Intramolecular versus Intermolecular Hydrogen Bonding of Coordinated Acetate to Organic Acids: A Neutron, X-ray, and Database Study

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ABSTRACT: The effect of strong intra- and intermolecular hydrogen bonding on molecular geometry in carboxylate coordination complexes is examined by means of a search of the Cambridge Crystallographic Database. Accurate hydrogen-bonding parameters for two representative examples, $[Cu_2(\mu\text{-}O_2CCH_3)_4(CH_3CO_2H)_2]$ (**1**; intramolecular) and $[Cu_2(\mu\text{-}O_2CCH_3)_4(H_2O)_2]\cdot 2CH_3CO_2H$ (**2**; intermolecular), are determined by single-crystal neutron diffraction. Electronic effects are probed by the synthesis and characterization of a further mixed carboxylate derivative, $[Cu_2(\mu\text{-}O_2CCH_3)_2(\mu\text{-}O_2CCF_3)_2 (H_2O)_2]\cdot 2CH_3CO_2H$ (**5**).

Introduction

Hydrogen bonds have been described as the "master-key interaction" in supramolecular chemistry and crystal engineering because of their strength and directionality.[1] These qualities are particularly relevant in the case of strongly acidic species and charge-assisted hydrogen bonding (hydrogen bonding between species bearing a formal electrostatic charge) in which short D···A and H···A distances are generally coupled with DH···A angles in the region of 150-180°.[2-4] A large number of studies have focused on the structural systematics of strongly hydrogen-bonded systems, and in some cases, this has led to the identification of common motifs, which have been used or proposed as supramolecular synthons—reproducible structure-organizing noncovalent motifs that can be incorporated into larger arrays, typically as part of an infinite solid state material[5-8] (e.g., the centrosymmetric carboxylic acid dimer, which is predictably and reproducibly obtained in carboxylic acid structures in the absence of stronger acceptors than the acid carbonyl and in the absence of sterically bulky substituents[1,9,10]). The situation is dramatically changed, however, with the introduction of inorganic species. Coordination of a protic ligand to a metal center can frequently greatly enhance its acidity, while hydrogen bond basicity is lowered upon coordination. The presence of a metal center also often introduces rigid steric requirements into the system.[1]

We have recently highlighted a number of examples in which hydrogen-bonding interactions may have a marked effect on the coordination geometry of relatively "soft" metal complexes with moderate to strong hydrogen bonds competing effectively with coordination interactions as structure-organizing elements.[11-13] Such effects have also been noted in several isolated examples

of metal carboxylate complexes,[14] and they can be of crucial importance in the assembly of the highly topical metal–organic frameworks (MOF).[15-19] The Cambridge Structural Database (CSD)[20,21] contains the coordinates of two particularly interesting, unstable complexes of one of the simplest and most well-understood carboxylic acids, acetic acid. These materials were originally studied in order to gain insight into the nature of the Cu–Cu bonding. The dimeric acetic acid adduct of copper(II) acetate, $Cu_2(\mu\text{-}O_2CMe)_4(O_2HCMe)_2$ (**1**; CSD refcode ACACCV10[14]), comprises a dicopper tetraacetate dimer with axially coordinated, unidentate acetic acid molecules. The acidic OH group forms an intramolecular hydrogen bond with the oxygen atom of one of the bridging acetato ligands, an $S(6)$ motif in graph set terminology.[22] The X-ray crystal structure of the complex is shown in Figure 1a. Independently, the hydrated form of **1**, $[Cu_2(\mu\text{-}O_2CMe)_4(OH_2)_2]\cdot 2MeCO_2H$ (**2**; CSD refcode VATNOT[23]), has also been reported. In this material, the axial ligands are water molecules that form (i) an intermolecular hydrogen bond to the oxygen atom of a coordinated acetato ligand on an adjacent molecule and (ii) a hydrogen bond to a molecule of acetic acid enclathrated solvent. This uncoordinated acetic acid, in turn, hydrogen bonds to the oxygen atom of a coordinated acetato ligand on the same $Cu_2(\mu\text{-}O_2CMe)_4$ unit as the aqua ligand thus forming a $R_2^2(8)$ hydrogen-bonded motif (Figure 1b). The literature suggests that hydrogen-bonded interactions in these and related systems result in marked changes to the geometry of the relatively rigid dimetal tetracarboxylate framework with metal–oxygen distances being elongated in cases where the carboxylate oxygen forms part of a hydrogen-bonded system.[14]

In this paper, we report a detailed analysis of the hydrogen-bonded characteristics of **1** and **2** determined by single-crystal neutron diffraction as a means to precisely determine hydrogen-bonding characteristics and place them in context against related species found in the CSD. Precise conditions for the crystallization of

