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Density Functional Calculations Reveal a Flexible Version of the Copper Paddlewheel Unit: Implications for Metal Organic Frameworks

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Density functional theory calculations on $[\text{Cu}_2(\text{O}_2\text{CR})_4\text{L}]$ systems reveal a change in ground state with increasing Cu-L bond strength. For L = N-heterocyclic carbene (NHC), the Jahn-Teller axis switches from parallel to orthogonal to the Cu-Cu vector and the copper coordination geometry becomes highly flexible. While the calculated dimer/monomer equilibrium for isolated complexes slightly favours monomers, the preformed paddlewheel units embedded in many metal organic frameworks are potential targets for developing novel materials.

Metal Organic Frameworks (MOFs) are porous materials with many potential applications in gas storage, separations and catalysis.¹ They consist of nodes, either transition metal centres or small clusters, connected by organic linkers, often polytopic carboxylates. The resulting frameworks are often sufficiently rigid to allow molecules adsorbed in the pores to be removed or replaced without the framework collapsing.

Flexible MOFs are an interesting development.² The pore size and/or shape responds to the adsorbed species, a property which suggests applications in selectivity and separations. An early example of such flexible MOFs was $[\text{Zn}(\text{bdc})_2(\text{dabco})]_n$ (bdc = 1,4-benzenedicarboxylate; dabco = 1,4-diazabicyclo(2.2.2)octane) which contains layers of four-bladed paddle-wheel $\{\text{Zn}_2(\text{O}_2\text{CR})_4\}$ units connected by dabco pillars.³ The unit cell of this material is sensitive to adsorbed species (Figure 1).

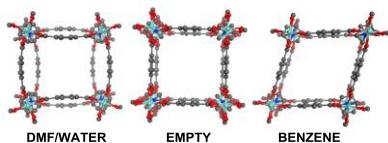


Figure 1 Unit cell of $[\text{Zn}(\text{bdc})_2(\text{dabco})]_n$. Left: as-synthesised material with four dimethylformamides and a water molecule; centre: after evacuation; right: after uptake of four benzene molecules. (Adsorbed species and H atoms omitted for clarity.)

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 Electronic Supplementary Information (ESI) available: full computational details, Cartesian coordinates and total/binding energies. See DOI: 10.1039/x0xx00000x

The paddle-wheel motif (Figure 2) is common in flexible MOFs with many zinc and copper examples. Zn(II)-based systems are considered to be more flexible than comparable Cu(II) paddlewheel (CPW) MOFs and this has been attributed to their respective electronic structures.⁴ The d^{10} Zn(II) centres have no particular electronic preference so a pentacoordinated Zn(II) would be expected to adopt a trigonal bipyramidal (TBP) structure. This occurs when the axial group is a water ligand⁵ but N donors favour a square pyramidal (SQP) structure.⁶ However, the TBP and SQP coordination geometries have similar energies (c.f. the Berry pseudorotation) and the transition from TBP to SQP or vice versa is relatively easy. Hence, the zinc paddlewheel (ZPW) unit is relatively flexible.

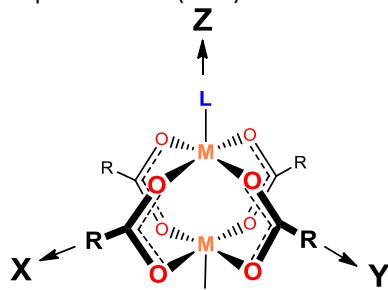


Figure 2 Schematic representation of four-bladed paddlewheel complex.

In contrast, d^9 Cu(II) CPW centres show a preference for planar CuO_4 coordination with the unpaired electron being in the $d_{x^2-y^2}$ orbitals on each metal. We will call this state T_0 since geometry optimisations are carried out on the ferromagnetic spin triplet surface. We note that while the true ground states are the anti-ferromagnetically coupled singlet states (*vide infra*), the structures of CPWs are not sensitive to this coupling (see ESI). For T_0 , the ‘hole’ in the otherwise filled d shell on each metal is localised in the equatorial plane leading to a ‘stereochemical activity’ which shortens the Cu-O distances and concomitantly lengthens the bond to the axial ligand.⁷ This is the same mechanism by which the Jahn-Teller elongation of six-coordinate Cu(II) complexes may be rationalised.⁸

