



DINUCLEAR COPPER(II) COMPLEXES WITH THE NEW [Cu₂(μ-OR)(μ-OAc)₂]⁺ (R = ALKYL) CORE: PREPARATION AND CHARACTERIZATION OF [Cu₂(OR)(OAc)₂(bpy)₂]⁺ (R = Me, Et, Prⁿ) SALTS

SPYROS P. PERLEPES,* JOHN C. HUFFMAN and
GEORGE CHRISTOU†

Department of Chemistry and Molecular Structure Center, Indiana University,
Bloomington, IN 47405-4001, U.S.A.

and

SOFIA PASCHALIDOU

Department of Chemistry, University of Patras, 26500 Patra, Greece

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Abstract—Procedures are described for the synthesis of complexes containing the cations [Cu₂(μ-OR)(μ-O₂CMe)₂(bpy)₂]⁺ (R = Me, Et, Prⁿ). Treatment of Cu₂(O₂CMe)₄(H₂O)₂ with 2 equivs of bpy and 1 equiv. of NaOH in anhydrous EtOH, followed by addition of NBu₄PF₆ in MeCN gave highly crystalline blue [Cu₂(OEt)(O₂CMe)₂(bpy)₂](PF₆) (**1a**) in ~70% yield. The corresponding reaction in dry MeOH–MeCN led to green crystals of the methoxo analogue [Cu₂(OMe)(O₂CMe)₂(bpy)₂](PF₆) (**2a**), also in ~70% yield. Layering of a methanolic solution of **1a** with a mixture of Et₂O and hexanes led to clean, high-yield conversion to complex **2a**. Complexes **1a**, **2a** and [Cu₂(OPrⁿ)(O₂CMe)₂(bpy)₂](PF₆) (**3**) were also prepared from the reactions of the compound [Cu₂(OH)(O₂CMe)₂(bpy)₂](PF₆) · 3DMF with an excess of the appropriate alcohol. In order to study the influence of the counterion on the structure of the [Cu₂(OR)(O₂CMe)₂(bpy)₂]⁺ ions, the blue–turquoise complex [Cu₂(OEt)(O₂CMe)₂(bpy)₂](ClO₄) (**1b**) and the corresponding green methoxo-bridged compound [Cu₂(OMe)(O₂CMe)₂(bpy)₂](ClO₄) (**2b**) were obtained in the same manner as complexes **1a** and **2a**, respectively. The structure of the cations of both complexes determined by X-ray diffraction consisted of triply-bridged pairs of copper(II) atoms. Two of the bridging ligands are *syn,syn* η¹:η¹:μ₂ acetate groups, the third being the OR⁻ ion; a terminal bpy molecule completes five-coordination at each metal atom. The Cu···Cu separations are 3.093(1) and 3.230(1) Å for **2a** and **1a**, respectively. In **1a**, the metal coordination geometry is best described as square pyramidal; the oxygen atoms [O(30) and O(32)] of one acetate occupy basal positions while the oxygens of the other acetate [O(34) and O(36)] occupy the apical positions of the two square pyramids. The cation of **2a** consists of two distorted trigonal bipyramids sharing the methoxo oxygen as a common apex. The solid-state electronic and IR spectra of the complexes are discussed in terms of the nature of the bonding and structures of **1a** and **2a**. A cyclic voltammetry study of **1a** and **2a** in MeCN reveals a quasi-reversible reduction at ~−0.75 V vs ferrocene, and an irreversible reduction at E_p = −1.83 V for **1a** and −1.63 V for **2a**, yielding copper metal, which deposits on the electrode.

*On sabbatical leave from the University of Ioannina, Ioannina, Greece. Present address: Department of Chemistry, University of Patras, 26500 Patra, Greece

†Author to whom correspondence should be addressed.

The development of carboxylate chemistry is a central theme in transition metal chemistry,¹ research in this area ranging from catalysis² to bioinorganic³ and materials chemistry.⁴ Over the last several years, we have been concerned with transition metal carboxylate chemistry employing 2,2'-bipyridine (bpy) as a terminal ligand.⁵⁻⁹ In particular, our interest⁷⁻⁹ in $M_2(O_2CR)_4/bpy$ chemistry stems from a desire to understand the factors that influence the binding of neutral nitrogen-donor chelates to systems with four relatively rigid bridging groups. Novel perturbations of the tetra-bridged structures were found for products of bpy reactions with $Cu_2(O_2CMe)_4(H_2O)_2$,⁷ $Rh_2(O_2CMe)_4(MeOH)_2$ ⁸ and $Mo_2(O_2CCF_3)_4$.⁹ For the 4d 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 $Rh_2(O_2CMe)_4(bpy)$ ⁸ and *syn*- and *anti*- $Mo_2(O_2CCF_3)_4(bpy)_2$.⁹ The rhodium complex was found to exhibit an asymmetrical structure containing a chelating acetate ligand, and the latter pair of molybdenum complexes have been of particular interest because they are isomers. In contrast, for the 3d metal carboxylate $Cu_2(O_2CMe)_4(H_2O)_2$, the absence of metal–metal bonding permits a greater structural versatility. Thus, we have found that reactions of $Cu_2(O_2CMe)_4(H_2O)_2$ with bpy lead⁷ to the neutral species $[Cu_2(O_2CMe)_4(bpy)_2] \cdot 2H_2O$ and $[Cu_4(O_2CMe)_8(bpy)_2]_n$, and salts of the cations $[Cu_2(O_2CMe)_3(bpy)_2]^+$, $[Cu_2(O_2CMe)_2(H_2O)_2(bpy)_2]^{2+}$, $[Cu_2(OH)(H_2O)(O_2CMe)(bpy)_2]^{2+}$ and $[Cu_2(OH)Cl(O_2CMe)(bpy)_2]^+$. Related work has more recently been reported by others,¹⁰⁻¹² including the trinuclear species $[Cu_3(O_2CMe)_4(H_2O)(bpy)_3]^{2+}$.

