A New Class of Bipyridine-ligated Metal Carboxylate Complexes: Characterization of the Triply-bridged Ferromagnetically-coupled Complexes [Cu₂(OAc)₃(bpy)₂](ClO₄) and [Cu₂(OH)(H₂O)(OAc)(bpy)₂](ClO₄)₂

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Treatment of $Cu_2(OAc)_4 \cdot 2H_2O$ with 2,2'-bipyridine (bpy) and $NaClO_4$ in EtOH yields [Cu₂(OAc)₃(bpy)₂](ClO₄) (1) whereas the same reaction in hot water yields [Cu₂(OH)(H₂O)(OAc)(bpy)₂](ClO₄)₂ (2); the novel structures of the complexes are described, together with the results of magnetic susceptibility studies which show that both complexes possess intramolecular ferromagnetic coupling.

In recent years, we have been reporting our progress towards developing 3d transition metal carboxylate chemistry employing 2,2'-bipyridine (bpy) as a terminal ligand, seeking models for the various Mn biomolecules being identified.[1] Most of our efforts have hitherto been concentrated in Mn, and a growing family of complexes of various nuclearities has been obtained.[1] We recently reported preliminary extension of our work to Fe.[2] We have now extended our efforts still further to Cu, and we wish to report our first successes in this area, the preparation of two new dinuclear Cu^II complexes with novel bridging units.

Treatment of a stirred slurry of $Cu_2(OAc)_4 \cdot 2H_2O$ (1.00 g, 2.5 mmol) in EtOH (70 cm³) with solid bpy (0.78 g, 5.0 mmol) gave a clear blue solution. Addition of $NaClO_4$ (0.61 g, 5.0 mmol) in EtOH (10 cm³) rapidly precipitated sky-blue microcrystalline [Cu₂(OAc)₃(bpy)₂](ClO₄) (1) in 95% yield that can be recrystallized from hot MeCN or MeCN/Et₂O.†

In a similar fashion, a slurry of $Cu_2(OAc)_4 \cdot 2H_2O$ (1.00 g, 2.5 mmol) and $NaClO_4$ (0.61 g, 5.0 mmol) in H₂O (65 cm³) was treated with bpy (0.78 g, 5.0 mmol) dissolved in EtOH (10 cm³). The resulting slurry was heated to 75 °C and all solids dissolved to give a deep-blue solution. The solution was left to cool slowly overnight to ambient temperature to produce well-formed dark-blue crystals of [Cu₂(OH)(H₂O)-(OAc)(bpy)₂](ClO₄)₂ (2) in 69% yield. The product can be recrystallized from hot water.†

The structures‡ of the two cations are shown in Figures 1 and 2. The structure of (1) consists of two Cu^II centres bridged by three AcO⁻ groups, two in the familiar η¹ : η¹ : μ₂ mode and the third in the rarer mono-atomic bridging mode,[3—5] with C(36)–O(35) [1.319(4) Å] significantly longer than C(36)–

O(37) [1.224(4) Å] as a result. A terminal bpy group completes five-co-ordination at each metal. As is sometimes[4] (but not always[5]) observed for mono-atomic bridging RCO_2^- groups, there is evidence for an additional weak interaction between Cu(1) and O(37). The Cu(1)···O(37) distance is only 2.716(2) Å, and the AcO⁻ group is clearly tilted towards Cu(1) as manifested in the Cu(1)–O(35)–C(36) angle [108.4(2)°] being significantly smaller than Cu(2)–O(35)–C(36) [127.3(2)°]. Also, the Cu(1)–O(35) bridging distance [1.977(2) Å] is noticeably shorter than the Cu(2)–O(35) distance [2.169(2) Å]. Further, the co-ordination geometries of the two Cu atoms are significantly different, and we assign this as also due to the Cu(1)···O(37) interaction. Thus, Cu(2) is intermediate between square pyramidal and trigonal bipyramidal whereas Cu(1) is approximately square pyramidal with O(31) at the apex. Indeed, this places O(37) approximately at the vacant sixth position of the Cu(1) square pyramid [O(31)–Cu(1)–O(37), 149.4(2)°].
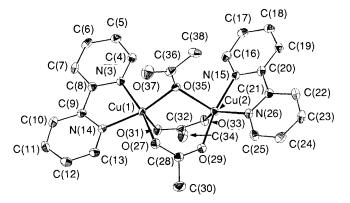