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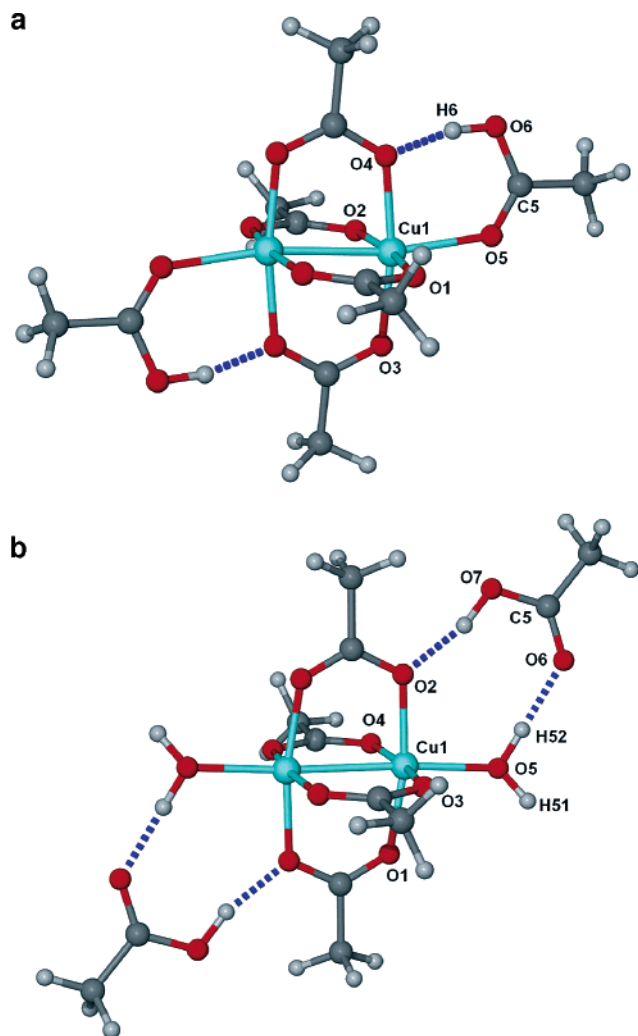
a

b

Figure 1. Structures of (a) **1** and (b) **2**.

the highly unstable **1** and **2** are elucidated, and a further hexafluoro analogue is reported.

Results and Discussion

Database Analysis. A search of the CSD[20,21,24] revealed a total of 145 fragments in 90 separate structure determinations that contain either an OH or a NH group within van der Waals contact distance of an oxygen atom of a bridged transition metal carboxylate complex. Of these, some 63 fragments were intramolecular over four or more bonds (as in **1**). A plot of the of the O⋯H hydrogen-bonded distance against the M−O bond length for the whole data set showed no significant correlation (Figure 2a). However, subtracting out the intermolecular contacts to leave the 45 structures loosely related to **1** gives the plot shown in Figure 2b. This shows a distinct, although nonlinear, correlation of hydrogen bond distance with M−O bond length. No such correlation is noted for the C−O distance of the carboxylate. Examination of Figure 2b suggests that the very shortest intramolecular hydrogen bonds can have a marked, although variable, effect on the MO distance, or conversely, weakly bound metal carboxylates make better hydrogen bond acceptors. This effect rapidly drops off with increasing hydrogen bond length. A histogram of intramolecular donor⋯oxygen distances
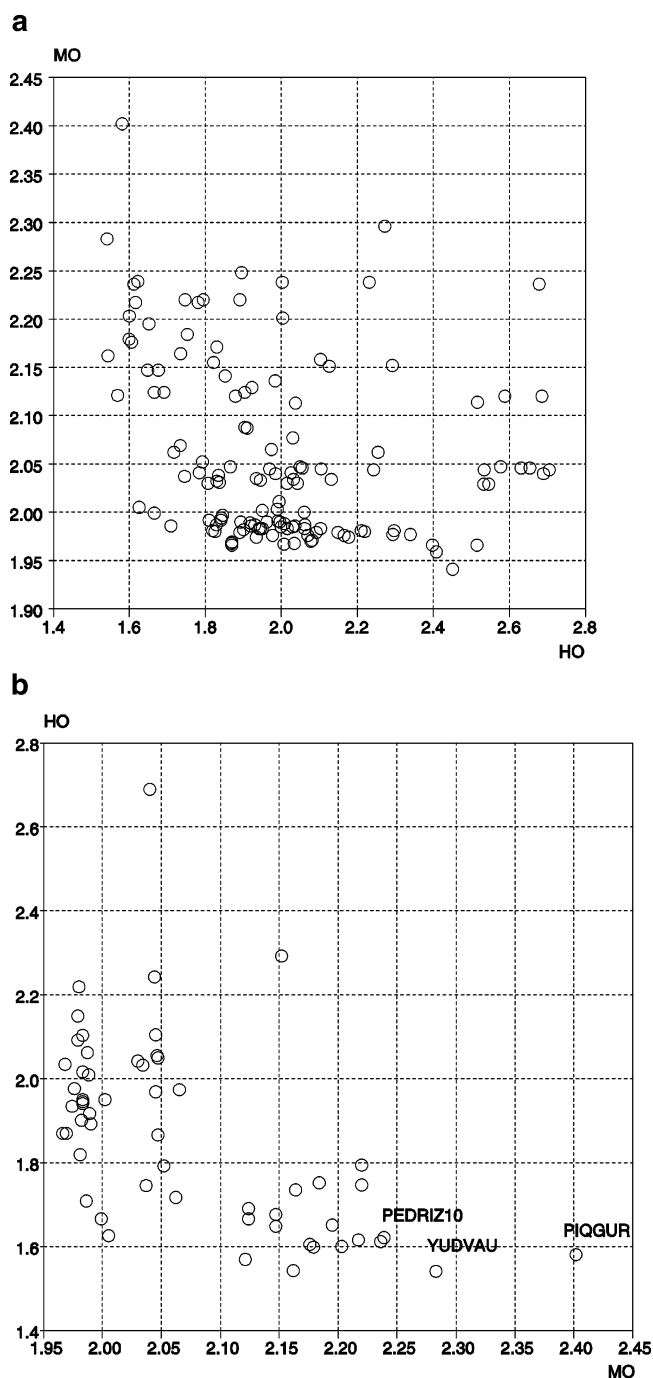
a

