

THE REACTIONS OF $\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{H}_2\text{O})_2$ WITH 2,2'-BIPYRIDINE (bpy): INFLUENCE OF THE Cu:bpy RATIO, AND THE STRUCTURE OF A LINEAR POLYMER COMPRISING TWO ALTERNATING TYPES OF Cu_2 UNITS

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Abstract—Further investigation of the $\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{H}_2\text{O})_2/\text{bpy}$ reaction system is described, including the determination of the influence of the $\text{Cu}^{\text{II}}:\text{bpy}$ ratio (x) on the identity of the reaction products. Values of x in the 1–2 range have been employed. Reaction of $\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{H}_2\text{O})_2$ with two equivalents of bpy ($x = 1$) in MeCN yields $[\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{bpy})_2] \cdot 2\text{H}_2\text{O}$ (**1**) in 79% yield. Treatment of $\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{H}_2\text{O})_2$ with 1.33 equivalent of bpy ($x = 1.5$) in MeCN leads to precipitation of the polymeric compound $[-\text{Cu}_2(\text{O}_2\text{CMe})_2(\text{bpy})_2-\text{O}_2\text{CMe}-\text{Cu}_2(\text{O}_2\text{CMe})_4-\text{O}_2\text{CMe}-]_n$ (**2**); from the filtrate **1** slowly crystallizes in 15% yield. A high yield (89%) of pure **2** can be obtained by increasing x from 1.5 to 2. Treatment of **1** with $\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{H}_2\text{O})_2$ in MeCN provides an additional route to **2**. Compound **2** reacts with equimolar bpy in EtOH to yield complex **1**. Complex **1** undergoes facile carboxylate substitution in MeCN with an excess of PhCOOH, leading to reasonable yields (40–65%) of $[\text{Cu}_2(\text{O}_2\text{CPh})_4(\text{bpy})_2] \cdot \text{MeCN}$ (**3a**) or $[\text{Cu}_2(\text{O}_2\text{CPh})_4(\text{bpy})_2] \cdot 2\text{H}_2\text{O}$ (**3b**), depending on the rate of crystallization. Complex **2** is converted to the known compound $\text{Cu}_2(\text{O}_2\text{CPh})_4(\text{EtOH})_2$ (**4**) or **3b** by treatment with excess PhCOOH in EtOH or MeCN, respectively. Complexes **1** and **2** undergo a variety of additional reactions that lead to the dinuclear complexes $[\text{Cu}_2(\text{O}_2\text{CMe})_3(\text{bpy})_2](\text{ClO}_4)$ (**5**), $[\text{Cu}_2(\text{OH})(\text{H}_2\text{O})(\text{O}_2\text{CMe})(\text{bpy})_2](\text{ClO}_4)_2$ (**6**), $\text{Cu}_2(\text{OH})_2(\text{bpy})_2(\text{ClO}_4)_2$ (**7**), $[\text{Cu}_2(\text{O}_2\text{CMe})_2(\text{H}_2\text{O})_2(\text{bpy})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**8**) and $\text{Cu}_2(\text{O}_2\text{CMe})_2(\text{ClO}_4)_2(\text{bpy})_2$ (**9**). Complex **1** crystallizes in the triclinic space group $P\bar{1}$ with (at -143°C) $a = 8.842(2)$, $b = 12.266(2)$, $c = 7.708(1)$ Å, $\alpha = 98.72(1)$, $\beta = 106.35$, $\gamma = 109.68(1)^\circ$, $Z = 1$ and $V = 726.68$ Å³. A total of 2318 unique reflections with $F > 3.00\sigma(F)$ were refined to values of R and R_w of 2.67 and 2.87%, respectively. Compound **2** crystallizes in the triclinic space group $P\bar{1}$ with (at -155°C) $a = 9.272(2)$, $b = 14.718(3)$, $c = 8.023(1)$ Å, $\alpha = 102.66(1)$, $\beta = 103.89(1)$, $\gamma = 94.00(1)^\circ$, $Z = 1$ and $V = 1028.21$ Å³. A total of 2319 unique reflections with $F > 3.00\sigma(F)$ were refined to values of R and R_w of 3.68 and 3.96%, respectively. The structure of **1** consists of a $[\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{bpy})_2]$ molecule located at a centre of symmetry with two *syn,anti* acetate bridges. The molecules of **1** form infinite ladder-like chains as a result of hydrogen-bonding interactions with the water molecules. The structure of **2** is composed of one-dimensional, well-separated polymeric chains and contains two different types of copper(II) dinuclear units, each at a crystallographic centre of symmetry. The chains are formed by alternating $\text{Cu}_2(\text{O}_2\text{CMe})_4$ and $[\text{Cu}_2(\text{O}_2\text{CMe})_2(\text{bpy})_2]^{2+}$ units which are linked by *syn,anti* bridging acetates. The $\text{Cu}_2(\text{O}_2\text{CMe})_4$ unit has a tetra-bridged structure with four *syn,syn* bridging acetates and two oxygens from the two *syn,anti* acetates occupying the axial positions. The other dinuclear unit has a structure with two acetate groups

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forming mono-atomic bridges. From the IR and UV-vis solution spectra, it is concluded that the polymeric structure of **2** is not retained in MeCN. A cyclic voltammetric study of **1** in MeCN reveals a quasi-reversible reduction at -0.82 V vs ferrocene, and an irreversible reduction at -1.82 V yielding copper metal which deposits on the electrode. Complex **3b** displays almost identical processes. Compound **2** displays two reduction processes at -0.84 and -1.82 V.

In recent reports,¹ we have described the initial results from a systematic investigation of the reactivity characteristics of $\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{H}_2\text{O})_2$ with 2,2'-bipyridine (bpy). This investigation had been stimulated by a variety of reasons, not least of which is the continuing utility of non-mononuclear Cu^{II} complexes for magnetochemical study to assist in understanding how structural features can affect the nature (ferromagnetic or antiferromagnetic) and magnitude of intramolecular magnetic exchange interactions.² In addition, we have been exploring in detail over the last few years the reactions of a variety of manganese carboxylates with bpy,³ and had recently extended this work to Fe.⁴ It thus seemed natural to seek to extend this work further to copper, and allow better comparisons and contrasts to be made concerning the influence of 3d metal identity on the reaction product(s).

In the previous papers,¹ we reported that treatment of $\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{H}_2\text{O})_2$ with two equivalents of bpy in EtOH or H_2O , followed by addition of NaClO_4 , leads to the isolation of salts containing the cations $[\text{Cu}_2(\text{O}_2\text{CMe})_3(\text{bpy})_2]^+$ and $[\text{Cu}_2(\text{OH})(\text{H}_2\text{O})(\text{O}_2\text{CMe})(\text{bpy})_2]^{2+}$, respectively. These ions contain bridging units not seen before in dinuclear Cu^{II} chemistry and provided two new examples of species with ferromagnetic exchange interactions. It was suspected that we had merely scratched the surface of this area, and decided to investigate carefully the influence on product identity of a number of experimental parameters. In this report, we describe the identity of the products obtained from the $\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{H}_2\text{O})_2/\text{bpy}$ reaction system in the absence of added ClO_4^- , and the influence on product identity of small changes to the Cu:bpy ratio.

EXPERIMENTAL

Compound preparation

All manipulations were performed under aerobic conditions using materials as received.

CAUTION: *Perchlorate salts are potentially explosive.*

Although no detonation tendencies have been observed in this work, caution is advised and handling of only small quantities is recommended.

(1) $x = 1$: $[\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{bpy})_2] \cdot 2\text{H}_2\text{O}$ (**1**). Solid $\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{H}_2\text{O})_2$ (1.00 g, 2.50 mmol) was slowly dissolved with stirring in a solution of bpy (0.78 g, 5.0 mmol) in MeCN (100 cm^3). A deep blue homogeneous solution was obtained. This was allowed to stand undisturbed for 3 days, and the resulting well-formed blue crystals were collected by filtration, washed with MeCN and Et_2O , and dried in air; yield, 1.40 g (79%). The product was recrystallized from MeCN/ Et_2O . The complex can also be prepared using MeCN/EtOH (1:1) as a solvent mixture. Found: C, 47.5; H, 4.5; N, 7.9. Calc. for $\text{C}_{28}\text{H}_{32}\text{N}_4\text{O}_{10}\text{Cu}_2$: C, 47.2; H, 4.5; N, 7.9%. Magnetic moment per Cu^{II} (Faraday method): $1.82 \mu_{\text{B}}$ at 25.2°C . Solid-state (diffuse-reflectance) electronic spectrum: λ_{max} , nm; 375, 402 (sh), 715 (sh), 735. Electronic spectrum in MeCN: λ_{max} , nm ($\epsilon_{\text{M}}/\text{Cu}_2$, $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$); 384 (154), 670 (174).