In the present work, we have extended our efforts to encompass reactions of $Cu_2(O_2CMe)_4(H_2O)_2$ with bpy and OH^- in alcohol solution, and have encountered products containing the new $[Cu_2(\mu-OR)(\mu-O_2CMe)_2]^+$ ($R = alkyl$) core. We herein describe the preparation and characterization of these species.

EXPERIMENTAL

Starting materials

All manipulations were performed under aerobic conditions using materials as received. MeCN and Et_2O –hexanes were dried by distillation from CaH_2 and sodium–benzophenone, respectively. The synthesis of the hydroxo complex $[Cu_2(OH)(O_2CMe)_2(bpy)_2](PF_6) \cdot 3DMF$ will be described in a subsequent report.¹³

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

Preparation of $[Cu_2(OEt)(O_2CMe)_2(bpy)_2](PF_6)$ (1a). Method A. Solid $Cu_2(O_2CMe)_4(H_2O)_2$ (1.00 g, 2.50 mmol) was slowly dissolved in a solution of bpy (0.78 g, 5.0 mmol) in anhydrous EtOH (50 cm³). The resulting deep blue solution was stirred while a solution of NaOH (0.10 g, 2.5 mmol) in anhydrous EtOH (20 cm³) was added to give a darker blue solution. To the latter was added a solution of $NBu_4^+PF_6^-$ (1.9 g, 4.0 mmol) in MeCN (10 cm³), and the flask was stored overnight at ambient temperature; the resultant blue crystals were collected by filtration, washed with EtOH and Et_2O , and dried *in vacuo* over P_4O_{10} . Some crystals were suitable for X-ray crystallography. Yield 1.23 g (66%). Recrystallization can be effected from anhydrous EtOH– Et_2O . An IR feature at ~ 3400 cm⁻¹ assignable to H_2O suggested the dried solid to be hygroscopic, and this was supported by the analytical data, which gave a reasonable fit for $[Cu_2(OEt)(O_2CMe)_2(bpy)_2](PF_6) \cdot 2H_2O$. Found: C, 39.7; H, 3.6; N, 7.3; P, 4.1; Cu, 16.0. Calc. for $C_{26}H_{31}N_4O_7PF_6Cu_2$: C, 39.9; H, 4.0; N, 7.2; P, 4.0; Cu, 16.2%. IR spectrum (KBr pellet, cm⁻¹): 3396 (w, br). Effective magnetic moment per copper(II): 1.99 μ_B at 26°C. Solid-state (diffuse reflectance) electronic spectrum: λ_{max} 360 sh, 705 nm. Electronic spectrum in MeCN: λ_{max} (ϵ_M/Cu_2 , dm³ mol⁻¹ cm⁻¹): 694 nm (150). When the whole procedure was repeated using 96% EtOH and MeCN as received, crystals of **1a** were again obtained, but these were contaminated with $[Cu_2(OH)(O_2CMe)_2(bpy)_2](PF_6) \cdot H_2O$.¹³

Method B. A slurry of complex $[Cu_2(OH)(O_2CMe)_2(bpy)_2](PF_6) \cdot 3DMF$ ¹³ (0.40 g, 0.43 mmol) in anhydrous EtOH (20 cm³) was stirred at 50°C for 2 h. A colour change from turquoise to blue occurred. After cooling the reaction mixture to room temperature, the blue solid was collected by filtration, washed with cold EtOH and Et_2O , and dried *in vacuo*; yield 0.27 g (84%). The product was spectroscopically identical to authentic material prepared by Method A.

Preparation of $[Cu_2(OEt)(O_2CMe)_2(bpy)_2](ClO_4)$ (1b). This complex was prepared in a manner analogous to that for **1a** (Method A) using NEt_4ClO_4 (0.58 g, 2.5 mmol). Storage of the reaction solution in a freezer for 2 days yielded blue–turquoise crystals suitable for crystallography. The yield was 0.90 g (51%). Found: C, 44.4; H, 3.9; N, 7.8. Calc. for $C_{26}H_{27}N_4O_9ClCu_2$:

C, 44.5; H, 3.9; N, 8.0%. Effective magnetic moment per copper(II): $1.97 \mu_B$ at 26°C. Solid-state (diffuse reflectance) electronic spectrum: λ_{\max} 370, 717 nm.