b

Figure 2. Scatterplot showing variation of Cu−O bond length with H⋯O hydrogen-bonded distances (Å). (a) All 145 inter- and intramolecular contacts and (b) 63 intramolecular contacts.

(Figure 3) shows that the observed contacts fall into two very distinct categories. Examination of the structures confirms that the very shortest distances involve hydrogen bonds to either OH groups (typically of carboxylic acids) or highly acidic NH groups, often as part of a charge-assisted interaction. The second group contains predominantly neutral NH donors (e.g., ureas). Close examination of the chemical nature of the entries on the bottom right of Figure 2b reveals the majority to contain ligands with a strong trans influence. This is exemplified by entry PEDRIZ10, $Rh_2(\mu\text{-}CF_3CO_2)_3$- $(\mu\text{-}PPh_2\text{-}o\text{-}C_6H_4)(CF_3CO_2H)_2$,[25] (Figure 2b) in which the Rh−O distance to the hydrogen-bonded acetate oxygen
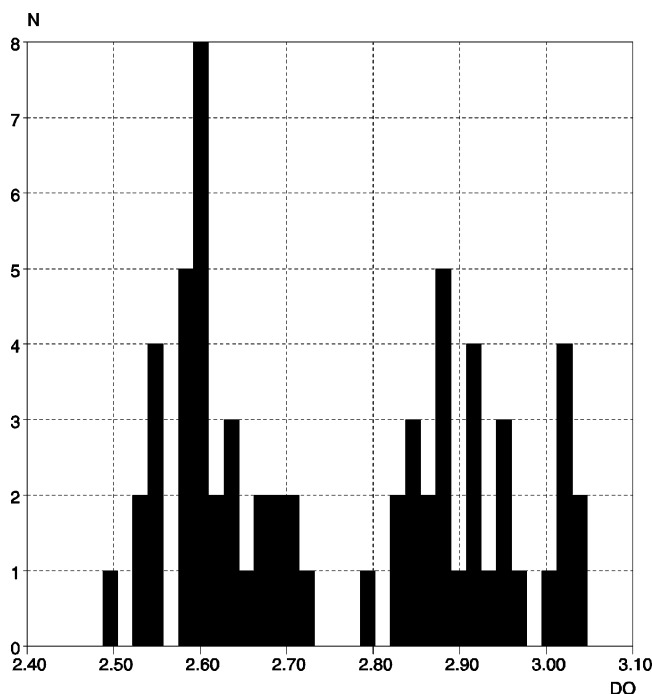
Figure 3. Histogram of donor (N or O) to acceptor distances in intramolecularly hydrogen-bonded adducts of transitional metal-bridged carboxylates.

is elongated by the strong σ-donor nature of the carbanion ligand and it is the most weakly bound oxygen atoms that form hydrogen bonds. Furthermore, extreme examples such as PIQGUR, bis(μ_3-acetato-O,O,O′)-hexakis(μ_2-acetato-O,O′)diacetato-di-cadmium(II)-di-palladium(II), are influenced by additional ligand coordination. Nevertheless, hydrogen bonding seems to be a factor of significance in the structure of YUDVAU, catena-(cis-bis(hydrogen maleato-O,O′)-di-silver(I)), and more generally, in all cases where the carboxylato oxygen environment is comparable in two cases, the metal centers forms a longer interaction to the hydrogen-bonded atom. Thus, overall, the MO bond length and complex geometry as a whole are subject to perturbation by strong or charge-assisted hydrogen bonds despite the lowered basicity of the metal coordinated carboxylate anion and the rigid "lantern" geometry of the complexes in cases where there are distinct geometric constraints on the hydrogen bonds, effectively resulting in the formation of a strained hydrogen-bonded ring system.