These observations also lead to a dilemma. Since pentacoordinate species are inherently flexible and Cu(II) centres are strongly Jahn-Teller active, CPW units should be more flexible than their zinc counterparts. In mononuclear CuL₆ complexes, the first-order Mexican hat potential energy surface shows that all the structures in the circular minimum have the same energy despite the large bond length fluctuations associated with the change from a tetragonal elongation along one Cartesian axis through a series of rhombic distortions to a tetragonally compressed structure along a different axis.⁹ Evidently, the copper centres in the CPW moiety behave differently to a typical CuL₆ system. The first indication of this was the anomalously low magnetic moment for the archetypal CPW [Cu₂(acetate)₄(OH₂)₂].¹⁰ The structure of copper acetate dihydrate was unknown but when its dinuclear nature was revealed,¹¹ the magnetic behaviour could be correlated with anti-ferromagnetic coupling between the two unpaired d_{x2-y2} electrons. All subsequent studies on copper acetate and related CPW systems have concentrated on characterising the details of this coupling. There does not appear to have been any previous attempt to locate other local minima.

Our first step was to search for a ‘compressed’ CPW form. Using the spin triplet surface of [Cu₂(formate)₄(OH₂)₂] as a model, all our DFT optimisations¹² collapsed back to the elongated form. However, for [Cu₂(formate)₄(NH₃)₂] a second stable configuration was located (Figure 3). Interestingly, this does not correspond to a fully compressed structure which would have d_{z2} as the singly occupied d orbital on each copper. Instead, the spin density distribution corresponds to a mixed d_{x2-y2}/d_{z2} configuration (state T_M, Figure 3, left).

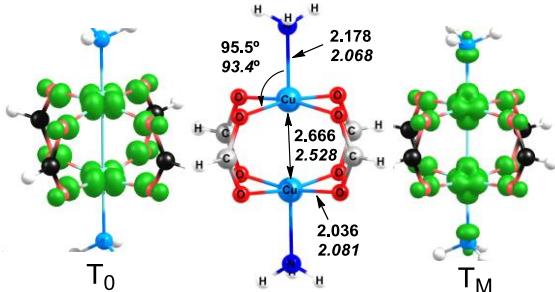


Figure 3 Centre: selected calculated geometrical data for [Cu₂(formate)₄(NH₃)₂]. Normal text for elongated d_{x2-y2}/d_{x2-y2} state (T₀) structure; italics for mixed d_{x2-y2}/d_{z2} state (T_M) structure. Spin density plots to left and right.

Qualitatively, the presence of this new state is easy to understand. Following Hay, Thibeault and Hoffmann’s analysis,¹³ the ‘normal’ (i.e. elongated) CPW electronic structure arises from joining two isolated square pyramidal copper species where the apical direction lies parallel to the Cu-Cu vector. This leads to d_{x2-y2} lying above d_{z2} as shown on the left of Figure 4. Focusing on the valence, mainly-d orbitals, we generate symmetric (S) and antisymmetric (A) combinations in the dimer. Since the ‘equatorial’ d_{x2-y2} orbitals are oriented for metal-metal δ -bonding which is, at best, very weak, the splitting of the symmetric (S_{Eq}) and antisymmetric (A_{Eq}) molecular orbitals is relatively small, the triplet and anti-ferromagnetic singlet states are close in energy and, at least from a structural perspective, the two ends of the CPW behave like isolated

pentacoordinate SQP copper complexes with comparatively short Cu-O_{eq} bond lengths and a relatively long Cu-L_{ax} bond.

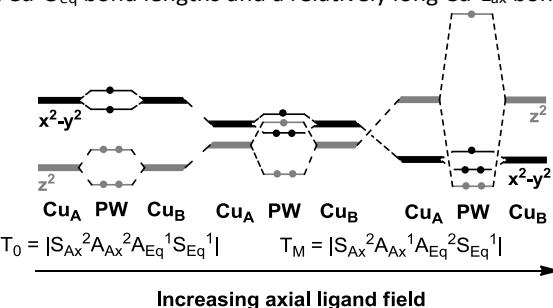


Figure 4 Schematic partial valence molecular orbital (MO) energy level diagram for copper paddlewheel systems as a function of increasing the axial ligand field. For the MOs, S refers to a symmetric (in-phase) combination of d orbitals, A to an asymmetric combination, Ax = d_{z2} and Eq = d_{x2-y2}.