*Preparation of $[\text{Cu}_2(\text{OMe})(\text{O}_2\text{CMe})_2(\text{bpy})_2](\text{PF}_6)$ (**2a**). Method A.* To a stirred green solution of $\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{H}_2\text{O})_2$ (1.00 g, 2.50 mmol) in anhydrous MeOH (110 cm³) was added solid bpy (0.78 g, 5.0 mmol). To the resultant deep blue solution was added a solution of NaOH (0.10 g, 2.5 mmol) in anhydrous MeOH (15 cm³), followed by a solution of $\text{NBu}_4^+\text{PF}_6^-$ (1.08 g, 2.8 mmol) in MeCN (20 cm³). The resultant dark blue solution was stirred for a further 10–15 min, and Et₂O (140 cm³) added to initiate crystallization. The flask was stored overnight in a refrigerator, and the well-formed green crystals (suitable for crystallography) were collected by filtration, washed with Et₂O and dried *in vacuo*; yield 1.30 g (71%). The product was recrystallized from anhydrous MeOH–Et₂O. Found: C, 41.8; H, 3.4; N, 7.3. Calc. for $\text{C}_{25}\text{H}_{25}\text{N}_4\text{O}_5\text{PF}_6\text{Cu}_2$: C, 40.9; H, 3.4; N, 7.6%. Effective magnetic moment per copper(II): $2.01 \mu_B$ at 21°C. Solid-state (diffuse reflectance) electronic spectrum: λ_{\max} 350, 740, 825 nm. Electronic spectrum in MeCN: λ_{\max} 695 nm (150); in MeOH, 634 nm (95).

Method B. Method B for complex **1a** was repeated using MeOH in place of EtOH; the yield of **2a** was ~60%. The identity of the product was deduced by spectroscopic comparison with material from Method A.

Method C. A blue solution of **1a** (0.20 g, 0.27 mmol) in anhydrous MeOH (25 cm³) was layered with a 1:1 mixture of hexanes and Et₂O (30 cm³). Slow mixing yielded green crystals of **2a**. The crystals were collected by filtration, washed with Et₂O and dried *in vacuo*; yield 0.17 g (87%). The green product was spectroscopically identical to that from Method A.

*Preparation of $[\text{Cu}_2(\text{OMe})(\text{O}_2\text{CMe})_2(\text{bpy})_2](\text{ClO}_4)$ (**2b**).* The procedure for the preparation of complex **1b** [but in anhydrous MeOH (120 cm³)–MeCN (12 cm³)] was followed to the formation of the final dark blue solution. The solution was layered with an equal volume of Et₂O and left undisturbed at ambient temperature for 2 weeks. The resulting green crystals were collected by filtration, washed with Et₂O and dried *in vacuo* over silica gel; yield 0.84 g (49%). The product was recrystallized from MeOH–Et₂O. Found: C, 43.7; H, 3.7; N, 7.9. Calc. for $\text{C}_{25}\text{H}_{25}\text{N}_4\text{O}_9\text{ClCu}_2$: C, 43.6; H, 3.7; N, 8.1%. Effective magnetic moment per copper(II): $1.99 \mu_B$ at 20°C. Solid-state (diffuse reflectance) electronic spectrum: λ_{\max} 352, 745, 820 nm.

*Preparation of $[\text{Cu}_2(\text{OPr}^n)(\text{O}_2\text{CMe})_2(\text{bpy})_2](\text{PF}_6)$ (**3**).* A slurry of $[\text{Cu}_2(\text{OH})(\text{O}_2\text{CMe})_2(\text{bpy})_2](\text{PF}_6)$ ·3DMF¹³ (0.56 g, 0.60 mmol) in anhydrous PrⁿOH (290 cm³) was stirred under reflux for 30 min. The solid dissolved to give a green solution, which slowly turned blue upon cooling to room temperature. The blue solution was filtered and the filtrate was stored for 3 days at –10°C. The product formed as small blue crystals that were isolated by filtration, washed with Et₂O and dried *in vacuo* over P₄O₁₀; yield 0.22 g (48%). Found: C, 42.5; H, 3.9; N, 7.5; Cu, 17.0. Calc. for $\text{C}_{27}\text{H}_{29}\text{N}_4\text{O}_5\text{PF}_6\text{Cu}_2$: C, 42.6; H, 3.8; N, 7.4; Cu, 16.7%. Effective magnetic moment per copper(II): $2.00 \mu_B$ at 24°C. Solid-state (diffuse reflectance) electronic spectrum: λ_{\max} 365, 710 nm.

X-ray crystallography and structure solution

Data for **1a** and **2a** were collected on a Picker four-circle diffractometer at –155°C; details of the diffractometry, low-temperature facilities and computational procedures employed by the Molecular Structure Center are available elsewhere.¹⁴ Data collection parameters are summarized in Table 1. For both complexes, a systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with no symmetry or systematic absences, indicating a triclinic space group. The choice of the centrosymmetric space group $P\bar{1}$ was confirmed by the successful solution and refinement of the structures. The structures were solved by a combination of direct methods (MULTAN) and Fourier techniques and refined by full-matrix least-squares.

