

## COORDINATION CHEMISTRY

## Copper comeuppance

“the description of physical  $d^8$   $\text{Cu}^{\text{III}}$  in any case is likely unjustified”

Copper has a central role in many biological and synthetic catalysts. Although copper complexes typically have formal oxidation states of +I and +II, high-valent  $\text{Cu}^{\text{III}}$  has been implicated in reactive intermediates. For example, the  $\text{Cu}^{\text{III}}$  redox pair is suggested to perform analogously to  $\text{Pd}^{\text{IV}}$  in bond formation chemistries. Several complexes formally assigned as  $\text{Cu}^{\text{III}}$  have been isolated, but peculiarities remain in understanding their electronic structures. For instance,  $[\text{Cu}(\text{CF}_3)_4]^-$  can formally be considered to have four  $\text{CF}_3^-$  ligands surrounding a  $\text{Cu}^{\text{III}}$  centre, yet the frontier orbitals have predominantly ligand character. This suggests that the monoanion may better be described as a  $d^{10}$   $\text{Cu}^{\text{I}}$  complex. Such ‘ligand field inversion’ contrasts the typical assignment of ligand field molecular orbitals as being metal-centred. Oftentimes,  $d^9$   $\text{Cu}^{\text{II}}$  is distinguished from  $d^8$   $\text{Cu}^{\text{III}}$  by means

of Cu K-edge X-ray absorption spectroscopy (XAS), in particular the energy of the  $\text{Cu } 1s \rightarrow 3d$  electronic transition. However, interpreting these features is complicated by metal–ligand covalency, a hallmark of ligand field inversion. Writing in *Journal of the American Chemical Society*, Kyle Lancaster and colleagues challenge the formal assignment of  $d^8$   $\text{Cu}^{\text{III}}$  using a combination of Cu multi-edge X-ray spectroscopic measurements and time-dependent density functional theory (TDDFT) calculations.

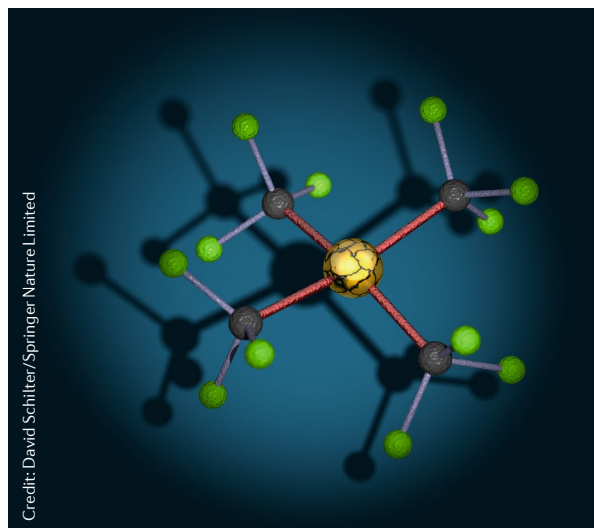
The team collected a diverse set of 17 representative Cu complexes, which feature a variety of ligands and have oxidation states ranging from +I to +III. The Cu complexes were interrogated by Cu K and  $L_{2,3}$ -edge XAS, and the set of complexes gave rise to peak energies in the range 8,977.6–8,981.8 eV, which were in excellent agreement with TDDFT calculations. Notably, these also exceed the proposed  $8,981 \pm 0.5$  eV range considered diagnostic of  $\text{Cu}^{\text{III}}$  and some fall in the  $8,979 \pm 0.5$  eV range normally ascribed to  $\text{Cu}^{\text{II}}$  species, emphasizing the ambiguity in using the Cu K-edge energy to assign oxidation states. However, Lancaster and colleagues find that the  $L_{2,3}$ -edges observed for the formally  $\text{Cu}^{\text{III}}$  species, which arise from  $2p \rightarrow 3d$  transitions, have intensities reflective of physically more reduced Cu centres. The team compared these data with robust covalency standards, thereby extracting the  $d$ -orbital contributions to the lowest unoccupied molecular orbital (LUMO) and singly occupied

molecular orbital (SOMO) of each complex. Importantly, the LUMOs/SOMOs of all formally  $\text{Cu}^{\text{III}}$  complexes have <50% Cu  $3d$  character, suggesting that these species each have an inverted ligand field and substantial covalent character. Experimental Cu  $3d$  contributions were very closely matched by values calculated using hybrid DFT. Given the strong correlation between the calculated and experimental results, modelling nine additional reported Cu complexes revealed all but one ( $[\text{CuF}_6]^{3-}$ ) to have bonds with similarly covalent bonding (and its Cu–F bonds, with 61% Cu  $3d$  character, would still be considered covalent).

Altogether, the XAS data and computational modelling emphasize an important distinction between formal and spectroscopic oxidation states. Indeed, careful examination of a range of Cu complexes by multi-edge XAS does not reveal any signature that is unambiguous evidence for the physical  $\text{Cu}^{\text{III}}$  oxidation state. Instead, the highly covalent bonding present in ‘ $\text{Cu}^{\text{III}}$ ’ complexes suggests substantial hole character to remain on the ligands. Importantly, Lancaster posits that “the description of physical  $d^8$   $\text{Cu}^{\text{III}}$  in any case is likely unjustified, with the exception perhaps of  $[\text{CuF}_6]^{3-}$ .” This conclusion has implications for understanding ligand reactivity and reaction mechanisms. For instance, instead of undergoing redox, a metal may simply modulate the charge on its ligands, such that they are more non-innocent than we think.

Adam Weingarten, Senior Editor,  
Nature Communications

**ORIGINAL ARTICLE** DiMucci, I. M. et al. The myth of  $d^8$  copper(III). *J. Am. Chem. Soc.* **141**, 18508–18520 (2019)



Credits: David Schilter/Springer Nature Limited