 0.21, indicating a distorted square-pyramidal Cu coordination geometry. The larger τ value is primarily a consequence of a twist of the two bpy groups (while still remaining parallel) about the crystallographic two-fold rotation axis. Cu(1) lies 0.123 Å above the O(19)O(21′)N(3)N(14) least-squares basal plane [max. deviation 0.158 Å by N(3)] towards O(15). The angle between the two CuO_2N_2 planes is 23.4°, and the angle between the two bpy planes is 3.60°. The Cu(1)···Cu(1′) distance is 3.035(1) Å. The Cu(1)—O(15) distance [2.268(3) Å] indicates a rather strong[15,16] copper(II)–perchlorate bond, comparable to the $Cu—OH_2$ bonds in **3**, and thus the Cu atoms are truly five-coordinate.

Complexes **3** and **4** represent the second and third, respectively, structurally-characterized examples of $[Cu_2(syn,syn\text{-}\eta^1:\eta^1:\mu_2\text{-}O_2CMe)_2]^{2+}$ complexes, i.e. dinuclear complexes containing two *syn,syn* acetates as the only bridging ligands. There are also four other, structurally-related complexes with a $[Cu_2(\mu\text{-}O_2CR)_2]^{2+}$ core. All these complexes are collected in Table 4, together with selected structural parameters for comparison. All contain two five-coordinate Cu ions with square-pyramidal coordination about each metal. The oxygen atoms of the bridging carboxylates and the donor atoms from the chelating ligands (phen, bpy, L) occupy the basal planes around the two Cu^{II} atoms. There is a significant stacking interaction (*vide infra*) between the aromatic ligands in the isolated dimers (the first five entries in Table 4). Cu···Cu separations are in the range 3.002–3.197 Å, and there is no correlation between Cu···Cu separation and O—C—O and Cu—O—C angles. Variations in $Cu—O_{axial}$(terminal) distances are again small in the isolated dimers. The mean Cu—O—C angles are all in the narrow range 127.5–129.9°, with the greater range of angles seen in **3** (123.3–131.9°).

Bpy stacking interactions and structural consequences

It is instructive to relate the structures of **3** and **4** to those of the tetra-bridged $Cu_2(O_2CR)_4L_2$ complexes[17,18] with a view to rationalizing the precise structural details of the former. In particular, for reasons outlined in the Introduction, it is important to establish the precise effect of the bpy–bpy stacking interactions on the observed structures. As originally pointed out elsewhere for related complexes,[10] the core structures of **3** and **4** can be derived from the $Cu_2(\mu\text{-}O_2CMe)_4$ core by replacement of two bridging $MeCO_2^-$ groups by two chelating bpy groups. Indeed, it is interesting that of the many products that we have obtained to date from the reactions of $Cu_2(O_2CMe)_4(H_2O)_2$ with bpy, **3** and **4** are the first to have a recognizable structural relationship to the starting Cu_2 dimer. Given that there are only two bridging acetates and no metal–metal bonding, we agree[10] that the structure of this family of complexes is maintained by attractive aromatic ring stacking interactions. Further, however, we believe these interactions are also the origin of the observed deviations from the "ideal" $Cu_2(O_2CMe)_4(H_2O)_2$ structure. The positioning of the two bpy groups in *syn* positions to facilitate stacking interactions defines the inter-bpy separation at ~ 3.4 Å. For the rings to stay parallel, the Cu···Cu separation must also be ~ 3.4 Å. However, this causes a problem at the bridging acetate groups whose intramolecular O···O bite distance (~ 2.24 Å) precludes them spanning a distance of ~ 3.4 Å if the Cu—O bonds are required to be parallel. Thus, the molecules distort by tilting of the two N_2O_2 square planes permitting the acetates to bridge. This, however, tilts the bpy rings away from each other, weakening the stacking interaction, and to compensate, the bpy rings tilt back towards each other. Thus, although the dihedral angle between the two N_2O_2 planes is 22.6° in **3** and 23.4° in **4**, the dihedral angle between the bpy rings is only 8.24° in **3** and 3.60° in **4**. These processes are facilitated by (or put another way, are the cause of) the Cu adopting square-pyramidal geometry with the Cu above the N_2O_2 plane, allowing the *trans* N—Cu—O angles to be less than 180°; note how the various tilts prevent, for example, O(4)—Cu(2)—Cu(1)—O(3) (Fig. 1) from being linear. Thus, the observed structures of **3** and **4** and their deviations from $Cu_2(O_2CR)_4L_2$ species are a compromise of various steric and electronic factors resulting from the incorporation of the *syn* bpy groups.