With a stronger axial field generated by shortening the Cu-NH₃ and lengthening the Cu-O bonds, d_{z2} becomes the highest energy d orbital for the *isolated* pentacoordinate system (Figure 4, right). In the dimer, these orbitals are oriented for metal-metal σ -bonding and the splitting between the S and A combinations is no longer small. The more one tries to force a stronger axial ligand field, the more stabilised the symmetric d_{z2} MO (S_{Ax}) becomes while the antisymmetric d_{z2} MO (A_{ax}) is increasingly destabilised. The system becomes trapped in an intermediate ‘mixed’ state in which one unpaired electron occupies the A_{Ax} d_{z2} MO and the other the higher of the two d_{x2-y2} combinations which turns out to be S_{Eq}.

This new mixed d_{x2-y2}/d_{z2} state, T_M, is interesting in that the unpaired electron on each copper centre is shared between the d_{x2-y2} and d_{z2} orbitals. In the localised picture, we have a resonance mixing of two configurations, one with an unpaired electron in the d_{z2} orbital on Cu_A and the other unpaired electron in the d_{x2-y2} orbital on Cu_B, and vice versa.

For [Cu₂(formate)₄(NH₃)₂], the mixed state is a local minimum but some 5–6 kcal mol⁻¹ higher than the elongated state. However, it provides the clue that using stronger axial donors may eventually favour the mixed state.

In order to maintain strict control over the electronic states, we carried out a series of symmetry-restricted optimisations.¹⁴ These structures are only local minima with respect to the applied point group so the calculated values of $\Delta E(T_M - T_0)$ serve only as an approximate guide.

Complex	Point Group	BP86/DZP $\Delta E(T_M - T_0)$	B3LYP/TZVP $\Delta E(T_M - T_0)$
CuPH ₂ H ₂ O	D _{2h}	16.42	
CuPCH ₃ .2H ₂ O	D ₂	18.38	
CuPCH ₃ .2NH ₃	C _{2h}	6.73	
CuPCH ₃ .2py	D ₂	7.07	
CuPCH ₃ .2CN	D ₂	4.46	
CuPCH ₃ .2NHC	C _{2v}	0.03	
CuPCF ₃ .2NHC	C _{2v}	-6.17	-2.42

Table 1 Energy differences (kcal mol⁻¹) between T_M and T₀ states for symmetry restrained optimised CPW systems. The B3LYP/TZVP energy difference employed the BP86/DZP-optimised structures.

Table 1 shows that $\Delta E(T_M - T_0)$ decreases with decreasing electronegativity of the axial donor, L, and decreasing pK_a of the

equatorial carboxylate. The former corresponds to increasing the covalency (and hence strength) of the axial ligand field while the latter corresponds to a progressive weakening of the equatorial field. The calculations suggest that the combination of a strong carboxylic acid (hence weak conjugate base) and a highly covalent axial group such as an N heterocyclic carbene (NHC) may be sufficient to make the T_M (i.e. mixed) state the lowest energy spin triplet.

To explore this possibility, we relaxed all symmetry constraints and carried out full optimisations and frequency calculations for N-methyl NHC complexes. The structures changed significantly compared to the symmetry-constrained cases and the T_M state becomes the lowest triplet state already for the acetato species.

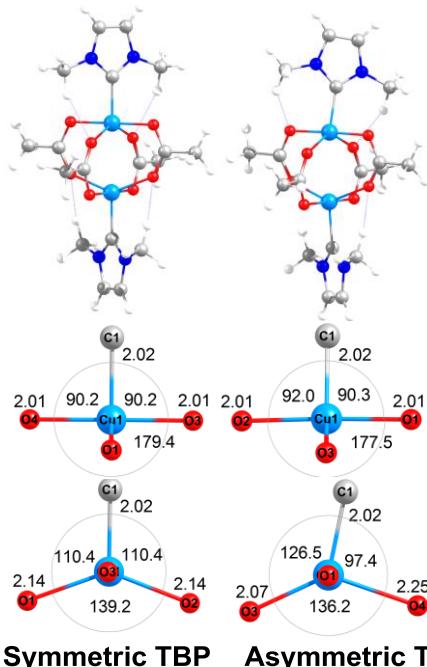


Figure 5 Optimised geometries for $[Cu_2(\text{acetate})_4(\text{Me}_2\text{NHC})_s]$. Top: complete structures; Middle and bottom: local geometrical detail around the metal centres. Numbers with two decimal places are distances in Å; those to one decimal place are angles in °.