All non-hydrogen atoms were readily located and refined with anisotropic thermal parameters. For both complexes, all hydrogen atoms were clearly visible in a subsequent difference Fourier map, and they were included in the final cycles and refined with isotropic thermal parameters. Final difference Fourier maps were essentially featureless. Final values of R and R_w are included in Table 1. Selected bond distances and angles are given in Tables 2 and 3.

Physical 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 or KBr discs using a Nicolet 510P Fourier transform spectrometer or a Perkin–Elmer 283 spectrophotometer. Solid-state (diffuse reflectance, 890–330 nm) and solution (800–350 nm) electronic spectra were

Table 1. Crystallographic data for complexes **1a** and **2a**

Parameter	1a	2a
Formula	C ₂₆ H ₂₇ N ₄ O ₅ PF ₆ Cu ₂	C ₂₅ H ₂₅ N ₄ O ₅ PF ₆ Cu ₂
M _r (g mol ⁻¹)	747.58	733.55
Space group	P $\bar{1}$	P $\bar{1}$
a (Å)	10.514(2)	9.376(3)
b (Å)	16.485(2)	18.111(6)
c (Å)	8.910(1)	8.515(3)
α (°)	105.05(1)	103.01(2)
β (°)	90.50(1)	100.40(1)
γ (°)	92.28(1)	93.46(1)
V (Å ³)	1489.81	1377.96
Z	2	2
ρ_{calc} (g cm ⁻³)	1.667	1.768
Radiation (λ , Å)	Mo-K _α (0.71069)	Mo-K _α (0.71069)
μ (cm ⁻¹)	15.623	16.874
2 θ range (°)	6.00–45.00	6.00–45.00
Scan speed (deg min ⁻¹)	4.0	8.0
Scan width (°)	2.0 + dispersion	2.0 + dispersion
Data collected	5036	6168
Unique data	3900	3593
Data with $F > 2.33\sigma(F)$	3396	3321
Averaging R	0.040	0.020
$R(R_w)$ (%)	3.76 (3.98)	2.83 (3.19)
Goodness of fit for last cycle	1.032	1.103

Table 2. Selected bond distances (Å) and angles (°) for [Cu₂(OEt)(O₂CMe)₂(bpy)₂](PF₆) (**1a**)

Bond distances			
Cu(1)…Cu(2)	3.230(1)		
Cu(1)—O(27)	1.954(3)	Cu(2)—O(27)	1.939(3)
Cu(1)—O(30)	1.945(3)	Cu(2)—O(32)	1.982(3)
Cu(1)—O(34)	2.155(3)	Cu(2)—O(36)	2.164(3)
Cu(1)—N(3)	2.047(3)	Cu(2)—N(15)	2.026(3)
Cu(1)—N(14)	2.013(3)	Cu(2)—N(26)	2.023(3)
Bond angles			
Cu(1)—O(27)—Cu(2)	112.1(1)		
O(34)—Cu(1)—O(27)	100.1(1)	O(36)—Cu(2)—O(27)	97.0(1)
O(34)—Cu(1)—O(30)	97.0(1)	O(36)—Cu(2)—O(32)	99.9(1)
O(34)—Cu(1)—N(3)	104.8(1)	O(36)—Cu(2)—N(15)	95.8(1)
O(34)—Cu(1)—N(14)	89.9(1)	O(36)—Cu(2)—N(26)	97.3(1)
O(27)—Cu(1)—O(30)	94.7(1)	O(27)—Cu(2)—O(32)	95.7(1)
O(27)—Cu(1)—N(3)	154.3(1)	O(27)—Cu(2)—N(15)	165.9(1)
O(27)—Cu(1)—N(14)	94.1(1)	O(27)—Cu(2)—N(26)	92.5(1)
O(30)—Cu(1)—N(3)	88.6(1)	O(32)—Cu(2)—N(15)	87.8(1)
O(30)—Cu(1)—N(14)	167.8(1)	O(32)—Cu(2)—N(26)	160.0(1)
N(3)—Cu(1)—N(14)	79.8(1)	N(15)—Cu(2)—N(26)	80.1(1)

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. Cyclic voltammetry was performed using an IBM Model EC 225 voltammetric analyser, a PAR Model 175 universal programmer and a stan-

Table 3. Selected bond distances (\AA) and angles ($^\circ$) for $[\text{Cu}_2(\text{OMe})(\text{O}_2\text{CMe})_2(\text{bpy})_2](\text{PF}_6)$ (2a)