Room-temperature μ_{eff} values, UV–vis and IR spectroscopy

The room-temperature μ_{eff} values for **3** and **4** appear to exclude strong antiferromagnetic coupling; most probably they indicate a weak antiferromagnetic interaction. It is worth noting that the other complexes with the $[Cu_2(\mu\text{-}O_2CR)_2]^{2+}$ core are weakly antiferromagnetically coupled ($2J$ between -125 and -86 cm^{-1}).[10–13] These $-2J$ values are much less than those found in the $Cu_2(O_2CR)_4L_2$ complexes ($2J$ between -250 and -560 cm^{-1}).[17–19] This decrease has been rationalized[11] in terms of the decrease in the number of bridging carboxylato groups by which the superexchange interaction is mediated.

Complexes **3** and **4** possess similar solid-state electronic spectra, in agreement with their similar structures. Both exhibit one LMCT ($MeCO_2^-$-to-Cu^{II}) transition[20] at 365(3) and 355(4) nm and two *d–d* transitions at lower energies. The *d–d* frequencies are typical of square-pyramidal structures with a CuN_2O_3 chromophore.[11,20] The *d–d* spectra of both **3** and **4** in dry MeCN consist of a broad, featureless band at ~ 625 nm. These spectra are different from the solid-state spectra, indicating structural changes upon dissolution. It is unlikely that the solid-state structure is retained on dissolution in MeCN.[10] Instead, mononuclear, solvated $Cu/MeCO_2^-/bpy$ species are undoubtedly present.

In the IR spectrum, complex **3** exhibits bands at 3580 and ~ 3450 cm^{-1}, assignable to bound and lattice water groups, respectively.[21] The broadness and relatively low frequency of the second band are both indicative of hydrogen bonding. The $\nu_{as}(COO)$ and $\nu_s(COO)$ bands of **3** and **4** are at 1580–1576 and ~ 1450 cm^{-1}, respectively; the difference Δ [$\Delta = \nu_{as}(COO) - \nu_s(COO)$] (125 cm^{-1} for **3**, 121 cm^{-1} for **4**) is less than that for NaO_2CMe (164 cm^{-1}), as expected for the bidentate bridging mode of carboxylate ligation.[21,22] The number and the frequencies of the ClO_4^- modes in **4** are consistent with monodentate perchlorato groups of C_{3v} symmetry.[15,21] In **3**, bands assignable to ClO_4^- groups of both T_d and C_{3v} symmetry are observed, suggesting that one ClO_4^- group is involved in hydrogen-bonding interactions with H_2O groups.[23]

CONCLUSIONS

Facile methods to complexes with the $[Cu_2(\mu\text{-}O_2CMe)_2(bpy)_2]^{2+}$ core have been developed, allowing detailed consideration of the structural perturbation on the copper acetate core of two *syn*- and π-stacked bpy groups. This information will be vital in our continuing study of the isomerization of $[Mo_2(O_2CMe)_2(bpy)_2]^{2+}$, as described earlier. It is clear from the structural descriptions of **3** and **4** that the *syn*-bpy groups have a *significant* structural effect; it is also readily apparent how significant will be the additional requirement that the metal–metal distance in the $[M_2(O_2CMe)_2(bpy)_2]^{2+}$ unit decreases from ~ 3.0 Å for M = Cu^{2+} to ~ 2.5 Å for M = Rh^{2+}, and to ~ 2.1 Å for M = Mo^{2+}. These matters are the subjects of ongoing investigations, and will be reported in due course.

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