(2) $x = 1.5$: *Complex 1 and* $[\text{Cu}_4(\text{O}_2\text{CMe})_8(\text{bpy})_2]_n$ (**2**). To a stirred solution of $\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{H}_2\text{O})_2$ (1.00 g, 2.50 mmol) in warm MeCN (100 cm^3) was added bpy (0.52 g, 3.3 mmol) in small portions to give a deep blue solution. The flask was stored at ambient temperature for 2 days, and the resulting blue crystals of **2** were collected by filtration, washed with MeCN and Et_2O (not added to the filtrate) and dried *in vacuo*; yield 0.82 g (63% based on copper). Recrystallization can be effected from EtOH/ Et_2O . The filtrate was allowed to slowly concentrate by evaporation at room temperature to give blue crystals of **1** (identified by IR), which were collected by filtration, washed with Et_2O and dried in air; yield, 0.27 g (15%). Data for **2**: Found: C, 41.4; H, 3.8; N, 5.4; Cu, 24.2. Calc. for $\text{C}_{36}\text{H}_{40}\text{N}_4\text{O}_{16}\text{Cu}_4$: C, 41.6; H, 3.8; N, 5.4; Cu, 24.5%. Magnetic moment per Cu^{II} (Faraday method): $1.68 \mu_{\text{B}}$ at 21.1°C . Solid-state (diffuse-reflectance) electronic spectrum: λ_{max} , nm; 385, 405, 680, 805. Electronic spectrum in MeCN: λ_{max} , nm ($\epsilon_{\text{M}}/\text{Cu}_4$, $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$); 378 (237), 672 (564).

(3) $x = 2$: *Complex 2*. To a stirred slurry of $\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{H}_2\text{O})_2$ (1.50 g, 3.75 mmol) in MeCN (120 cm^3) was slowly added solid bpy (0.58 g, 3.75 mmol). The resulting dark blue solution was stirred for a further 10–15 min and the flask stored in a freezer for 2 days. The large blue crystals of **2** thus obtained were collected by filtration, washed with

MeCN/Et₂O (1 : 1) and dried *in vacuo*; yield 1.7 g (87%). The crystals had an IR spectrum identical to that from method (2). The same synthetic procedure [1.50 g of $\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{H}_2\text{O})_2$, 0.58 g of bpy] in EtOH (110 cm³) gave no precipitate in the freezer. Addition of Et₂O (180 cm³) to the solution resulted in the formation of a blue microcrystalline precipitate, which was collected by filtration, washed with Et₂O and dried *in vacuo*; yield 1.4 g (72%). The product was identical to **2** on spectroscopic examination.

Conversion of 1 to 2. To a stirred solution of $\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{H}_2\text{O})_2$ (0.50 g, 1.25 mmol) in MeCN (40 cm³) was added a solution of complex **1** (0.89 g, 1.25 mmol) in MeCN (20 cm³) to give a blue solution. Stirring was continued for a further 30 min; precipitation of a microcrystalline pale blue solid began almost immediately. After overnight storage in a freezer, the resulting precipitate was collected by filtration, washed with MeCN/Et₂O (1 : 1) and dried *in vacuo*; yield 0.82 g (63%). The product was recrystallized from EtOH/Et₂O. The IR of the solid was identical to that of complex **2**.

Conversion of 2 to 1. To a stirred, filtered, blue solution of complex **2** (0.50 g, 0.48 mmol) in 96% EtOH (70 cm³) was slowly added solid bpy (0.15 g, 0.96 mmol) in small portions to give a darker blue solution. After the solution was stirred overnight, it was allowed to slowly concentrate until the volume was *ca* 20 cm³. Addition of Et₂O (40 cm³) gave blue flakes of **1**, which were collected by filtration, washed with Et₂O and dried in air; yield 0.54 g (79%). The IR of the solid was identical to that of complex **1**.

$[\text{Cu}_2(\text{O}_2\text{CPh})_4(\text{bpy})_2] \cdot \text{solv}$ [solv = MeCN (**3a**) or 2H₂O (**3b**)]. A solution of complex **1** (0.21 g, 0.30 mmol) in freshly distilled MeCN (20 cm³) was treated with a solution of PhCOOH (0.29 g, 2.4 mmol) in the same solvent (5 cm³). No noticeable colour change occurred. Overnight storage of the flask containing the undisturbed solution in a refrigerator yielded dark blue crystals which were collected by filtration and washed with Et₂O; yield 0.19 g (65%). Found: C, 62.1; H, 4.3; N, 7.6. Calc. for C₅₀H₃₉N₅O₈Cu₂: C, 62.2; H, 4.1; N, 7.3%. Magnetic moment per Cu^{II} (Faraday method): 1.84 μ_B at 21.0°C. Solid-state (diffuse-reflectance) spectrum: λ_{max}, nm; 384, 400 (sh), 730. The crystalline solid is slightly hygroscopic; this is supported by the H₂O peaks observed in an IR spectrum of an aged sample. Stirring of the reaction solution to **3a** initiated precipitation of a blue powder, which, after overnight storage in a refrigerator, was collected by filtration, washed with Et₂O and dried *in vacuo*; the yield was *ca* 40%. Analytical data for the powder indicated the composition $[\text{Cu}_2(\text{O}_2\text{CPh})_4(\text{bpy})_2] \cdot$

2H₂O (**3b**). Found: C, 60.3; H, 4.1; N, 6.0. Calc. for C₄₈H₄₀N₄O₁₀Cu₂: C, 60.0; H, 4.2; N, 5.8%. The IR spectrum of **3b** is very similar to that of **3a**; the main differences are the absence of the MeCN band at 2250 cm⁻¹ and the presence of a medium broad band at *ca* 3350 cm⁻¹, due to the water stretching mode.

Reaction of 2 with PhCOOH. PhCOOH (0.28 g, 2.29 mmol) was dissolved in a stirred, filtered, blue solution of complex **2** (0.24 g, 0.23 mmol) in MeCN (80 cm³). No noticeable colour change occurred. Slow evaporation of solvent at ambient temperature yielded long blue needles, which were collected by filtration, washed with Et₂O and dried in air; yield, 0.07 g (16% based on total available copper). The product had an IR spectrum identical with that of compound **3b**. A stirred, filtered, blue solution of complex **2** (0.50 g, 0.48 mmol) in EtOH (70 cm³) was treated with PhCOOH (0.70 g, 5.73 mmol). Stirring was continued for a further 5 min. After overnight storage in a freezer, the resulting greenish-turquoise needles of the known⁵ compound $\text{Cu}_2(\text{O}_2\text{CPh})_4(\text{EtOH})_2$ (**4**) were collected by filtration, washed with EtOH and dried in air; yield 0.24 g (36% based on total available copper). Found: C, 53.8; H, 4.4; Cu, 18.2. Calc. for C₃₂H₃₂O₁₀Cu₂: C, 54.6; H, 4.6; Cu, 18.1%. The dark blue filtrate was allowed to slowly concentrate by evaporation at ambient temperature. After several days, long blue needles of **3b** and a turquoise microcrystalline precipitate of **4** were obtained. These were carefully collected by filtration, washed with a little EtOH and dried in air. The two products were readily separable manually, and complexes **3b** and **4** were obtained in yields (based on total available copper) of 20% and 10%, respectively; their identity was confirmed by IR spectroscopy.