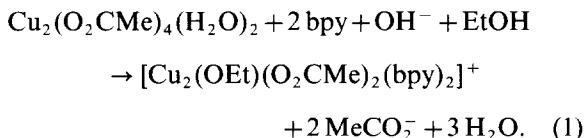
Bond distances			
$\text{Cu}(1)\cdots\text{Cu}(2)$	3.093(1)	$\text{Cu}(2)-\text{O}(35)$	1.931(2)
$\text{Cu}(1)-\text{O}(35)$	1.922(2)	$\text{Cu}(2)-\text{N}(15)$	2.001(3)
$\text{Cu}(1)-\text{N}(3)$	1.988(3)	$\text{Cu}(2)-\text{O}(33)$	1.993(2)
$\text{Cu}(1)-\text{O}(31)$	2.000(2)	$\text{Cu}(2)-\text{O}(29)$	2.099(2)
$\text{Cu}(1)-\text{O}(27)$	2.066(2)	$\text{Cu}(2)-\text{N}(26)$	2.059(3)
$\text{Cu}(1)-\text{N}(14)$	2.093(3)		
Bond angles			
$\text{Cu}(1)-\text{O}(35)-\text{Cu}(2)$	106.8(1)	$\text{O}(35)-\text{Cu}(2)-\text{N}(15)$	173.8(1)
$\text{O}(35)-\text{Cu}(1)-\text{N}(3)$	175.2(1)	$\text{O}(35)-\text{Cu}(2)-\text{O}(33)$	93.6(1)
$\text{O}(35)-\text{Cu}(1)-\text{O}(31)$	94.1(1)	$\text{O}(35)-\text{Cu}(2)-\text{O}(29)$	97.6(1)
$\text{O}(35)-\text{Cu}(1)-\text{O}(27)$	98.0(1)	$\text{O}(35)-\text{Cu}(2)-\text{N}(26)$	95.6(1)
$\text{O}(35)-\text{Cu}(1)-\text{N}(14)$	96.5(1)	$\text{O}(33)-\text{Cu}(2)-\text{O}(29)$	116.2(1)
$\text{O}(31)-\text{Cu}(1)-\text{O}(27)$	122.8(1)	$\text{O}(33)-\text{Cu}(2)-\text{N}(26)$	138.7(1)
$\text{O}(31)-\text{Cu}(1)-\text{N}(14)$	135.6(1)	$\text{O}(29)-\text{Cu}(2)-\text{N}(26)$	102.3(1)
$\text{O}(27)-\text{Cu}(1)-\text{N}(14)$	98.1(1)	$\text{N}(15)-\text{Cu}(2)-\text{O}(33)$	87.5(1)
$\text{N}(3)-\text{Cu}(1)-\text{O}(31)$	86.9(1)	$\text{N}(15)-\text{Cu}(2)-\text{O}(29)$	87.4(1)
$\text{N}(3)-\text{Cu}(1)-\text{O}(27)$	85.4(1)	$\text{N}(15)-\text{Cu}(2)-\text{N}(26)$	79.6(1)
$\text{N}(3)-\text{Cu}(1)-\text{N}(14)$	79.6(1)		

dard three-electrode assembly (glassy carbon working, platinum wire auxiliary, SCE reference), with 0.1 M $\text{NBu}_4^+\text{ClO}_4^-$ as supporting electrolyte. The scan rate was 100 mV s⁻¹. No IR compensation was employed. Quoted E values (± 0.01 V) are vs the ferrocene/ferricinium couple under the same conditions.

RESULTS AND DISCUSSION

Syntheses

Treatment of $\text{Cu}_2(\text{O}_2\text{CMe})_4(\text{H}_2\text{O})_2$ with 2 equivs of bpy and 1 equiv. of NaOH in anhydrous EtOH followed by addition of $\text{NBu}_4^+\text{PF}_6^-$ in anhydrous MeCN gave highly crystalline **1a** in $\sim 70\%$ yield. A structural characterization (see below) established the formulation $[\text{Cu}_2(\text{OEt})(\text{O}_2\text{CMe})_2(\text{bpy})_2](\text{PF}_6)$. The preparation of this blue complex is summarized in eq. (1).



The parallel investigation of this reaction in anhydrous MeOH–MeCN surprisingly led to the formation of green crystals in $\sim 70\%$ yield, on adding Et₂O to the blue reaction solution. An X-ray crystallographic study (see below) showed this material to be $[\text{Cu}_2(\text{OMe})(\text{O}_2\text{CMe})_2(\text{bpy})_2](\text{PF}_6)$.

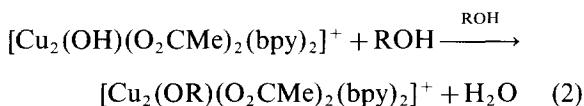
(**2a**). Complexes **1a** and **2a** have a significant structural difference which is responsible for their different colours; in **1a** the metal coordination geometry is best described as square pyramidal, while in **2a** it is distorted trigonal bipyramidal. Initially we suspected that the isolation of the two structurally different complexes was due to the different method of crystallization. We therefore added Et₂O to the reaction solution of **1a** after treatment with $\text{NBu}_4^+\text{PF}_6^-$; blue crystals of **1a** were again isolated.

In order to then probe the possible influence of another parameter on the structure of the $[\text{Cu}_2(\text{OR})(\text{O}_2\text{CMe})_2(\text{bpy})_2]^+$ ($\text{R} = \text{Me, Et}$) ions, we decided to seek the isolation and identification of these cations with another counterion. The blue–turquoise complex $[\text{Cu}_2(\text{OEt})(\text{O}_2\text{CMe})_2(\text{bpy})_2](\text{ClO}_4^-)$ (**1b**) and the corresponding green methoxo-bridged complex **2b** were obtained in an almost exactly analogous manner as compounds **1a** and **2a**, respectively, using $\text{NEt}_4^+\text{ClO}_4^-$ as the anion source. A crystal structure of **1b** (not shown) confirmed that the cation of **1b** is very similar to the cation of **1a**, i.e. the copper(II) coordination geometry is again square pyramidal. In addition, the solid-state electronic spectrum of **2b** is almost identical to that of **2a**, suggesting that the two complexes have similar structures. The identity of the counterion (PF_6^- vs ClO_4^-) is thus not of importance in determining the structures of the $[\text{Cu}_2(\text{OR})(\text{O}_2\text{CMe})_2(\text{bpy})_2]^+$ ($\text{R} = \text{Me, Et}$) cations. Presumably, minor changes in crystal-packing forces as the OR^- alkyl size is varied account for the variability in coordination

geometry in the crystalline state, since MeO^- and EtO^- are similar ligands from both electronic and steric points of view.¹⁵ In fact, electronic spectral data indicate both complexes are identical in solution (see below).