Neutron Studies. To assess the effects of hydrogen-bonded ring strain by precise location of hydrogen atoms, complexes **1** and **2**, closely comparable examples containing an intra- and intermolecular acetic acid to coordinated acetate hydrogen bond, were characterized by single-crystal neutron diffraction at 20 K using the D19 instrument at the ILL.[26] Crystals of **1** were prepared by refluxing copper(II) acetate monohydrate in glacial acetic acid/acetic anhydride (20:1) followed by slow cooling. Mixtures of **1** and **2** were obtained from 95 to 98% aqueous acetic acid, while a solution of 93% aqueous acetic acid afforded pure **2** in the same manner. In our hands, the presence of more than 10% water resulted in the crystallization of the starting material, copper(II) acetate monohydrate.

The neutron determinations are of good to very good precision and reproduce well the heavy atom skeleton
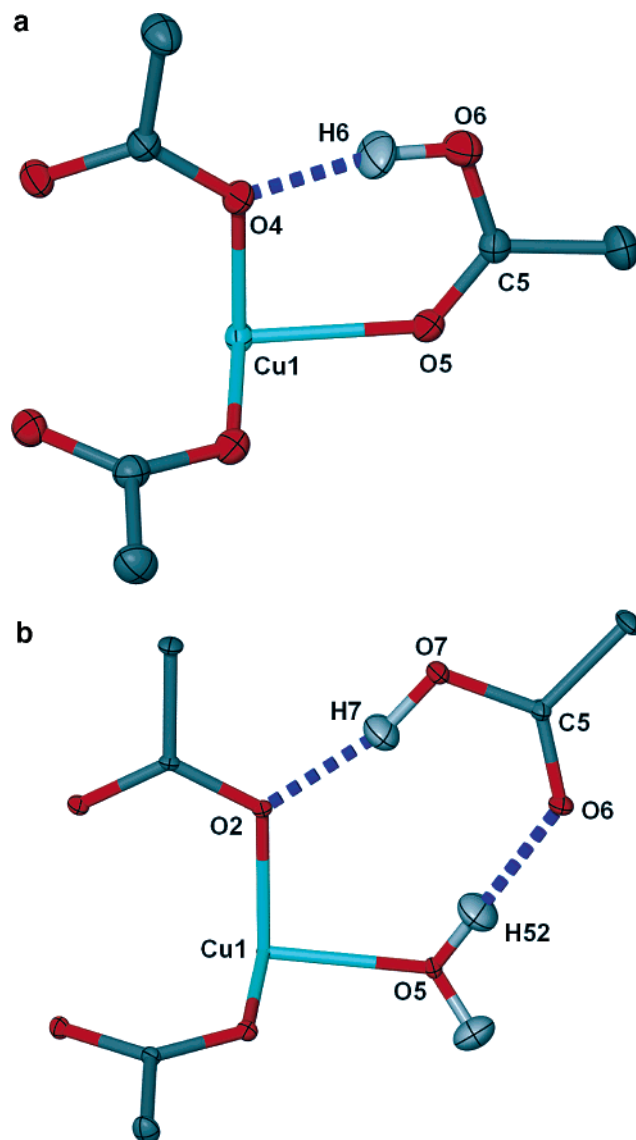

Figure 4. Thermal ellipsoid plot (70% probability) of hydrogen-bonded ring motifs determined by neutron diffraction (a) $S(6)$ in **1** and (b) $R_2^2(8)$ in **2**.

Table 1. Hydrogen Bond Distances and Angles in 1 and 2 (Neutron Data) and 5 (X-ray Data)

D−H···A	d(D−H)	d(H···A)	d(D···A)	<(DHA)
		compound **1**		
O(6)−H(6)···O(4)′	1.004(6)	1.628(6)	2.615(4)	166.5(5)
		compound **2**		
O(7)−H(7)···O(2)′	1.000(3)	1.736(3)	2.7165(17)	165.8(2)
O(5)−H(51)···O(3)′	0.964(3)	1.887(3)	2.8166(18)	161.2(2)
O(5)−H(52)···O(6)	0.979(3)	1.758(3)	2.7360(18)	175.9(3)
		compound **5**		
O(6)−H(6)···O(2)	0.71(7)	1.97(7)	2.636(4)	156(7)

determined by X-ray methods.[14,23] Compound **1** contains a single intramolecular hydrogen bond characterized by an H···O distance of 1.628(6) Å and a relatively short O···O contact of 2.615(4) Å (Table 1 and Figure 4a). The Cu−O bond distance to the coordinated oxygen atom is 1.996(3) Å, much longer than the remaining three independent bond lengths of 1.959 Å (average) (Table 2). The hydrogen-bonded angle is 166.5(5)° consistent with a strong hydrogen-bonding interaction.