Strong-field NHC groups completely change the coordination geometry compared to copper acetate dihydrate. The lowest-energy NHC structure has a ‘symmetric’ TBP geometry but with relatively long equatorial carboxylate bond lengths (2.14 Å) and short ‘axial’ carboxylate contacts of 2.01 Å (Figure 5, left). At almost the same energy is an ‘asymmetric’ TBP geometry (Figure 5, right) where the NHC moiety tilts towards an equatorial oxygen resulting in a lengthening of that Cu-O bond by ~0.1 Å while the other ‘equatorial’ Cu-O distance shortens by 0.07 Å. This type of structural change is well known for pentacoordinate Cu(II) species such as $[\text{Cu}(\text{bipy})_2\text{Cl}]^+$ where the Cu-Cl distance increases from 2.26 Å to 2.36 Å as the equatorial N-Cu-N angle opposite opens up from ~97 ° to ~124 °. Here, the energy difference between ‘symmetric’ and ‘asymmetric’ TBP-like structures is less than 1 kcal mol⁻¹ which now mirrors simple mononuclear Cu(II) complexes where the d_{z^2} and $d_{x^2-y^2}$ orbitals mix freely. The shape of the ‘hole’ in the d shell, and its stereochemical activity, is thus highly variable resulting in significant changes in structure for almost no change in energy.

The structural change destroys the nominal tetragonal symmetry assumed in the construction of Figure 4 and thus muddies the distinction between Ax and Eq with regard to the d orbitals containing the unpaired spin. The dominant axis is now aligned along the shorter Cu-O_{eq} bonds (Figure 6). Broken symmetry B3LYP calculations still show that the ground state is antiferromagnetically coupled ($J = -140 \text{ cm}^{-1}$ ¹⁵).

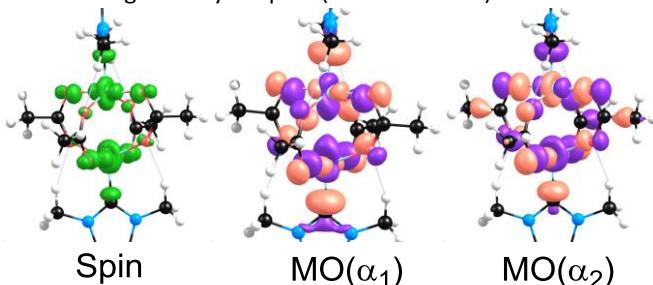


Figure 6 Spin density (left) and plots of the molecular orbital housing the two unpaired electrons for the symmetric TBP structure shown in Figure 5, left.

The change in electronic structure thus has a significant effect on the geometric structure and flexibility of the CPW. As shown schematically in Figure 7, the tilting of the NHC causes significant structural changes, more so when we consider that there is an equivalent tilting motion at right angles to that shown at the bottom of Figure 7.

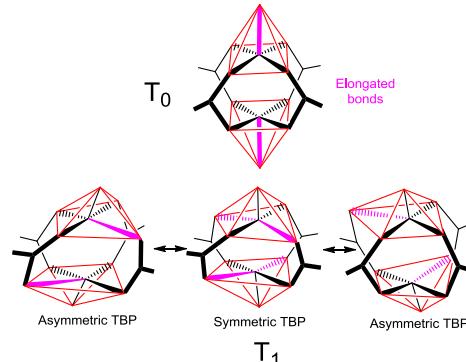


Figure 7 Schematic diagram of the sense of Jahn-Teller elongation (highlighted in pink) for CPW-NHC systems