Conversion of 1 to $[\text{Cu}_2(\text{O}_2\text{CMe})_3(\text{bpy})_2](\text{ClO}_4)$ (5**) with NaClO₄.** To a stirred blue solution of **1** (0.20 g, 0.28 mmol) in MeCN (25 cm³) was added a solution of NaClO₄ (0.035 g, 0.28 mmol) in EtOH (10 cm³). No noticeable colour change occurred. Stirring was continued for a further 10 min. Slow evaporation of solvents at ambient temperature yielded sky blue crystals of $[\text{Cu}_2(\text{O}_2\text{CMe})_3(\text{bpy})_2](\text{ClO}_4)$ (**5**), which were collected by filtration, washed with Et₂O and dried *in vacuo*; yield 0.14 g (70%). The identity of the product was deduced by IR and electronic spectral comparison with authentic material.¹

Conversion of 1 and 2 to $[\text{Cu}_2(\text{OH})(\text{H}_2\text{O})(\text{O}_2\text{CMe})(\text{bpy})_2](\text{ClO}_4)_2$ (6**).** Complex **1** (0.43 g, 0.6 mmol) was dissolved in H₂O (15 cm³). The resulting deep blue solution was stirred while solid NaClO₄ (0.15 g, 1.2 mmol) was added to give the blue powder of $[\text{Cu}_2(\text{OH})(\text{H}_2\text{O})(\text{O}_2\text{CMe})$

(bpy)₂](ClO₄)₂ (**6**).¹ The reaction mixture was stirred for a few minutes and the precipitate was collected by filtration, washed with EtOH and Et₂O, and dried *in vacuo*; yield 0.15 g (34%). To a solid mixture containing complex **2** (0.50 g, 0.48 mmol) and bpy (0.15 g, 0.96 mmol) was added EtOH (10 cm³). To the resulting slurry was added H₂O (10 cm³). The mixture was stirred to yield a blue homogeneous solution which was treated with NaClO₄ (0.24 g, 1.96 mmol). The resulting solution began to precipitate blue microcrystals of **6** within minutes. The solid was collected by filtration, washed with THF and Et₂O, and dried *in vacuo*; yield 0.39 g (56%). The identity of **6** was deduced by IR and electronic spectral comparison with authentic material.¹

*Conversion of 1 and 2 to Cu₂(OH)₂(bpy)₂(ClO₄)₂ (**7**).* A deep blue solution of complex **1** (0.43 g, 0.6 mmol) in H₂O (10 cm³) was treated with an aqueous solution (15 cm³) containing NaOH (0.048 g, 1.2 mmol) and NaClO₄ (0.15 g, 1.2 mmol). This gave a lavender precipitate of the known⁶ compound Cu₂(OH)₂(bpy)₂(ClO₄)₂ (**7**). The powder was collected by filtration, washed with EtOH and Et₂O, and dried *in vacuo*; yield 0.36 g (90%). A blue solution of complex **2** (0.50 g, 0.48 mmol) in H₂O (10 cm³) was treated with a solution of bpy (0.15 g, 0.96 mmol) in EtOH (10 cm³) to give a deep blue homogeneous solution. Addition of an aqueous solution (12 cm³) containing NaClO₄ (0.24 g, 1.96 mmol) and NaOH (0.77 g, 1.92 mmol) immediately yielded a lavender powder of **7**. The reaction mixture was stirred for 10 min at room temperature and the solid was collected by filtration, washed with EtOH and Et₂O, and dried *in vacuo*; yield 0.59 g (92%). The identity of **7** was confirmed by IR and electronic spectral comparison with authentic material.⁶

*Conversion of 2 to [Cu₂(O₂CMe)₂(H₂O)₂(bpy)₂](ClO₄)₂·H₂O (**8**).* A solution of complex **2** (0.62 g, 0.6 mmol) in H₂O (15 cm³) was treated with a solution of bpy (0.19 g, 1.2 mmol) in glacial MeCOOH (5 cm³) to give a royal blue solution. To this was added a solution of NaClO₄ (0.3 g, 2.4 mmol). The homogeneous solution obtained was allowed to stand undisturbed at 5°C and the resulting large dark blue crystals of [Cu₂(O₂CMe)₂(H₂O)₂(bpy)₂](ClO₄)₂·H₂O (**8**) were collected by filtration, washed with Et₂O and dried in air; yield 0.53 g (55%). The identity of **8** was deduced by IR and electronic spectral comparison with authentic material.⁷

*Conversion of 2 to Cu₂(O₂CMe)₂(ClO₄)₂(bpy)₂ (**9**).* To a solution of complex **2** (0.62 g, 0.6 mmol) in H₂O (7 cm³) was added a solution of bpy (0.19 g, 1.2 mmol) in a glacial MeCOOH (3 cm³) with

stirring. The resulting royal blue solution was treated with solid NaClO₄ (0.3 g, 2.4 mmol) to yield the fine royal blue powder of Cu₂(O₂CMe)₂(ClO₄)₂(bpy)₂ (**9**). When precipitation was judged to be complete, the solid was filtered, washed with a little H₂O, EtOH and Et₂O, and dried *in vacuo* overnight; yield 0.28 g (31%). The product had IR and electronic spectra identical with those of authentic complex **9**.⁷

X-ray crystallography and structure solution

Data were collected on a Picker four-circle diffractometer at -143 and -155°C for **1** and **2**, respectively; details of the diffractometry, low-temperature facilities and computational procedures employed by the Molecular Structure Center are available elsewhere.⁸ Data collection parameters are summarized in Table 1. The structures were solved by a combination of direct methods (MULTAN) and Fourier techniques and refined by full-matrix least-squares. For both complexes **1** and **2**, a systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with no symmetry or systematic absences. The maxima were indexed using a triclinic lattice and the space group *P* $\bar{1}$ was confirmed by the subsequent solution and refinement of the structures.

For both complexes, all non-hydrogen atoms were readily located and refined with anisotropic thermal parameters. For **1**, all hydrogen atoms were clearly visible in a subsequent difference Fourier map; for **2**, essentially all hydrogen atoms were located. All hydrogen atoms were included in the final cycles and refined with isotropic thermal parameters. Final difference Fourier maps were essentially featureless, the largest peaks being 0.32 and 0.4 e Å⁻³ for **1** and **2**, respectively. Final values of *R* and *R_w* are listed in Table 1.

Other measurements

Elemental analyses were performed at the Microanalytical Laboratory, Department of Chemistry, Manchester University, England. IR spectra were recorded as Nujol mulls or KBr discs using a Nicolet 510P or Perkin-Elmer 283 spectrophotometer. Solid-state (diffuse-reflectance, 890–340 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(NCS)₄. The molar susceptibilities were corrected for the diamagnetism of the constituent atoms using Pascal's constants.

Table 1. Crystallographic data for complexes 1 and 2

| Parameter | 1 | 2 |
|---|--|--|
| Formula | $\text{C}_{28}\text{H}_{32}\text{N}_4\text{O}_{10}\text{Cu}_2$ | $\text{C}_{36}\text{H}_{40}\text{N}_4\text{O}_{16}\text{Cu}_4$ |
| M_r (g mol^{-1}) | 711.67 | 1038.91 |
| Space group | $P\bar{1}$ | $P\bar{1}$ |
| Temperature ($^\circ\text{C}$) | -143 | -155 |
| a (\AA) | 8.842(2) | 9.272(2) |
| b (\AA) | 12.266(2) | 14.718(3) |
| c (\AA) | 7.708(1) | 8.023(1) |
| α ($^\circ$) | 98.72(1) | 102.66(1) |
| β ($^\circ$) | 106.35(1) | 103.89(1) |
| γ ($^\circ$) | 109.68(1) | 94.00(1) |
| V (\AA^3) | 726.68 | 1028.21 |
| Z | 1 | 1 |
| ρ_{calc} (g cm^{-3}) | 1.626 | 1.678 |
| λ (\AA) | 0.71069 | 0.71069 |
| μ (cm^{-1}) | 15.288 | 21.198 |
| Data collected | $6^\circ \leq 2\theta \leq 50^\circ$ | $6^\circ \leq 2\theta \leq 45^\circ$ |
| Observed data | 2318 ^a | 2319 ^a |
| $R(R_w)$ (%) | 2.67 (2.87) | 3.68 (3.96) |

^a $F > 3.00\sigma(F)$.

Cyclic and differential pulse voltammograms were recorded on an IBM Model EC 225 voltammetric analyser, a PAR Model 175 universal programmer, and a standard three-electrode assembly (glassy carbon working, platinum wire auxiliary, SCE reference) with 0.1 M $\text{NBu}_4^+\text{ClO}_4^-$ as supporting electrolyte. No IR compensation was employed. Quoted $E_{1/2}$ values (± 0.01 V) are vs the ferrocene/ferricinium couple under the same conditions. The scan rate was 100 mV s^{-1} for CV, unless otherwise indicated. Differential Pulse Voltammograms (DPV) were carried out at 5 mV s^{-1} with a 25 mV pulse amplitude.