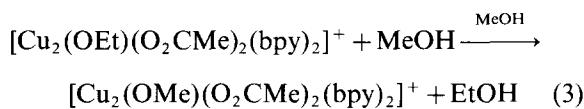
It should be noted that the concentration of water in the solvents affects the above reactions. As will be described in a future report,¹³ the H_2O concentration has an important influence on the core identity in the case of PF_6^- , leading to $[\text{Cu}_2(\text{OH})(\text{O}_2\text{CMe})_2(\text{bpy})_2]^+$ species. We have already explained that if the reaction solution to **1b** contains ~5% H_2O and an excess of ClO_4^- , $[\text{Cu}_2(\text{O}_2\text{CMe})_2(\text{H}_2\text{O})_2(\text{bpy})_2]$ is converted to $[\text{Cu}_2(\text{OH})_2(\text{bpy})_2](\text{ClO}_4)_2$ and $[\text{Cu}_2(\text{O}_2\text{CMe})_3(\text{bpy})_2](\text{ClO}_4)$.^{7a}

Complexes containing the cations $[\text{Cu}_2(\text{OR})(\text{O}_2\text{CMe})_2(\text{bpy})_2]^+$ ($\text{R} = \text{Me, Et, Pr}^n$) may also be prepared from $[\text{Cu}_2(\text{OH})(\text{O}_2\text{CMe})_2(\text{bpy})_2]^+$.¹³ Three reactions that convert complex $[\text{Cu}_2(\text{OH})(\text{O}_2\text{CMe})_2(\text{bpy})_2](\text{PF}_6) \cdot 3\text{DMF}$ ¹³ to **1a**, **2a** and **3** are detailed in the Experimental section; these procedures are summarized in eq. (2).



Further detail and discussion of these alcoholysis reactions will be included in the full report on the $[\text{Cu}_2(\text{OH})(\text{O}_2\text{CMe})_2(\text{bpy})_2]^+$ complexes. The solid-state UV-vis spectral characteristics of **3** are almost identical to those of **1a**, supporting similar structures and coordination geometries. The procedure summarized in eq. (2) could no doubt be extended to a variety of R groups.

A third synthetic route to **2a** is provided by the alkoxide substitution reaction of **1a** with an excess of MeOH [eq. (3)]. This procedure demonstrates the lability to substitution of the bound ethoxo group and it could no doubt also be extended to more alkoxides and carboxylates.



Complexes **1a** and **2a** hydrolyse slowly in moist air over several days to give powders having the composition $[\text{Cu}_2(\text{OH})(\text{O}_2\text{CMe})_2(\text{bpy})_2](\text{PF}_6) \cdot x\text{H}_2\text{O}$ ($x = 1-2$), as indicated by IR spectroscopy and elemental analysis. This type of substitution of alkoxide by hydroxide in the solid state has been observed previously.¹⁶

Description of structures

ORTEP projections of the cations of complexes **1a** and **2a** are shown in Figs 1 and 2, respectively.

The important structural parameters are listed in Tables 2 and 3.

The structure of **1a** consists of a dinuclear, triply-bridged $[\text{Cu}_2(\text{OEt})(\text{O}_2\text{CMe})_2(\text{bpy})_2]^+$ cation and a well-separated PF_6^- anion; the latter will not be discussed. The cations are well separated from each other. The two acetates are in the familiar bidentate *syn, syn* $\eta^1:\eta^1:\mu_2$ -bridging mode; a terminal bpy molecule and the bridging ethoxo group complete five-coordination at each copper(II) atom. The coordination geometry about each copper(II) is well described as square pyramidal, with the acetate oxygens O(34) and O(36) occupying the apical positions for Cu(1) and Cu(2), respectively. As expected, the axial bonds are longer than bond lengths in the basal planes. Cu(1) lies 0.274 Å and Cu(2) lies 0.261 Å out of their respective least-squares basal planes towards O(34) and O(36), respectively [max. deviation from the least-squares basal planes of Cu(1) and Cu(2) is 0.174 Å by N(3) and 0.041 Å by N(15), respectively]. The dihedral angle between the two planes is 34.5°. The Cu(1) ··· Cu(2) distance is 3.230(1) Å. Analysis of the shape-determining angles using the approach of Addison *et al.*¹⁷ yields τ values of 0.23 for Cu(1) and 0.10 for Cu(2) ($\tau = 0$ and 1 for perfect square pyramidal and trigonal bipyramidal geometries, respectively). Thus, the geometry around Cu(1) deviates from ideal square pyramidal geometry more than that around Cu(2).

