Inverted Ligand Fields – Implications on Electronic Structure and Reactivity

Sagnik Chakrabarti Literature Seminar July 23rd, 2020

Oxidation state formalisms are often not fully capable of capturing the nuances of electronic partitioning in metal-ligand bonds. The dichotomy between the formal oxidation state and the physical oxidation state has become more pronounced with the advent of advanced methods of characterizing the electronic structure of molecules, both by means of theory and experiments. Inversion of Ligand Fields was first proposed by Snyder in 1995[1], in describing the electronic structure of $[Cu(CF_3)_4]^-$. He proposed that the complex, formally with a Cu(III) center, is better described as Cu(I) with oxidized trifluoromethyl ligand sets. In his molecular orbital description (Fig. 1), the antibonding orbitals are predominantly based on the ligand atomic orbitals. His proposal was roundly criticized, which was met with an immediate response from him[2,3].

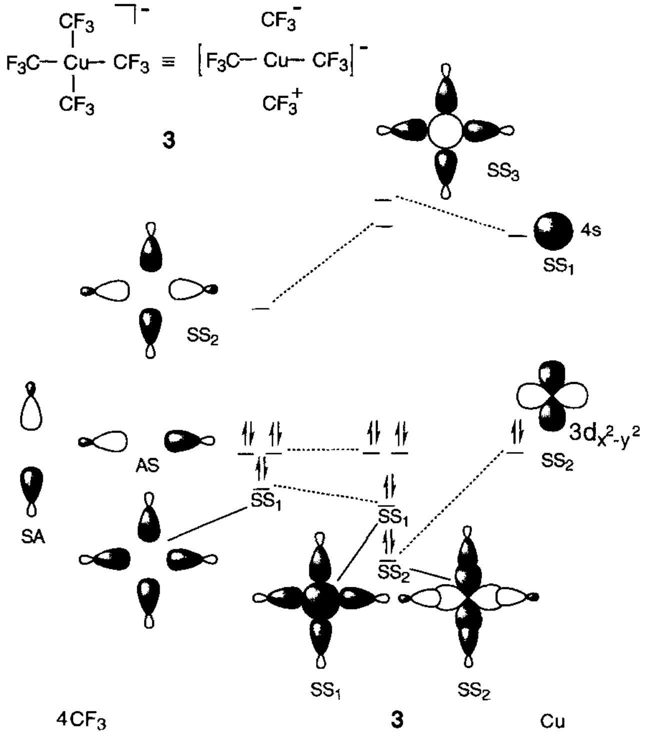

Fig 1: Correlation Molecular Orbital diagram of $[Cu(CF_3)_4]^-$. Adapted from Ref. 1.

The relative ease[4] of synthesizing the complex by a method reported by Grushin and coworkers in 2014[5] meant that the complex became amenable to spectroscopic experiments. In 2016, the Lancaster lab[6] employed Electronic and X-Ray absorption spectroscopy (Cu K-edge, Cu $L_{2,3}$-edge, Cu_{1s2p}-RIXS) to elucidate its electronic structure and their results lent support to Snyder's assignment of an inverted ligand field for the formally Cu(III) complex. The electronic spectrum showed no d-d transition in the NIR/visible regions. From XAS and TD-DFT simulation of XAS spectra, they came up with a molecular orbital energy ordering as shown below –

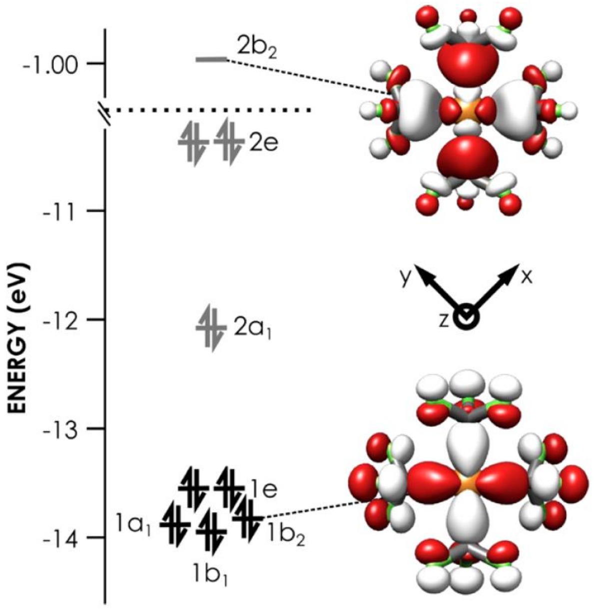

Fig 2: ωB97X/def2-TZVP(-f)-ZORA optimized M.O. diagram of $[Cu(CF_3)_4]^-$. Metal based M.O.s are shown in black, ligand-based M.O.s are shown in grey. Adapted from Ref. 4.