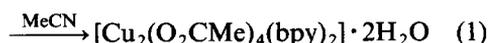
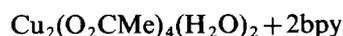
RESULTS AND DISCUSSION

Syntheses and reactivity studies

For convenience, the syntheses and transformations described in this work are summarized in schematic form in Fig. 1.

In our initial studies of $\text{Cu}^{\text{II}}/\text{RCO}_2^-/\text{bpy}$ chemistry,¹ we had employed with success the fact that chelating bpy cannot be accommodated by the quadruply-bridged $\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{H}_2\text{O})_2$ unit without serious structural perturbation. Reaction of $\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{H}_2\text{O})_2$ with two equivalents of bpy in EtOH followed by addition of ClO_4^- or PF_6^- led to $[\text{Cu}_2(\text{O}_2\text{CMe})_3(\text{bpy})_2]^+$ products possessing a novel type of triply-bridged core. In extending the investigation of this system, the product in the absence of added counter-ion has been determined.

Preliminary efforts showed clean reactions could be obtained in several solvents, but MeCN was found to yield a nicely crystalline product with minimal work-up. Thus, an MeCN reaction mixture containing one equivalent of $\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{H}_2\text{O})_2$ and two equivalents of bpy gave a deep blue solution from which pure, highly crystalline $[\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{bpy})_2] \cdot 2\text{H}_2\text{O}$ (1) can be obtained in high yield (79%). Its formation can be summarized in eq. (1). The structure of this compound was determined by X-ray



crystallography; the $[\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{bpy})_2]$ unit possesses two $\eta^1:\eta^1:\mu_2$ acetate bridging ligands and two monodentate hydrogen-bonded acetate groups (*vide infra*).

Having obtained and identified complex 1, the next question addressed was whether, and in what manner, small changes to the $\text{Cu}^{\text{II}}:\text{bpy}$ ratio (x) might affect the product identity. In particular, we wondered whether it might be possible to prepare a linear trinuclear complex of formula $\text{Cu}_3(\text{O}_2\text{CMe})_6(\text{bpy})_2$, akin to the Mn^{II} analogue,³ employing $x = 1.5$. Such linear trinuclear Cu^{II} complexes are rare and possess interesting structural and magnetic features.⁹ However, the $x = 1.5$ reaction did not yield a trinuclear product. Instead, treatment of $\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{H}_2\text{O})_2$ with 1.33 equivalents of bpy ($x = 1.5$) in MeCN led to the slow

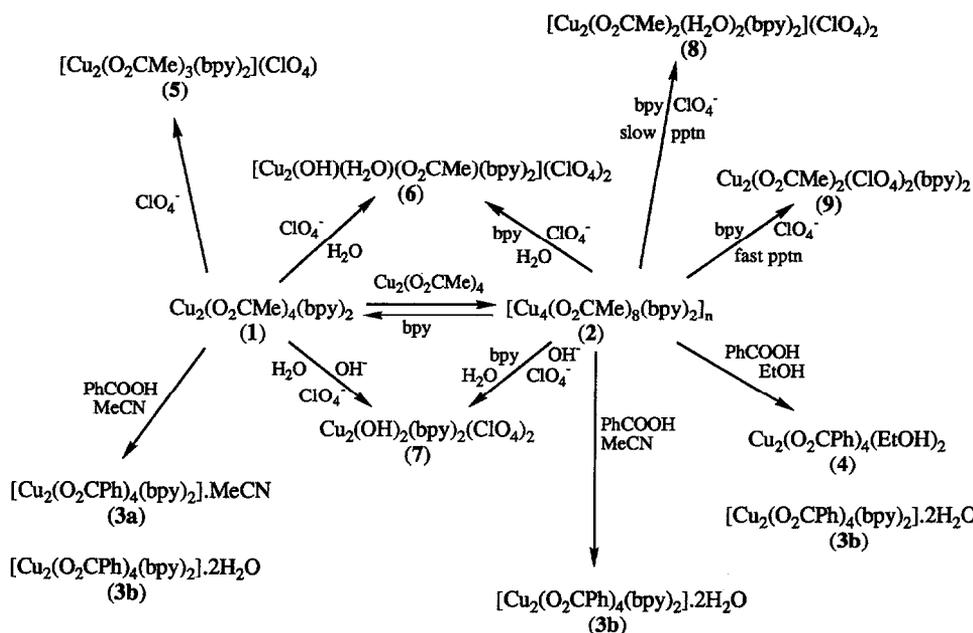
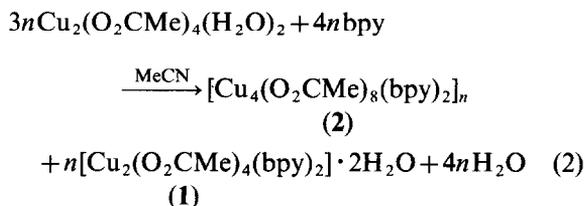
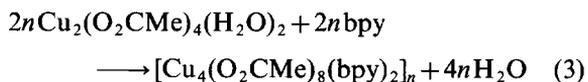


Fig. 1. The transformations of $[\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{bpy})_2] \cdot 2\text{H}_2\text{O}$ (1) and $[\text{Cu}_4(\text{O}_2\text{CMe})_8(\text{bpy})_2]_n$ (2) described in the text.

precipitation of $[-\text{Cu}_2(\text{O}_2\text{CMe})_2(\text{bpy})_2-\text{O}_2\text{CMe}-\text{Cu}_2(\text{O}_2\text{CMe})_4-\text{O}_2\text{CMe}-]_n$ (2), hereafter written as $[\text{Cu}_4(\text{O}_2\text{CMe})_8(\text{bpy})_2]_n$, possessing an interesting one-dimensional polymeric structure. The blue, highly crystalline precipitate was collected by filtration (yield 63%); from the filtrate 1 slowly crystallized in 15% yield. A reasonable rationalization of these observations, based on the reaction stoichiometry, is presented in eq. (2); this balanced equation predicts that the yields of 2 and 1 should be 67 and 33%,

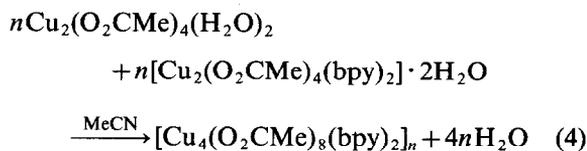


respectively, consistent with the experimental values. With the identity of 2 established, a high-yield preparative route was devised by adjusting x from 1.5 to 2 [eq. (3)]. The same reaction in EtOH instead of MeCN also gave 2 although Et₂O had to be added to initiate precipitation of the product as blue microcrystals.

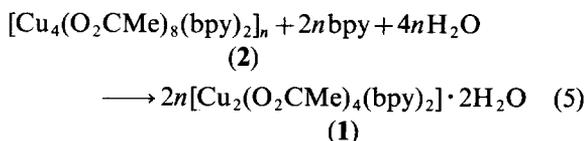


Since complexes 1 and 2 result from the use of different Cu : bpy ratios (x), it seemed reasonable to suspect that they could be interconverted by

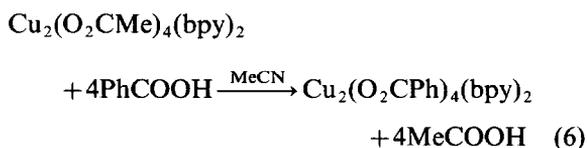
treatment of the preformed materials with appropriate reagents. The conversion of 1 to 2 can be accomplished quite easily by treatment of 1 with $\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{H}_2\text{O})_2$ [eq. (4)]; indeed, this reaction has potential



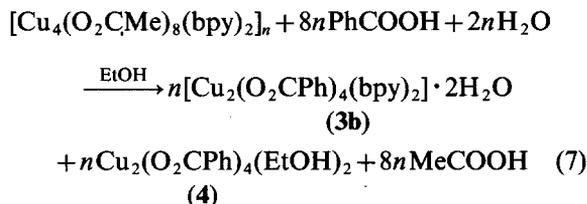
as a route to mixed-metal chains composed of alternating dinuclear units by employment of other $\text{M}_2(\text{O}_2\text{CMe})_4$ species (e.g. M = Mo, Cr, Rh, etc.). In a similar fashion, complex 2 can be converted to 1 by treatment with bpy [eq. (5)].