Figure 1. The structure of the cation of complex (1). Selected distances (Å) and angles (deg). Cu(1)···Cu(2), 3.392(1); Cu(1)–O(27), 1.939(2); Cu(1)–O(31), 2.238(2); Cu(1)–O(35), 1.977(2); Cu(1)–N(3), 2.001(2); Cu(1)–N(14), 2.019(2); Cu(2)–O(29), 1.930(2); Cu(2)–O(33), 1.974(2); Cu(2)–O(35), 2.169(2); Cu(2)–N(15), 1.992(2); Cu(2)–N(26), 2.033(2); C(36)–O(35), 1.319(4); C(36)–O(37), 1.224(4); C(32)–O(31), 1.245(3); C(32)–O(33), 1.270(3); C(28)–O(27), 1.255(3); C(28)–O(29), 1.259(4); O(27)–Cu(1)–O(31), 97.4(1); O(27)–Cu(1)–O(35), 93.6(1); O(31)–Cu(1)–O(35), 96.5(1); O(27)–Cu(1)–N(3), 168.8(1); O(27)–Cu(1)–N(14), 88.3(1); O(31)–Cu(1)–N(3), 87.6(1); O(31)–Cu(1)–N(14), 102.4(1); O(31)–Cu(1)–O(37), 149.4(2); O(35)–Cu(1)–N(3), 95.9(1); O(35)–Cu(1)–N(14), 160.6(1); N(3)–Cu(1)–N(14), 80.8(1); Cu(1)–O(35)–C(36), 108.4(2); Cu(1)–O(35)–Cu(2), 109.8(1); O(29)–Cu(2)–O(33), 94.9(1); O(29)–Cu(2)–O(35), 96.0(1); O(29)–Cu(2)–N(15), 168.3(1); O(29)–Cu(2)–N(26), 88.6(1); O(33)–Cu(2)–O(35), 96.7(1); O(33)–Cu(2)–N(15), 90.6(1); O(33)–Cu(2)–N(26), 140.1(1); O(35)–Cu(2)–N(15), 93.7(1); O(35)–Cu(2)–N(26), 122.6(1); N(15)–Cu(2)–N(26), 80.6(1); Cu(2)–O(35)–C(36), 127.3(2).
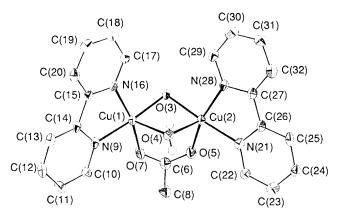

Figure 2. The structure of the cation of complex (2); OH⁻ and H₂O hydrogen atoms depicted as spheres of arbitrary size. Selected distances (Å) and angles (deg). Cu(1)···Cu(2), 3.035(2); Cu(1)–O(3), 1.927(4); Cu(1)–O(4), 2.405(4); Cu(1)–O(7), 1.931(4); Cu(1)–N(9), 2.006(5); Cu(1)–N(16), 2.008(5); Cu(2)–O(3), 1.930(4); Cu(2)–O(4), 2.379(4); Cu(2)–O(5), 1.944(4); Cu(2)–N(21), 2.010(5); Cu(2)–N(28), 2.009(4); C(6)–O(7), 1.267(7); C(6)–O(5), 1.264(7); Cu(1)–O(3)–Cu(2), 103.8(2); Cu(1)–O(4)–Cu(2), 78.7(1); O(3)–Cu(1)–O(4), 80.3(1); O(3)–Cu(1)–O(7), 95.2(2); O(3)–Cu(1)–N(9), 175.0(2); O(3)–Cu(1)–N(16), 93.9(2); O(4)–Cu(1)–O(7), 98.2(2); O(4)–Cu(1)–N(9), 100.5(2); O(4)–Cu(1)–N(16), 92.9(2); O(7)–Cu(1)–N(9), 89.6(2); O(7)–Cu(1)–N(16), 166.7(2); N(9)–Cu(1)–N(16), 81.2(2); O(3)–Cu(2)–O(4), 80.9(2); O(3)–Cu(2)–O(5), 94.2(2); O(3)–Cu(2)–N(21), 176.3(2); O(3)–Cu(2)–N(28), 95.4(2); O(4)–Cu(2)–O(5), 98.7(2); O(4)–Cu(2)–N(21), 99.4(2); O(4)–Cu(2)–N(28), 98.2(2); O(5)–Cu(2)–N(21), 89.4(2); O(5)–Cu(2)–N(28), 161.6(2); N(21)–Cu(2)–N(28), 80.9(2); Cu(2)–O(5)–C(6), 129.6(4); Cu(1)–O(7)–C(6), 129.4(4).