The structure of the cation of complex **2a** consists of a pair of copper(II) atoms bridged by two $\eta^1:\eta^1:\mu_2$ acetate groups and a $\mu_2\text{-OMe}^-$ ion. A terminal bpy molecule completes five-coordination at each metal atom. It is thus extremely similar to the cation of **1a**. However, the five donor atoms around each copper(II), while not disposed symmetrically in either a square pyramidal or trigonal bipyramidal array, adopt a distorted trigonal bipyramidal arrangement such that O(31), O(27) and N(14) comprise the trigonal plane around Cu(1), and O(33), O(29) and N(26) comprise the trigonal plane around Cu(2). Thus, the cation of **2a** consists of two trigonal bipyramids sharing a common apex, O(35). Cu(1) lies 0.212 Å and Cu(2) lies 0.191 Å out of their respective equatorial planes towards O(35). The dihedral angle between the two planes is 107.5°. An alternative description for both Cu(1) and Cu(2) is severely distorted square pyramidal with O(27) and O(29) in the apices, respectively. The preferred trigonal bipyramidal description is further supported by the τ values, which are 0.66 for Cu(1) and 0.59 for Cu(2). The Cu(1) ··· Cu(2) distance is 3.093(1) Å. The Cu—N distances, and their variation as a function of axial vs equatorial location at both Cu(1) and Cu(2), are typical of trigonal bipyramidal copper(II)/bpy complexes.^{7a,18}

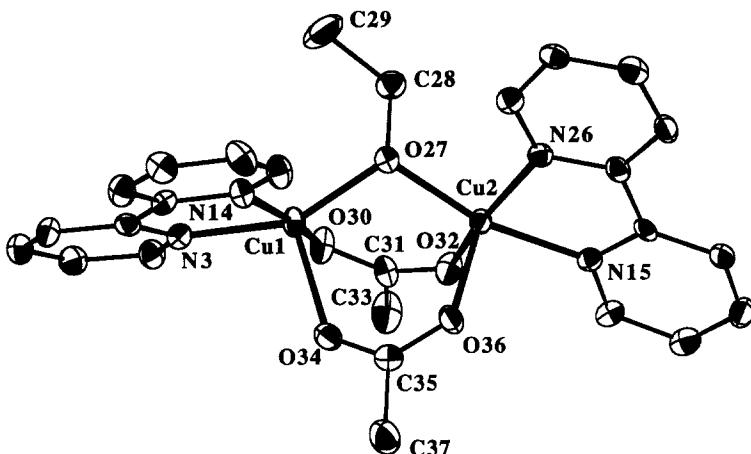


Fig. 1. ORTEP representation of the cation of complex **1a** at the 50% probability level. Bipyridine carbon atoms are labelled consecutively from N(3) and N(15).

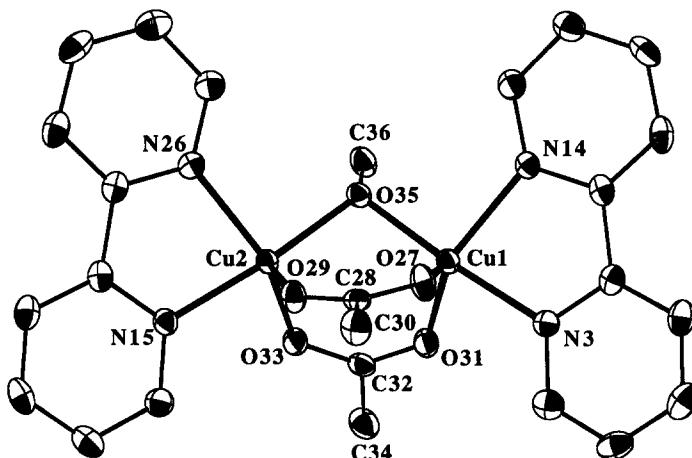


Fig. 2. ORTEP representation of the cation of complex **2a** at the 50% probability level. Bipyridine carbon atoms are labelled consecutively from N(3) and N(15).

The bond lengths to the bridging methoxy and acetate oxygens are typical.^{7,11,19}

Compound **2a** has the shorter Cu···Cu distance and the smaller Cu—O—Cu angle. We rationalize these features as due to (i) the methoxy oxygen atom being in an apical position of each trigonal bipyramidal copper(II) and (ii) the large dihedral angle (107.5°) between the two equatorial planes. From the sum of angles about the alkoxo bridging oxygen atoms (332.9–336.8°), it is clear that it has pyramidal rather than planar geometry in both structures. Note also that the Cu···Cu separations are much larger than those in the classic “Cu₂(O₂CR)₄L₂” structure, where the four bidentate bridging carboxylates allow a much closer approach of the metals (~2.6–2.7 Å).²⁰

Complexes **1a** and **2a** represent the first structurally characterized examples of copper(II) complexes with the [Cu₂(μ-OR)(μ-O₂CR')₂]⁺ (R = alkyl) core. Two other Cu₂ complexes are

structurally related to compounds **1a** and **2a** in that they both have two bidentate bridging carboxylates and one bridging aryloxide-type ligand: (i) [Cu₂L(OAc)₂]⁺ [L = monoanion of 2,6-bis((N-methylpiperazino)methyl)-4-chlorophenol]^{21a} and (ii) [Cu₂L'(O₂CPh)]⁺ [L' = monoanion of 2,6-bis(N-(2-diethylaminoethyl)-N-ethyl-amino-methyl)-4-methylphenol].^{21b} In these complexes, the bridging aryloxide oxygen is part of the pentadentate binucleating ligands L and L'.