Complex 1 has been found to undergo facile carboxylate exchange with the more acidic PhCOOH. Thus, treatment of 1 in MeCN with an excess of PhCOOH leads to clean isolation of $\text{Cu}_2(\text{O}_2\text{CPh})_4(\text{bpy})_2$ (3) [eq. (6)] in reasonable yields with either MeCN (3a) or

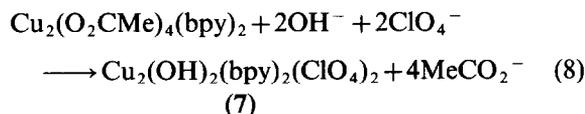


$2\text{H}_2\text{O}$ (**3b**) solvates of crystallization, depending on the rate of crystallization. Similar exchange reactions have been observed with other $\text{M}/\text{MeCO}_2^-/\text{bpy}$ ($\text{M} = \text{Cu}^2, \text{Mn}^4, \text{Fe}^5$) complexes. Attempts to carry out the analogous substitution on complex **2** were unsuccessful; in the same medium as eq. (6) (MeCN), only small amounts of complex **3b** were isolated (16% yield based on total copper). Employing EtOH as reaction medium, however, allowed isolation of both **3b** and the known complex $\text{Cu}_2(\text{O}_2\text{CPh})_4(\text{EtOH})_2$ (**4**).⁵ Since **3** and **4** are the constituent components of the target polymer $\text{Cu}_4(\text{O}_2\text{CPh})_8(\text{bpy})_2$, the failure to isolate the latter is presumably due to lattice energy effects and the precipitation of the least-soluble species. Polymers **2** and hypothetical $\text{Cu}_4(\text{O}_2\text{CPh})_8(\text{bpy})_2$ would undoubtedly dissociate into their constituent units in good donor solvents such as MeCN (*vide infra*). The reaction of **2** with PhCOOH is summarized in eq. (7).



Dissolution of **1** in MeCN and addition of NaClO_4 leads to isolation of $[\text{Cu}_2(\text{O}_2\text{CMe})_3(\text{bpy})_2](\text{ClO}_4)$ (**5**), as expected based on previously published work.¹ This transformation supports our previous suspicion of complex chemistry/

equilibria and the presence of multiple species in solution. Using an aqueous reaction medium, the product is $[\text{Cu}_2(\text{OH})(\text{H}_2\text{O})(\text{O}_2\text{CMe})(\text{bpy})_2](\text{ClO}_4)_2$ (**6**), again as expected from previous work.¹ Similarly, treatment of complex **1** with NaOH and NaClO_4 leads to the di- μ -hydroxo-bridged complex $\text{Cu}_2(\text{OH})_2(\text{bpy})_2(\text{ClO}_4)_2$ (**7**)¹⁶ [eq. (8)].



Complexes **5**, **6** and **7** can also be obtained by employing complex **2** and added bpy in the above reactions instead of complex **1**. This is as expected, given the conversion of **2** to **1** with added bpy.

Finally, we have found that the treatment of complex **2** with bpy and NaClO_4 in aqueous acetic acid leads not to $[\text{Cu}_2(\text{OH})(\text{H}_2\text{O})(\text{O}_2\text{CMe})(\text{bpy})_2](\text{ClO}_4)_2$ (**6**) as found at approximately neutral pH, but to either $[\text{Cu}_2(\text{O}_2\text{CMe})_2(\text{H}_2\text{O})_2(\text{bpy})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**8**) or $[\text{Cu}_2(\text{O}_2\text{CMe})_2(\text{ClO}_4)_2(\text{bpy})_2]$ (**9**), depending on the solvent's H_2O content and resulting rate of crystallization. In both complexes, the metal centres are bridged by only two MeCO_2^- groups. The crystal structures of both these complexes have been determined and a full description of this work will be reported elsewhere.⁶

Description of structures

ORTEP projections of complexes **1** and **2** are shown in Figs 2 and 4, respectively. A view of a

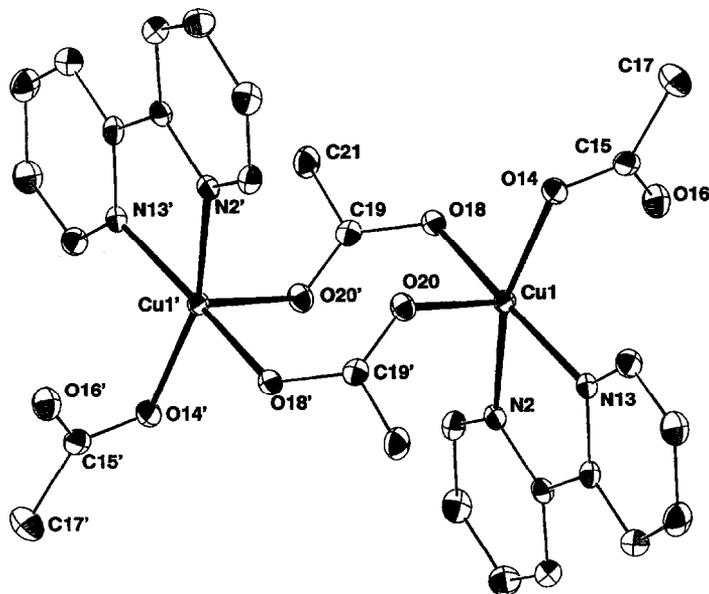


Fig. 2. ORTEP representation of **1** at the 50% probability level; the water molecules have been omitted. Bipyridine carbon atoms are labelled consecutively from N(2). Symmetry-related atoms are primed.

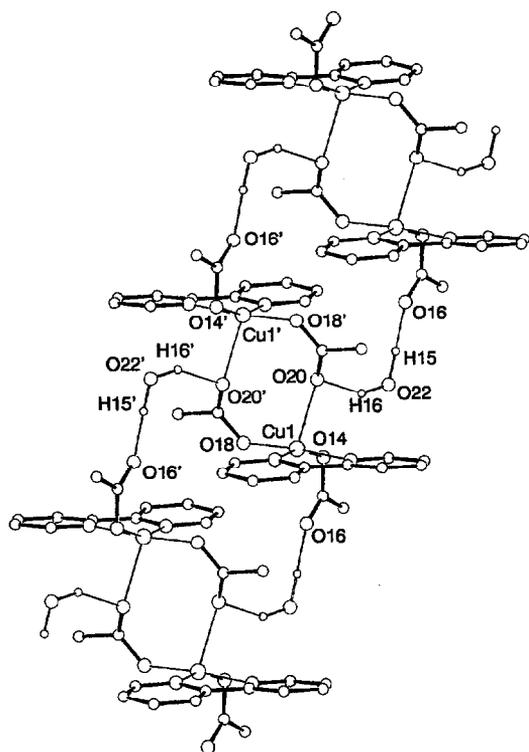


Fig. 3. A portion of the chain structure of $[\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{bpy})_2] \cdot 2\text{H}_2\text{O}$ (**1**) in the solid state showing the mode of inter-unit linkage by the hydrogen-bonded water molecules.

fragment of the chain structure of **1** is shown in Fig. 3. Selected structural parameters for **1** and **2** are listed in Tables 2–4.

Complex **1** crystallizes in triclinic space group $P\bar{1}$ with the asymmetric unit containing half the Cu^{II}

dimer and one molecule of H_2O . The structure of **1** consists of a dinuclear $[\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{bpy})_2]$ molecule located at a centre of symmetry with two *syn,anti* acetate bridges; a terminal bpy molecule and a monodentate acetate group complete five-coordination at each metal atom. The molecule represents a rare example of a discrete dinuclear Cu^{II} complex bridged by *syn,anti* carboxylates. This unusual bridging mode results in a significant lengthening of the $\text{Cu}(1) \cdots \text{Cu}(1')$ distance [4.554(1) Å], which is very long for a doubly-bridged complex.^{2,7,10,11} The coordination geometry at each Cu^{II} atom is distorted square-pyramidal. Three of the basal coordination sites are occupied by the nitrogen atoms of a chelating bpy and the oxygen atom of a monodentate acetate. The Cu—N bond lengths are normal.^{1,12} To the fourth basal site is coordinated an oxygen atom [O(18)] of a bridging acetate group. The two equatorial Cu—O bond lengths, 1.936(2) and 1.974(2) Å, are in the expected range.^{1,11,13} The apical site of each copper square pyramid is occupied by the second oxygen atom [O(20)] from the bridging acetate groups; the latter thus bridge by binding to a basal site at one copper and an apical site at the other (Fig. 2). Cu(1) lies only 0.186 Å above the N(2), N(13), O(14), O(18) least-squares plane toward O(20).