Table 2.   Copper Coordination Environments in 1 and 2

compound	Cu−O acetate hydrogen bonded (Å)	Cu−O acetate non-hydrogen bonded (Å)	Cu−O axial (Å)	O−Cu−O angles axial (°)	O−Cu−O equatorial angles (°)	Cu−Cu
1	1.996(3)	1.965(3) 1.949(3) 1.962(3)	2.184(3)	96.83(14) 100.22(14) 92.89(13) 89.52(12)[a]	89.15(13) 170.26(16) 89.72(14) 89.60(14) 170.26(16) 89.88(13)	2.581(4)
2	1.9996(14)[a] 1.9651(14)[b]	1.9578(14) 1.9764(14)	2.1325(14)	95.90(6) 94.98(6)[b] 94.36(6) 96.39(6)[a]	169.03(7) 90.56(6) 89.98(6) 87.52(6) 89.91(6) 169.22(6)	2.6128(16)
5	1.988(2)	1.946(3) 1.960(3) 1.971(3)	2.163(2)	100.32(10) 96.83(10) 94.06(10) 90.93(10)[a]	89.22(12) 89.29(12) 169.10(10) 168.74(10) 90.10(12) 89.27(11)	2.6206(7)

[a] Oxygen atom hydrogen bonded to acetic acid.   [b] Oxygen atom hydrogen bonded to water.

By contrast, compound **2** contains three unique hydrogen bonds. The axially coordinated water molecule interacts with an enclathrated molecule of acetic acid (Table 1, Figure 4b), which, in turn, hydrogen bonds to the carboxylate oxygen atom O(2). The H···O and O···O distances are longer than in **1** (1.736(3) and 2.7165(17) Å, respectively); however, the O−H···O angle of 165.8(2)° is still consistent with a strong interaction. The third unique hydrogen bond is from the remaining water proton to carboxylate oxygen atom O(3) on an adjacent molecule (Figure 5). This is markedly longer and less linear, consistent with the lower acidity of water as compared to acetic acid (the acetic acid covalent O−H bond lengths are much longer than the water distances; Table 1), and appears to have a relatively minor effect on the Cu−O distance to the acceptor (Table 2). This kind of interaction is analogous to that observed for copper(II) acetate monohydrate (**3**), which has also been characterized by neutron diffraction.[27]

Clearly, the *S*(6) hydrogen-bonded ring[22] in **1** is not so strained that formation of a strong, short hydrogen bond is prevented. Indeed, the acid OH···O interaction is markedly shorter than in **2**. This may be partially attributed to the enhanced acidity of the carboxylic acid ligand in **1** as a result of coordination to the metal center. However, the strain in the ring is clearly evident from the movement of the acetic acid ligand toward the acceptor, manifested in a Cu−Cu−O(5) angle of 170.75-(15)° as compared to 176.51(6)° in **2**. Similarly, the hydrogen-bonded O(5)−Cu−O(4) angle in **1** is acute, while all other $O_{equatorial}$−Cu−O_{axial} angles in both structures are obtuse (Table 2). Finally, the clear absence of strain in **2** is evident from the fact that the acidic proton H(7) lies within the ring defined by O(7), C(5), O(6), O(5), Cu(1), and O(2). In **1**, the proton is outside the hydrogen-bonded ring.

In summary, hydrogen bonding in **1** is strong and highly linear and results in small but significant distortions in the metal coordination sphere in order to maximize interactions. In **2**, the interaction is longer and presumably weaker despite the absence of strain and the more linear nature of the Cu−Cu−O(5) vector.

Synthesis and Structure of Further Derivatives. There are a number of reports of coordinated carboxylic