UV-vis and IR spectroscopy

The complexes in each of the groups **1a**, **1b**, **3** and **2a**, **2b** possess very similar solid-state electronic spectra, supporting similar structures for their cations. The *d-d* wavelength (705–717 nm) of **1a**, **1b** and **3** is fairly typical of square pyramidal species with a CuN₂O₃ chromophore.^{22a} These complexes also exhibit an absorption in the 360–370 nm range,

assigned to an OR⁻-to-copper(II) ligand-to-metal charge transfer (LMCT) transition.^{22b,c} The solid-state *d-d* spectra of **2a** and **2b** consist of two equally intense maxima, only just resolved, at 740, 825 nm and 745, 820 nm, respectively. The spectra are characteristic of distorted trigonal bipyramidal structures.^{23a} As expected,^{23a} the *d-d* transitions in the methoxy-bridged trigonal bipyramidal complexes occur at lower energies compared with the square pyramidal complexes **1a**, **1b** and **3**. The distortion of the equatorial angles from the ideal 120° value gives rise to the twin-peaked *d-d* spectra frequently seen in such distorted trigonal bipyramidal copper(II) systems.^{23b} Compounds **2a** and **2b** exhibit an OMe⁻-to-copper(II) LMCT transition at ~350 nm.^{22b,c,23a} Complexes **1a**, **1b** and **3** retain their colours in MeCN solution. The *d-d* spectra of the representative compounds **1a** and **2a** in dry MeCN consist of a broad, featureless band at ~695 nm. The slight difference in wavelength between the solid-state and solution spectra of **1a** indicates a cation-solvent interaction, and it is possible that MeCN may be bound as a sixth ligand.^{7a} The solution spectrum of **2a** is considerably different from the solid-state spectrum, indicating structural changes upon dissolution; indeed, the spectra of **1a** and **2a** in MeCN are essentially identical, indicating that the solid-state differences do not persist in solution.

In the IR spectra, the perchlorate compounds **1b** and **2b** exhibit very strong bands near 1090 and 620 cm⁻¹ due to the $\nu_3(T_2)$ and $\nu_4(T_2)$ modes of the uncoordinated ClO₄⁻, respectively.^{24a} The T_{1u} IR-active modes of the PF₆⁻ anion appear at ~840 and ~560 cm⁻¹ in the spectra of **1a**, **2a** and **3**. The $\nu_{as}(\text{COO})$ and $\nu_s(\text{COO})$ bands of the complexes are at 1554–1601 and ~1440 cm⁻¹, respectively; the difference Δ [$\Delta = \nu_{as}(\text{COO}) - \nu_s(\text{COO})$] is less than that observed for NaO₂CMe (164 cm⁻¹), as expected for the bidentate bridging mode of carboxylate ligation.^{24b} A medium-to-strong band at ~1020 cm⁻¹ is assigned to the C—O stretching vibration of the bridging alkoxy group.^{24c}

Cyclic voltammetry of **1a** and **2a**

Complexes **1a** and **2a** were studied using the cyclic voltammetry (CV) technique in MeCN. It is considered probable that these complexes retain their dinuclear nature on dissolution in this solvent; this belief is based on earlier work with the related complexes [Cu₂(O₂CMe)₃(bpy)₂](ClO₄)₂ and [Cu₂(OH)(H₂O)(O₂CMe)(bpy)₂](ClO₄)₂ (which also possess monoatomically bridging ligands), where a dinuclear structure in MeCN solution was confirmed.^{7a} Initial scans in the potential range 0.1 to -1.1 V indicated the presence of one quasi-

reversible reduction assigned as a two-electron process to give the 2 copper(I) state. These reductions had $E_{1/2}$ values of -0.72 (**1a**) and -0.76 V (**2a**). When the cathodic switching potential was made more negative (-2.1 V), a second, irreversible reduction was observed with $E_{p,c}$ values of -1.83 V for **1a** and -1.63 V for **2a**. This process is assigned to the reduction to the 2 copper(0) level, based on the absence of a return wave and the presence of a very large, anodic stripping wave at ~-0.6 V characteristic of oxidation of copper metal deposited on the electrode surface. This deposit was clearly visible in both cases when the working electrode was examined after stopping the experiment at the cathodic switching potential. Overall, the CV behaviour of complexes **1a** and **2a** is fairly similar to that observed for other dinuclear copper(II)/RCO₂⁻/bpy complexes.⁷

Supplementary material available

Atomic coordinates have been deposited with the Cambridge Crystallographic Data Centre. Complete MSC structure reports (Nos 89093 and 90047 for **1a** and **2a**, respectively) are available on request from the Indiana University Chemistry Library.

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