The $[\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{bpy})_2]$ units form infinite chains as a result of hydrogen-bonding interactions with the H_2O molecules (Fig. 3 and Table 3). The H_2O molecules [O(22)] hydrogen-bond to bridging acetate oxygen atom O(20) from one dinuclear unit and non-coordinated oxygen atom O(6) from a neighbouring dinuclear unit. As a result, the hydrogen-bonded network is a one-dimensional chain.¹

Table 2. Selected bond distances (Å) and angles (°) for **1**

| (a) Bonds | | | |
|-------------------|----------|--------------------|----------|
| Cu(1)···Cu(1') | 4.554(1) | Cu(1)—O(20) | 2.294(2) |
| Cu(1)—O(14) | 1.974(2) | C(19)—O(18) | 1.278(3) |
| Cu(1)—O(18) | 1.936(2) | C(19')—O(20) | 1.248(3) |
| Cu(1)—N(2) | 2.023(2) | C(15)—O(14) | 1.278(3) |
| Cu(1)—N(13) | 2.019(2) | C(15)—O(16) | 1.244(3) |
| (b) Angles | | | |
| O(20)—Cu(1)—O(14) | 85.6(1) | Cu(1)—O(14)—C(15) | 109.7(2) |
| O(20)—Cu(1)—O(18) | 97.2(1) | Cu(1)—O(18)—C(19) | 124.5(2) |
| O(20)—Cu(1)—N(2) | 110.3(1) | Cu(1)—O(20)—C(19') | 131.1(2) |
| O(20)—Cu(1)—N(13) | 87.9(1) | O(18)—C(19)—O(20') | 124.9(2) |
| O(14)—Cu(1)—O(18) | 89.8(1) | C(21)—C(19)—O(18) | 115.1(2) |
| O(14)—Cu(1)—N(2) | 161.8(1) | C(21)—C(19)—O(20') | 120.0(2) |
| O(14)—Cu(1)—N(13) | 91.7(1) | O(14)—C(15)—O(16) | 123.3(2) |
| O(18)—Cu(1)—N(2) | 96.8(1) | C(17)—C(15)—O(14) | 116.3(2) |
| O(18)—Cu(1)—N(13) | 174.7(1) | C(17)—C(15)—O(16) | 120.4(3) |
| N(2)—Cu(1)—N(13) | 80.4(1) | | |

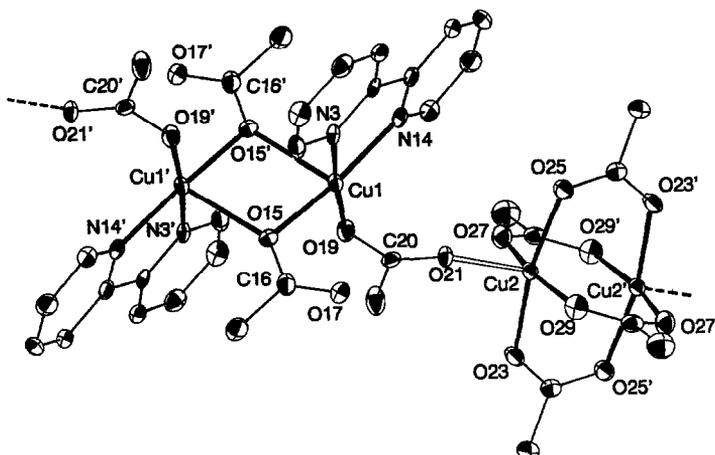


Fig. 4. ORTEP representation of **2** at the 50% probability level. Bipyridine carbon atoms are labelled consecutively from N(3). Symmetry-related atoms are primed.

Table 3. Hydrogen-bonding distances (Å) and angles (°) in **1**

| | | | |
|-------------------|----------|--------------------|----------|
| O(22)···O(16) | 2.768(3) | O(22)···O(20) | 2.956(3) |
| H(15)···O(16) | 1.94(5) | H(16)···O(20) | 2.23(4) |
| O(22)—H(15)—O(16) | 172.8(4) | O(22)—H(16)—O(20) | 153.9(4) |
| C(15)—O(16)—O(22) | 126.5(2) | C(19')—O(20)—O(22) | 111.9(2) |

Table 4. Selected bond distances (Å) and angles (°) for **2**

| (a) Bonds | | | |
|--------------------|----------|--------------------|----------|
| Cu(2)···Cu(2') | 2.669(1) | Cu(1)···Cu(1') | 3.358(1) |
| Cu(2)—O(23) | 1.974(3) | Cu(1)—O(15) | 1.968(3) |
| Cu(2)—O(25) | 1.972(3) | Cu(1)—O(19) | 1.949(3) |
| Cu(2)—O(27) | 1.975(4) | Cu(1)—N(14) | 2.003(4) |
| Cu(2)—O(29) | 1.981(4) | Cu(1)—N(3) | 2.018(4) |
| Cu(2)—O(21) | 2.162(3) | Cu(1)—O(15') | 2.353(3) |
| C(24)—O(23) | 1.264(6) | Cu(1)···O(17) | 2.870(4) |
| C(24)—O(25) | 1.263(6) | C(16)—O(15) | 1.292(6) |
| C(28)—O(27) | 1.246(6) | C(16)—O(17) | 1.232(6) |
| C(28)—O(29) | 1.259(6) | C(20)—O(19) | 1.272(6) |
| Cu(1)···Cu(2) | 5.441(1) | C(20)—O(21) | 1.241(6) |
| (b) Angles | | | |
| O(21)—Cu(2)—O(23) | 99.3(1) | O(15')—Cu(1)—O(15) | 78.4(1) |
| O(21)—Cu(2)—O(25) | 93.1(1) | O(15')—Cu(1)—O(19) | 92.9(1) |
| O(21)—Cu(2)—O(27) | 97.5(1) | O(15')—Cu(1)—N(14) | 99.5(1) |
| O(21)—Cu(2)—O(29) | 95.2(1) | O(15')—Cu(1)—N(3) | 92.8(1) |
| O(23)—Cu(2)—O(25) | 167.6(1) | O(15)—Cu(1)—O(19) | 89.4(1) |
| O(23)—Cu(2)—O(27) | 89.2(2) | O(15)—Cu(1)—N(14) | 173.1(2) |
| O(23)—Cu(2)—O(29) | 89.9(2) | O(15)—Cu(1)—N(3) | 93.0(2) |
| O(25)—Cu(2)—O(27) | 90.0(2) | O(19)—Cu(1)—N(14) | 97.2(2) |
| O(25)—Cu(2)—O(29) | 88.1(2) | O(19)—Cu(1)—N(3) | 174.1(2) |
| O(27)—Cu(2)—O(29) | 167.3(2) | N(3)—Cu(1)—N(14) | 80.6(2) |
| Cu(2)—O(23)—C(24) | 125.4(3) | Cu(1)—O(15)—Cu(1') | 101.6(1) |
| Cu(2)—O(25)—C(24) | 121.8(3) | Cu(1)—O(15)—C(16) | 114.6(3) |
| Cu(2)—O(27)—C(28) | 123.0(3) | Cu(1')—O(15)—C(16) | 143.5(3) |
| Cu(2)—O(29)—C(28) | 123.7(3) | Cu(1)—O(19)—C(20) | 133.6(3) |
| O(23)—C(24)—O(25') | 125.1(5) | O(19)—C(20)—C(22) | 115.3(5) |
| O(27)—C(28)—O(29') | 125.9(5) | O(19)—C(20)—O(21) | 125.2(5) |
| Cu(2)—O(21)—C(20) | 130.0(3) | | |
| C(22)—C(20)—O(21) | 119.5(5) | | |

The bpy rings are approximately perpendicular to the chain axis imparting a helical appearance to the network. The closest inter-dimer Cu...Cu distance is 5.665(2) Å [cf. Cu(1)...Cu(1') = 4.554(1) Å]. There are no close contacts between chains that may be considered bonding, and the chains are thus effectively isolated.