acids in various metal systems (e.g., $Cr_2(\mu$-$O_2CMe)_4$-$(O_2HCMe)_2$[28]); however, the instability of such adducts, particularly with respect to displacement of the acetic acid by other ligands, adventitious water, or solvent means that few systematic comparisons can be made. We have sought to prepare further complexes related to **1**. Dissolution of copper(II) acetate monohydrate in stronger acids than acetic acid (e.g., trifluoroacetic or aqueous benzoic acids) generally resulted in the displacement of the acetato ligands by the corresponding carboxylate anion. For example, refluxing copper(II) acetate monohydrate in trifluoroacetic acid followed by crystallization from diethyl ether solution resulted in the isolation of the trifluoroacetate diethyl etherate complex, $Cu_2(\mu$-$O_2CCF_3)_4(OEt_2)_2$ (**3**), which was characterized by X-ray crystallography (see Experimental Section). The analogous benzoate, $Cu_2(\mu$-$O_2CCF_3)_4$-$(OEt_2)_2$ (**4**), was also prepared. Compounds **3** and **4** were used as starting materials in further attempts to prepare compounds of type **1**. In the case of **4**, refluxing in acetic acid followed by slow cooling resulted in the back-displacement of benzoate to give **1**; however, the lower basicity of the trifluoroacetate ligands in **3** allowed the isolation of the mixed acetate−trifluoroacetate $[Cu_2(\mu$-$O_2CCH_3)_2(\mu$-$O_2CCF_3)_2(H_2O)_2]$·$2CH_3CO_2H$ (**5**) directly analogous to **1**. Consistent with the IR spectroscopic data observed for **1** (see Experimental Section), compound **5** displayed a ν(C=O) band at 1715 cm^{-1} and bands assignable to CF stretching modes. Compound **5** was analyzed by X-ray crystallography and proved to be isomorphous with **1**. The molecular structure is shown in Figure 6. The structure is centrosymmetric; hence, the two acetate (and two trifluoro acetate) ligands are mutually trans. The presence of both acetate and trifluoroacetate acceptor ligands sets up an interesting competition in that either OH···$O_{acetate}$ or OH···$O_{trifluoroacetate}$ interactions could be formed. As might be expected on electronic grounds, it is the more electron rich acetate oxygen atom that acts as the acceptor, analogous to **1**. Consistent with the more electron deficient nature of the complex, the Cu−O_{axial} distance is shorter than in **1**, while the intramolecular hydrogen bond is somewhat longer (although still markedly shorter than in **2**; Table 1). The same geometric
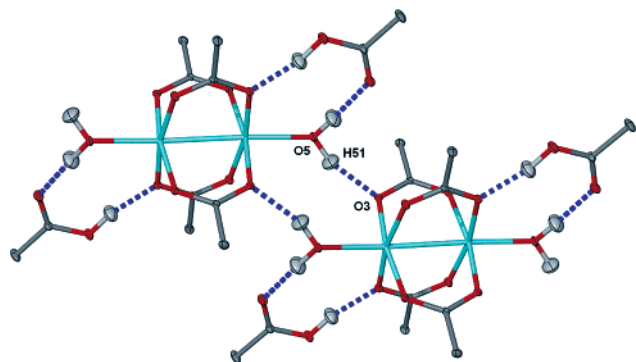
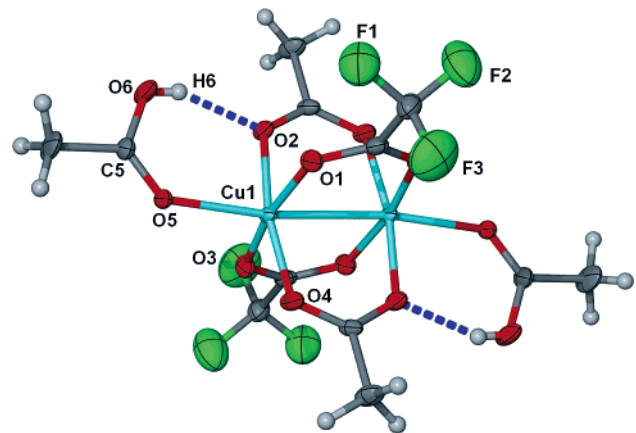**Figure 5.** Additional intermolecular hydrogen bonding in **2**.

Figure 6. Trifluoroacetate–acetic acid adduct [$Cu_2(\mu$-O_2-$CMe)_2(\mu$-$O_2CCF_3)_2(O_2CMe)_2$] (**5**).

distortions are seen as in **1** (Table 2), but consistent with the slightly elongated nature of the hydrogen bond, these distortions are less pronounced (as would be predicted from examination of Figure 2b). The Cu–Cu distance is markedly longer than in **1** and even than in **2**, supporting the σ-bonding model proposed previously.[14]

Conclusion

This study has shown using database, neutron, and X-ray techniques that strong metal–ligand coordination interactions within a rigid framework may be significantly perturbed by strong hydrogen-bonding interactions when part of a constrained ring system. While the system presented is a relatively simple model, such complexes are directly pertinent to the current intense interest in the design and control of solid state architecture in MOF materials and coordination polymers.[15–19,29–35]

Experimental Section

CSD Search. Searches of CSD version 5.23 (April 2002) were conducted using the CONQUEST software based on structures that contained no disorder with conventional R1 values of less than 7.5%. Distances to terminal hydrogen atoms were normalized to the conventional neutron values. Data analysis was performed using VISTA.