We believe these computational results might have significant implications for CPW MOFs. Given the existence of zinc paddlewheel complexes with NHC axial groups¹⁶ (e.g. Cambridge Structural Database recode AZOGOL, Figure 8, top) plus an example of a Cu(II)-carboxylate-NHC complex¹⁷ (refcode QAXKAC, Figure 8, bottom), it appears that synthesising a CPW with NHC groups might be feasible. Computational support for this assertion is, firstly, that the NHC CPWs are true local minima on the potential energy surface. Secondly, the estimated ΔG values for acetato CPW complexes with three carbenes which span a range of pK_a values¹⁸ (see ESI) is comparable to that for two corresponding QAXKAC-like monomers, being ~8 to 10 kcal mol⁻¹ in favour of the CPW at the BP86/SVP/D3 level and ~1-2 kcal mol⁻¹ less favourable at the B3LYP/TZVP/D3 broken symmetry level. Thus, while the thermodynamics may seem to favour monomers, a higher calculated free energy does not preclude the formation of the dimer and both monomer and dimer can be stable entities just as is observed for copper

acetate hydrate where both the ‘unexpected’ monomer¹⁹ and the ‘normal’ dimer¹¹ exist. However, obtaining the species with the higher free energy may require clever synthetic strategies. The formation of an NHC CPW directly from its components may fail but introducing the NHC to pre-formed CPWs, such as those often encountered in MOFs, may succeed.

Several CPW MOFs have large enough pores to accommodate NHC capping groups.^{20, 21} The question will be whether the NHCs will coordinate to the copper sites and whether any barriers to dissociation are high enough. Simply increasing the Cu-Cu separation in an isolated NHC CPW rapidly increases the energy (see ESI) so the system is at least stable with respect to this dissociation route. Partial capping should also help keep the framework stable. If synthetic strategies to generate CPW NHC MOFs can be developed, the comparison of the structures of AZOGOL with its copper analogue (Figure 8) suggests that a Cu-NHC MOF could behave quite differently to existing CPW MOFs.

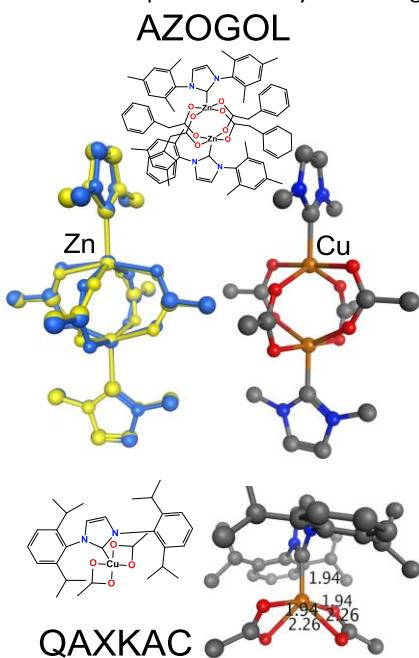


Figure 8 Illustrative metal-NHC complexes. AZOGOL is a zinc-NHC paddlewheel $[\text{Zn}_2(\text{OC}_2\text{CH}_2\text{Ph})_4(\text{N-MesitylNHC})_2]$ while QAXKAC is $\text{Cu}(\text{II})\text{-}\{\text{bis}(2,5\text{-PrPh})\text{NHC}\}(\text{acetate})_2$. For the Zn complex, yellow corresponds to the X-ray structure, blue to the DFT optimisation. The CPW is also the computed geometry (BP86/SVP/D3/COSMO).

Flexible MOFs are interesting²² and while NHCs have been incorporated into MOFs,²³ simply attaching NHCs to the copper paddlewheel centres has, to our knowledge, not yet been reported. Given the predicted effects on the structures and the fact that the $\text{Cu}(\text{II})\text{-NHC-carboxylate}$ complex is a hydrosilylation precatalyst,¹⁷ the properties of partially- or fully-capped NHC CPW MOFs, if they can be synthesised, are certain to be different and may potentially be very interesting compared to current systems. We are currently extending our first-principles ligand field molecular mechanics^{24, 25} force field for zinc paddlewheels²⁶ to CPWs in order to model such systems.

Notes and references

Full computational details including methods/basis sets/solvation models, coordinates etc. are included in the ESI.

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