The *syn,anti* conformation for the two bridging acetates is relatively uncommon. We are aware of a few previous examples in Cu^{II} carboxylate chemistry^{13,14} but, with one exception,¹⁴ these lead to polymeric structures. In addition to the unusual *syn,anti* acetates, complex **1** is also noteworthy because it contains both bridging and monodentate acetates (ignoring hydrogen bonding). Three other Cu₂ complexes are structurally related to **1** in that they also have both bridging and monodentate carboxylate ligands: (1) [Cu₂L₄(H₂O₄)]·4H₂O (L = hippurate anion),^{15a} (2) Cu₂(O₂CMe)₄L'₄(L' = 1-methylimidazole)^{15b} and (3) [Cu₂(H₂O)(O₂CCl₃)₄(proxyl)₂] (proxyl is the nitroxyl radical 2,2,4,4-tetramethylpyrrolinyl-1-oxy).^{15c} However, the first two complexes contain two monoatomic (and not triatomic) carboxylate bridges. Of relevance also are the structures of Cu₂(tsvalO)₄(bpy)₂^{16a} (tsvalO = N-tosylvalinate monoanion), [Cu₂(TsGlyH)₄(bpy)₂]·2H₂O^{16b} (TsGlyH = N-tosylglycinate monoanion) and Cu₂(tglyO)₄(bpy)₂^{16c} (tglyO = N-triphenylmethylglycinate monoanion). The structure of the first complex consists of two discrete crystallographically-independent dimeric units; the structure of one dimeric unit contains two monoatomic bridging carboxylates with a terminal bpy molecule and a monodentate carboxylate group completing five-coordination at each metal atom. A completely analogous carboxylate bonding situation exists in the other two complexes.

The structure of **2** (Fig. 4) is composed of one-dimensional, well-separated polymeric chains, containing two different types of Cu₂ units, each at a crystallographic centre of symmetry. The chains are formed by alternating Cu₂(O₂CMe)₄ and [Cu₂(O₂CMe)₂(bpy)₂]²⁺ units that are linked by *syn,anti* bridging acetates. The Cu—Cu vectors are not co-linear but form a zigzag line, with Cu(2')—Cu(2)—Cu(1) and Cu(2)—Cu(1)—Cu(1') angles of 166.0(1) and 135.9(1)°, respectively. The Cu₂(O₂CMe)₄ unit contains four bidentate bridging acetates as found in the parent Cu₂(O₂CMe)₄(H₂O)₂. The Cu(2)...Cu(2') separation is 2.669(1) Å, slightly larger than the 2.614(2) Å in Cu₂(O₂CMe)₄(H₂O)₂.¹⁷ Other bond distances and angles for the Cu₂(O₂CMe)₄ unit in **2** are fairly similar to those found for Cu₂(O₂CMe)₄(H₂O)₂; it thus appears that the Cu₂(O₂CMe)₄ units in **2** are relatively unperturbed. Cu(2) lies 0.216 Å above the

O(23), O(25), O(27) and O(29) least-squares plane towards O(21).

The other dinuclear unit in **2** has a centrosymmetric structure with two acetate groups providing mono-atomic bridges O(15) and O(15'); a terminal bpy molecule and an oxygen atom (O19) from a *syn,anti* bridging acetate complete five-coordination at each copper atom. The presence of mono-atomic bridging acetates results in a significant difference between the length of the two carboxylate CO bonds,¹⁸ the C(16)—O(15) distance [1.292(6) Å] being longer than the C(16)—O(17) distance [1.232(6) Å]. As is sometimes (but not always) observed for mono-atomic bridging RCO₂⁻ groups,¹⁹ there is evidence for an additional weak interaction between Cu(1) and Cu(1') and the non-bridging acetate oxygens O(17) and O(17'), respectively. The Cu(1)...O(17) distance is 2.870(4) Å and the two acetate groups are clearly tilted towards Cu(1) and Cu(1') as manifested in the Cu(1)—O(15)—C(16) angle [114.6(3)°] being significantly smaller than Cu(1')—O(15)—C(16) [143.5(3)°]. The Cu(1)...Cu(1') separation is 3.358(1) Å. The coordination geometry at the copper atoms is best described as distorted square-pyramidal. Each bridging oxygen simultaneously occupies a basal site at one Cu^{II} atom and the apical site of the other Cu^{II} atom. This is a common structural feature for dinuclear Cu^{II} complexes with two mono-atomic bridging acetates. As a result, the two Cu^{II}-bridging oxygen distances are significantly different [1.968(3) and 2.353(3) Å]. Cu(1) lies 0.029 Å out of the N(3), N(14), O(19), O(15) least-squares plane. The Cu(1), O(15), Cu(1'), O(15') rhomb is exactly planar owing to the inversion symmetry. The bridging angle Cu(1)—O(15)—Cu(1') is 101.6(1)°; this is in the range (96.1–103.0°) reported for other Cu^{II}₂ complexes containing two mono-atomic bridging acetates.¹

There are three distinct Cu...Cu separations along the chain which alternate according to the sequence ...ABCABC... where (using the viewpoint of Fig. 4) A = Cu(1)...Cu(1') = 3.358(1) Å, B = Cu(1)...Cu(2) = 5.441(1) Å and C = Cu(2)...Cu(2') = 2.669(1) Å. Note that the four *syn,syn* bridging acetates allow the closest approach of metal centres, with the Cu(2)...Cu(2') distance being typical of those found within a number of Cu₂(O₂CMe)₄L₂ complexes (2.6–2.7 Å).²

The chain of **2** can be described as being composed of Cu₂(O₂CMe)₄(bpy)₂ units "bridged" by Cu₂(O₂CMe)₄ units. In a sense, the structures of **1** and **2** are related, the Cu₂(O₂CMe)₄(bpy)₂ units of **2** being similar to those in **1**; the bridging acetates are mono-atomic instead of triatomic, however. Also, the Cu₂(O₂CMe)₄ units are functioning to

bridge the $\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{bpy})_2$ units, just as are the H_2O molecules in **1**. The ready conversion of **1** to **2** is thus quite understandable, as is the reverse reaction, which amounts to the bpy attacking the $\text{Cu}_2(\text{O}_2\text{CMe})_4$ units. The closest precedent to **2** is the polymer $[\text{Cu}_2\text{L}_2(\text{O}_2\text{CMe})_2 \cdot \text{Cu}_2(\text{O}_2\text{CMe})_4(\text{EtOH})_2]_n$ ²⁰ (L = a tridentate chelate ligand); this, however, has only hydrogen bonds linking the alternating Cu_2 units, not metal–ligand bonds as in **2**.

IR and UV–vis spectroscopy

In the solid-state IR spectra, complex **1** exhibits two broad water stretching bands at 3502 and 3370 cm^{-1} consistent with the two different types of hydrogen bonds in the structure (Fig. 3 and Table 5). The $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ bands of **1** are at 1575 and 1399 cm^{-1} , respectively. The absence of, for example, a $\nu_{\text{as}}(\text{COO})$ stretch at higher energy, as might be expected for a monodentate acetate group, is presumably due to the latter's involvement in hydrogen-bonding linkages.¹¹ A similar spectrum is observed for **3b**, supporting an analogous structure to **1** with similar hydrogen-bonding networks. Three distinct $\nu_{\text{as}}(\text{COO})$ (1640, 1622, 1566 cm^{-1}) and two $\nu_{\text{s}}(\text{COO})$ (1424 and 1377 cm^{-1}) are observed for **2** (the broad 1424 cm^{-1} feature undoubtedly representing two overlapping bands). The 1640 and 1377 cm^{-1} ($\Delta = 263 \text{ cm}^{-1}$) pair are assigned to the mono-atomic bridging acetates.^{1,18,21}

Solution IR spectra in MeCN were recorded to probe the species in solution. Complex **1** displays two broad $\nu_{\text{as}}(\text{COO})$ bands at ~ 1605 and $\sim 1590 \text{ cm}^{-1}$, indicating the presence of two types of acetate groups. This is slightly different from the solid-state spectrum. A fairly similar profile is seen in CHCl_3 , slightly shifted to ~ 1590 and $\sim 1580 \text{ cm}^{-1}$; a broad $\nu_{\text{s}}(\text{COO})$ band is also observable in the latter solvent, at $\sim 1400 \text{ cm}^{-1}$. It is considered unlikely that the dinuclear structure is totally retained on dissolution of **1** in MeCN; instead, a number of species in equilibrium are probably present.

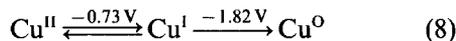
The high solubility of **2** in MeCN suggests that the chain structure is destroyed, and the most likely scenario is that discrete $\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{bpy})_2$ and $\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{MeCN})_2$ units are generated, the former then undergoing further transformations, as for **1**. Two $\nu_{\text{as}}(\text{COO})$ bands at 1590 and 1568 cm^{-1} are observed with no sign of the higher-energy (1640 cm^{-1}) band of the mono-atomic bridging groups. The spectrum is identical to that of an equimolar mixture of **1** and $\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{H}_2\text{O})_2$ in MeCN.