Synthesis. All chemicals and solvents were used without further purification from commercial sources. IR spectra were recorded on a PE Paragon 100 FTIR spectrometer as Nujol mulls. Microanalyses were performed at the University of North London. In the case of **1** and **4**, accurate elemental

analysis was not forthcoming as a result of the crystals' strong tendency to absorb moisture and, in the case of **1**, convert to **2**. Compound **1** has been prepared previously and the problem remarked upon.[14]

Preparation of 1. In a round-bottom flask, copper acetate monohydrate (0.50 g, 2.5 mmol) was added to a solution of 10 mL of glacial acetic acid with 0.5 mL of acetic acid anhydride. The mixture was stirred at reflux for 3 h using an oil bath. Then, heating was stopped and the solution was allowed to slowly cool overnight. Large dark blue crystals, suitable for neutron diffraction, were obtained. Yield: 0.49 g, 2.0 mmol, 81%. IR spectrum (cm^{-1}): ν(OH) = 3500, 3480, 3374, 3274; ν(CO) = 1701, 1607, 1454; other = 1290, 1048, 1032, 691.

Preparation of 2. In a round-bottom flask, copper acetate monohydrate (0.50 g, 2.5 mmol) was added to a solution of 10 mL of glacial acetic acid with 0.75 mL of distilled water. The mixture was stirred at reflux for 3 h using an oil bath. Then, the heating was stopped and the solution was allowed to cool slowly overnight. Large, light blue crystals, suitable for neutron diffraction, were obtained. Yield: 0.56 g, 2.15 mmol, 86%. IR spectrum (cm^{-1}): ν(OH) = 3450, 3369, 3277; ν(CO) = 1713, 1604, 1454, other = 1352, 1246, 1050, 1031, 689. Anal. calcd for $C_{12}H_{24}Cu_2O_{14}$: C, 27.75%; H, 4.66%. Found: C, 27.90%; H, 4.55%.

Preparation of 3. In a round-bottom flask, copper acetate monohydrate (2.0 g, 10 mmol) was dissolved in 10 mL of trifluoroacetic acid. The mixture was stirred at reflux for 3 h and allowed to cool overnight. Trifluoroacetic acid was removed using a high vacuum rotary evaporator. The blue solid (0.4 g) was dissolved in 0.5 mL of diethyl ether and put in the cold room resulting in the formation of the intermediate **3**, which was characterized by X-ray crystallography. This material was used without further analysis in the synthesis of **5**. The analogous benzoate, **4**, was prepared in an identical fashion and characterized by X-ray crystallography.

Preparation of 5. In a round-bottom flask, crystals of **3** (400 mg, 1.1 mmol) were dissolved in 1 mL of glacial acetic acid. The mixture was stirred at reflux in an oil bath for 2 h and then allowed to slowly cool overnight. Large green crystals were obtained. Conditions were optimized to produce X-ray diffraction quality crystals; however, yield was near-quantitative. IR spectrum (cm^{-1}): 1715 (ν(CO)), 1648 (ν(CO)), 1617, 1569, 1198 (CF), 734.

Neutron Structure Determinations. Crystals were mounted using quartz wool in quartz capillaries and cooled to 20 K using an Air Products 201 helium Displex[36] cryorefrigerator on the D19 instrument[26] at ILL equipped with both "banana" and square detectors. Reflections were collected on both detectors simultaneously using equatorial and normal beam geometry. Three standard reflections showed no change in intensity. Integration and geometric corrections were carried out using the "retreat" software.[37] Neutron scattering factors were taken from ref 38. X-ray coordinates were taken as a starting point for structure refinement using conventional alternating cycles of least squares refinement and difference Fourier synthesis (SHELXL-97).[39] The initial difference Fourier map showed clearly the positions of all acidic hydrogen atoms, and these were incorporated into the model with full anisotropic refinement. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre, CCDC 200174, 200175, 200176, 200177, and 200178 for compounds **1**–**5**, respectively. See Information for Authors, Issue No. 1.

(a) Crystal Data for 1. $C_6H_{10}CuO_6$, $M = 241.69$, blue block, 4.1 mm^3, monoclinic, space group $P2_1/n$ (no. 14), $a = 8.1015$-(10) Å, $b = 7.6022(10)$ Å, $c = 15.070(2)$ Å, $\beta = 103.613(6)°$, $V = 902.1(2)$ Å^3, $Z = 4$, $D_c = 1.780$ g/cm^3, $F_{000} = 180$, ILL D19, neutron radiation, $\lambda = 1.3150(1)$ Å, $T = 20.0(1)$ K, $2\theta_{max} = 134.3°$, 2183 reflections collected, 1243 unique ($R_{int} = 0.0389$). Final GooF = 1.126, $R1 = 0.0516$, $wR2 = 0.1183$, R indices based on 1056 reflections with $I > 2\sigma(I)$ (refinement on F^2), 209 parameters, 0 restraints. Absorption corrections not applied, $\mu = 2.08$ cm^{-1}.