Their experiments firmly established that the d-orbitals of copper were fully occupied with a hole in a ligand based molecular orbital ($2b_2$). Thus, Snyder's claim of a Cu(I) center, with an oxidized CF_3 ligand was experimentally validated.

The Lancaster and Betley groups then extended their experiments to other formally cupric complexes[7]. Their XAS experiments and DFT calculations suggested the phenomenon of ligand field inversion was ubiquitous in such complexes with diminishing contributions to the LUMO from Cu 3d orbitals in almost all of these complexes. The authors claimed that in complexes with formally high-valent, late 3d transition metals, the phenomenon of ligand field inversion is general. This is because the metal atomic orbitals are stabilized to a degree that they go beneath the ligand atomic orbitals. In fact, Hoffmann and others, in a recent perspective[8], underscored how this phenomenon is implicit in periodic trends - *"As we move from left to right in the periodic table,* *the d orbitals go deeper, become core-like in late transition metals and the Zn group, and core in the p-block, leading to hypervalency. There is a continuous path from normal ligand field to inverted ligand field to hypervalence."*

In terms of reactivity, considerations of an inverted ligand field may lead to a re-interpretation known reactivity pathways. For example, theoretical methods from the Klein and the Liu groups have shown that the charge change in formally reductive elimination reactions involving Cu(III) and Ni(IV)[9,10] is negligibly small. The reaction may be viewed as a redox-neutral process with electrophile-nucleophile recombination of the ligands.

A copper-nitrene complex displaying bona-fide ligand field inversion was isolated by the Betley group in 2019[11]. The steric protection offered by the bulky peralkylated hydridacene substituents meant that nitrene expulsion or dimerization was prevented. This was the first example of a terminal Cu(I)-triplet nitrene. The electronic structure was characterized to be a d^{10} Cu(I) center with a subvalent triplet nitrene, with one of the radicals being nitrogen centered, while the other one was delocalized in the aromatic ring.

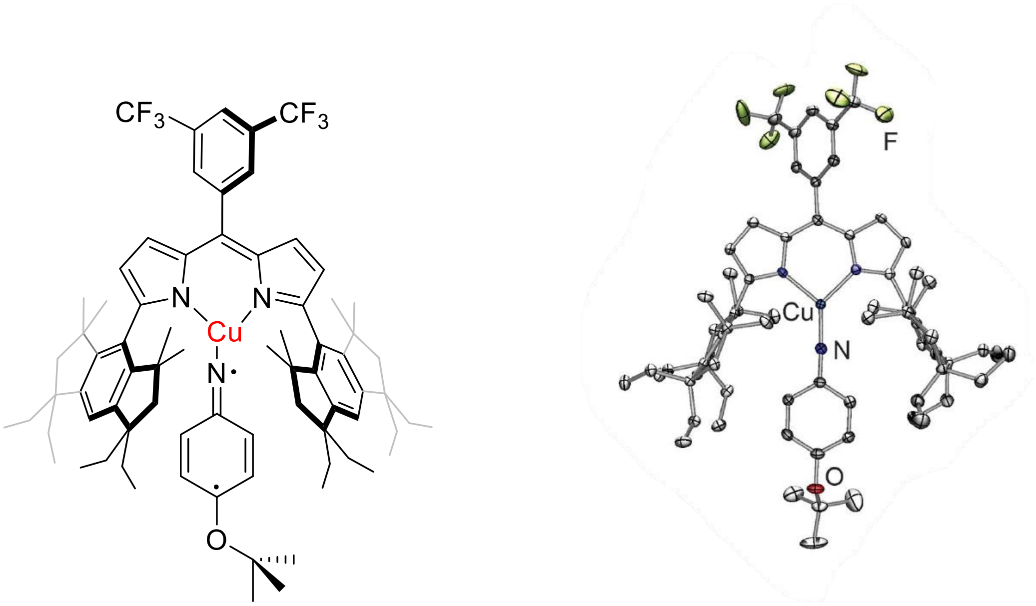

Fig. 3: The Cu(I)-nitrene complex, ball-and-stick representation (left) and the solid-state structure (right) at 50% displacement ellipsoid probability. Adapted from Ref. 9.

The existence of inverted ligand fields calls for a deeper analysis of physical *versus* formal oxidation states. While a metal center may formally be in a high oxidation state, the 'real' picture is that of an overall high *molecular* oxidation state, with ligand-centered holes. However, this does not necessarily mean that traditional ideas of oxidation state are redundant. As a first approximation, they are excellent guides to understanding and rationalizing reactivity, irrespective of normal or inverted ligand fields. However, convincing experimental evidence of such inversion can guide rational ligand design to selectively achieve unique reactivity.

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