Complexes **1** and **3a** display similar solid-state

electronic spectra, suggesting that they possess similar structures. Both exhibit two carboxylate-to-copper LMCT transitions²² and $d-d$ transitions at lower energies, typical of square-pyramidal species with a CuN_2O_3 chromophore.^{16a} The first two bands in the spectrum of **2** are assigned to acetate-to-copper LMCT transitions.²² The appearance of two main $d-d$ bands probably reflects the two different chromophores within the complex; the 680 nm transition is attributed to the CuN_2O_3 chromophore and the 805 nm transition to the CuO_5 chromophore.^{16b} The $d-d$ spectra of **1** and **2** in MeCN consist of a very broad and featureless band at 670 and 672 nm, respectively. The band position and intensity for **2** [672 nm ($\epsilon_m = 564$ per Cu_4)] is essentially that expected for a summation of the spectra of **1** [670 (174 per Cu_2)] and $\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{H}_2\text{O})_2$ [672 (456 per Cu_2)].

Electrochemical studies

The cyclic voltammogram (CV) of **1** in MeCN is shown in Fig. 5. A complete scan (bottom) displays two cathodic processes of comparable peak currents at E_p values of -0.82 and -1.82 V , and a large anodic feature on the reverse scan assignable to oxidation of copper metal deposited on the electrode surface. Assuming **1** has dissociated into mononuclear units in solution, the cathodic processes are assigned to two one-electron reductions. Reversal of the potential scan at -1.40 V reveals the first process to be quasi-reversible: $E_{1/2} = -0.73 \text{ V}$, $\Delta E_p = 0.17 \text{ V}$, $i_p^c/i_p^a = 1.13$; both i_p^c/i_p^a and $i_p/v^{1/2}$ are independent of scan rate (v) in the range 80–900 mV s^{-1} . The benzoate analogue, complex **3b**, gave identical CV features as **1** but at a potential of $E_{1/2} = -0.70 \text{ V}$ and $\Delta E_p = 0.16 \text{ V}$. The CV processes are summarized in eq. (8).



The CV of complex **2** is shown in Fig. 6. The same overall behaviour as **1** is observed although the first cathodic process is clearly consistent with multiple species in solution. It was hoped that the overlapping CV features might be resolved in the DPV scans but this was not the case; only a broad peak at -0.73 V and a distinct shoulder on its anodic side were seen. Complex **1** shows a well-formed DPV peak at -0.71 V , and $\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{H}_2\text{O})_2$ shows a broader feature at -0.69 V ; a 1:1 mixture of the latter two compounds displays an essentially superimposable asymmetric DPV as **2** supporting the previous conclusion on the dissociation of **2** in MeCN into $\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{bpy})_2$ (and derivatives) and $\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{MeCN})_2$.

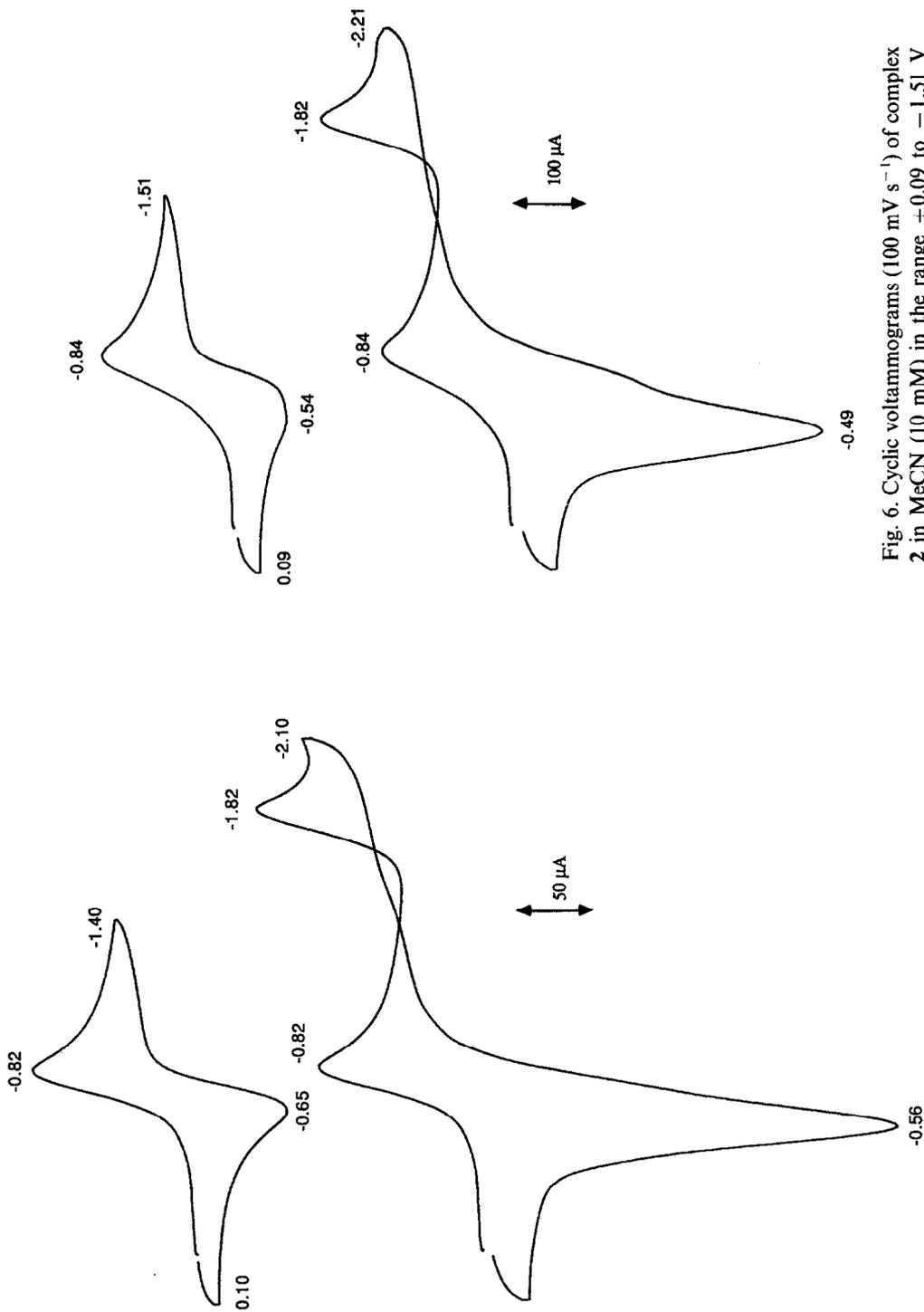


Fig. 5. Cyclic voltammograms (100 mV s^{-1}) of complex **1** in MeCN (1.0 mM) in the range +0.10 to -1.40 V (top) and +0.10 to -2.10 V (bottom). The quoted potentials are vs ferrocene/ferricinium.

Fig. 6. Cyclic voltammograms (100 mV s^{-1}) of complex **2** in MeCN (10 mM) in the range +0.09 to -1.51 V (top) and +0.09 to -2.21 V (bottom). The quoted potentials are vs ferrocene/ferricinium.

Concluding comments

The $\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{H}_2\text{O})_2/\text{bpy}$ reaction system continues to fulfill its promise as a source of a variety of new $\text{Cu}/\text{O}_2\text{CMe}/\text{bpy}$ complexes. In contrast to the charged species obtained in previous work,¹ the present work has unearthed one neutral and one polymeric species possessing unusual structural features. In addition to complexes **8** and **9** mentioned above, a number of other Cu_2 complexes belonging to this family have been characterized^{7,23} or are under characterization at the time of writing. The combined products of this reaction system comprise a remarkably wide variety of structural types, emphasizing the capability of the carboxylate group to adopt a number of different ligation modes, both terminal and bridging, and both monodentate and bidentate.^{10,12} The additional products obtained to date will be reported in due course.

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Supplementary material available. Complete listings of atomic coordinates, isotropic and anisotropic thermal parameters, bond lengths and angles (13 pages) and calculated and observed structure factors (12 pages). Ordering information is given on any current masthead page. Complete M.S.C. structure reports (Nos. 89094 and 90034) are available on request from the Indiana University Chemistry Library.

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