(b) Crystal Data for 2. $C_{12}H_{24}Cu_2O_{14}$, $M = 519.41$, blue-green block, triclinic, space group $P\bar{1}$ (no. 2), $a = 7.5216(10)$ Å, $b = 7.9866(10)$ Å, $c = 8.5058(10)$ Å, $\alpha = 93.000(5)°$, $\beta = 93.985(5)°$, $\gamma = 106.632(5)°$, $V = 487.00(11)$ Å^3, $Z = 1$, $D_c = 1.771$ g/cm^3, $F_{000} = 87$, ILL thermal beam instrument D19, neutron radiation, $\lambda = 1.3150(1)$ Å, $T = 20.0(1)$ K, $2\theta_{max} = 132.8°$, 2397 reflections collected, 1631 unique ($R_{int} = 0.0206$). Final GooF $= 1.274$, $R1 = 0.0311$, $wR2 = 0.0798$, R indices based on 1567 reflections with $I > 2\sigma(I)$ (refinement on F^2), 235 parameters, 0 restraints. Absorption correction not applied, $\mu = 2.31$ cm^{-1}.

X-ray Crystal Structures. General details of X-ray crystallographic procedures in our lab have been published elsewhere.[40]

(a) Crystal Data for 3. $C_{16}H_{20}Cu_2F_{12}O_{10}$, $M = 727.40$ g.mol^{-1}, $0.30 \times 0.10 \times 0.05$ mm^3, triclinic, space group $P\bar{1}$, $a = 8.3895(12)$ Å, $b = 8.9809(12)$ Å, $c = 9.7374(16)$ Å, $\alpha = 66.344(6)°$, $\beta = 88.319(6)°$, $\gamma = 77.646(8)°$, $V = 655.15(17)$ Å^3, $Z = 1$, $D_c = 1.844$ Mg/m^3, $F_{000} = 362$, Mo Kα radiation, $\lambda = 0.71073$ Å, $T = 120(2)$ K, $2\theta_{max} = 27.30°$, 2514 reflections collected, 1788 unique ($R_{int} = 0.0641$). Structures were solved and refined using the programs SHELXS-97 and SHELXL-97, respectively. The program X-Seed was used as an interface to the SHELX programs and to prepare figures. Final GooF $= 0.982$, $R1 = 0.0484$, $wR2 = 0.0931$, R indices based on 1788 reflections with $I > 2\sigma(I)$ (refinement on F^2), 184 parameters, 0 restraints. L_P and absorption corrections applied, $\mu = 1.755$ mm^{-1}.

(b) Crystal Data for 4. $C_{36}H_{40}Cu_2O_{10}$, $M = 759.76$, $0.4 \times 0.3 \times 0.25$ mm^3, triclinic, space group $P\bar{1}$ (no. 2), $a = 9.5744(17)$ Å, $b = 10.447(2)$ Å, $c = 18.068(5)$ Å, $\alpha = 94.352(10)°$, $\beta = 97.028(10)°$, $\gamma = 102.810(7)°$, $V = 1739.1(6)$ Å^3, $Z = 2$, $D_c = 1.451$ g/cm^3, $F_{000} = 788$, $T = 120(2)$ K, $2\theta_{max} = 50.0°$, 6317 reflections collected, 4637 unique ($R_{int} = 0.0908$). Final GooF $= 1.044$, $R1 = 0.0971$, $wR2 = 0.2030$, R indices based on 2446 reflections with $I > 2\sigma(I)$ (refinement on F^2), 437 parameters, 0 restraints. L_P and absorption corrections applied, $\mu = 1.279$ mm^{-1}.

(c) Crystal Data for 5. $C_{12}H_{14}Cu_2F_6O_{12}$, $M = 591.31$ g mol^{-1}, $0.60 \times 0.50 \times 0.40$ mm^3, monoclinic, space group $P2_1/n$ (no. 14), $a = 8.6160(3)$ Å, $b = 7.6784(3)$ Å, $c = 15.0095(5)$ Å, $\beta = 101.888(2)°$, $V = 971.69(6)$ Å^3, $Z = 2$, $D_c = 2.021$ Mg/m^3, $F_{000} = 588$, Mo Kα radiation, $\lambda = 0.71073$ Å, $T = 120(2)$ K, $2\theta_{max} = 27.49°$, 6126 reflections collected, 2197 unique ($R_{int} = 0.0498$). Final GooF $= 1.080$, $R1 = 0.0459$, $wR2 = 0.1316$, R indices based on 2197 reflections with $I > 2\sigma(I)$ (refinement on F^2), 152 parameters, 0 restraints. L_P and absorption corrections applied, $\mu = 2.306$ mm^{-1}.

Supporting Information Available: Crystallographic data in CIF format for the neutron structures of compounds **1** and **2** and X-ray data for **3**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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