The structure of complex (2) again consists of a triply-bridged pair of five-co-ordinate Cu atoms, but only one of the bridging ligands is an AcO⁻, the others being an OH⁻ and a H₂O molecule. As a result of more mono-atomic bridges, the Cu···Cu separation in (2) [3.035(2) Å] is shorter than that in (1) [3.392(1) Å]. The metal co-ordination geometries are square pyramidal with the Cu atoms lying in the basal planes§ and the H₂O molecule [O(4)] occupying the apical positions for both metals; the apical Cu(1)–O(4) and Cu(2)–O(4) distances are both quite long [2.405(4) and 2.379(4) Å, respectively] as expected. We are unaware of another structurally-characterized example of a triply-bridged dinuclear Cu complex possessing both OH⁻ and H₂O bridging groups.[6,7]

The only difference in the synthetic procedures to (1) and (2) is the identity of the solvents, complex (2) forming in the predominantly aqueous medium. We thus reasoned that (1) might convert to (2) in H₂O, and recrystallization of (1) from hot water does indeed yield (2), in essentially quantitative yield if the required extra ClO₄⁻ is added [equation (1)].

$$[Cu_2(OAc)_3(bpy)_2](ClO_4) + NaClO_4 + 2\ H_2O \rightarrow$$
$$(1)$$
$$[Cu_2(OH)(H_2O)(OAc)(bpy)_2](ClO_4)_2$$
$$(2)$$
$$+\ NaOAc + AcOH \qquad (1)$$

Variable temperature magnetic susceptibility data were collected on powdered samples of (1) and (2) in the

temperature range 5—300 K. The data were least-squares fit to the Bleaney–Bowers equation[8] replacing T with $(T - \theta)$ where θ is the Weiss constant. For complex (1), the effective magnetic moment, μ_{eff}, per Cu₂ decreases gradually from 2.96 μ_B at 295.0 K to a minimum of 2.69 μ_B at 60.0 K and then rises to 2.87 μ_B at 5.0 K. The behaviour is clearly characteristic of intramolecular ferromagnetic coupling, and the fitting parameters were $J = +3.6\ cm^{-1}$, $g = 2.1$ and $\theta = 0.20$ K.

Complex (2) is also ferromagnetically-coupled; μ_{eff}/Cu₂ rises from 2.64 μ_B at 200 K to 2.93 μ_B at 50.0 K and then is relatively constant with a value of 2.95 μ_B at 5.0 K. However, the low-temperature plateau could not be modelled satisfactorily, and we believe the cause to be weak intermolecular antiferromagnetic interactions mediated by the hydrogen bonds between the bridging OH⁻ and H₂O groups and the ClO₄⁻ anions which give one-dimensional H-bonded chains.¶ Therefore, only the higher temperature data were fit to provide an estimate of J, and the fitting parameters were $J = +19.3\ cm^{-1}$, $g = 2.1$ and $\theta = 4.5$ K. Although antiferromagnetically-coupled Cu dimers are by far the more common, ferromagnetic coupling is frequently seen and the values obtained for (1) and (2) fall in the typical range observed.[9]

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§ The largest deviation from the least-squares plane Cu(1), O(3), O(7), N(9), N(16) is 0.093 Å by N(16), and from the plane Cu(2), O(3), O(5), N(21), N(28) it is 0.159 Å by N(28). The dihedral angle between these planes is 61.7°.

¶ The one-dimensional chain of Cu₂ cations is formed by an O atom of one ClO₄⁻ being H-bonded both to the OH⁻ hydrogen of one Cu₂ cation and one of the H₂O hydrogens of an adjacent Cu₂ cation. The other ClO₄⁻ is H-bonded to the second H₂O hydrogen but does not bridge to a neighbouring Cu₂ cation.