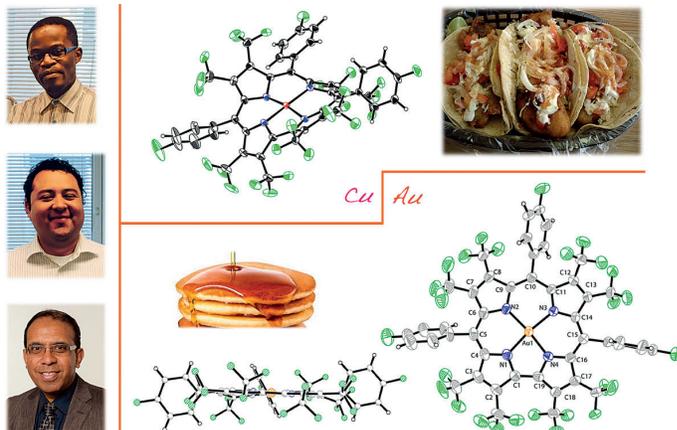


Ligand Noninnocence in Coinage Metal Corroles: A Silver Knife-Edge



Kolle E. Thomas (top left), who synthesized the compounds in question, Hugo Vazquez-Lima (middle left), who provided a coherent theoretical picture of the experimental data, and Abhik Ghosh (bottom left). Not pictured are Professor Karl Kadish and members of his research group at the University of Houston and collaborators at the Advanced Light Source, Berkeley, CA, who also made key contributions to this research.

Invited for the cover of this issue are Abhik Ghosh and his collaborators at UiT (The Arctic University of Tromsø, Norway) and in the United States. The image depicts a silver corrole complex poised on the summit ridge of Mount Sir Alexander, a peak of the Canadian Rockies (image courtesy of Chris Goulet), symbolizing the balance between innocent and noninnocent ligands. Read the full text of the article at [10.1002/chem.201502150](https://doi.org/10.1002/chem.201502150).

Why is ligand noninnocence important?

It's a fascinating problem. What inorganic chemists call 'noninnocent', theoreticians generally describe as 'multideterminantal'. The two terms are not quite synonymous, but noninnocent complexes are a major subset of multideterminantal systems. Describing these systems accurately, especially their excited states and electronic spectra, is something that today's quantum chemistry cannot do. That may, however, change over the next few years. Noninnocent systems are also very important in redox catalysis—both synthetic catalysts and enzymes, such as peroxidases and cytochromes P450. In essence, a noninnocent ligand acts as a reservoir of oxidizing or reducing equivalents.

What are your main contributions to the field?

We have worked in this field for a long time. An early contribution was to show that broken-symmetry DFT provides a decent, first-order description of most cases of ligand noninnocence. Then we got busy with corrole chemistry. Unlike in porphyrin chemistry, where ruffled, saddled, and other nonplanar conformations are widespread, metallocorroles are typically planar or mildly domed. Copper corroles are a major exception, being *inherently* saddled. The saddling of copper corroles is due to noninnocence, a specific metal–ligand orbital interaction, although it can be further enhanced by sterically demanding substituents. In the figure above, observe that a copper β -octakis(trifluoromethyl)corrole is folded like a taco, whereas the analogous gold complex is flat as a pan-

cake! That's why it was so interesting to get a crystal structure of a sterically hindered silver corrole. The silver case is utterly fascinating: silver corroles seem to straddle a knife-edge between the innocent and noninnocent. Depending on the substitution pattern, they may be either. My favorite contribution to our understanding of ligand noninnocence is in the field of electronic spectroscopy. The Soret maxima of noninnocent metallocorroles are exquisitely sensitive to *para*-substituents on the *meso*-aryl groups, providing a simple, spectroscopic signature of ligand noninnocence in this growing class of complexes. To my knowledge, these spectra are unique in the literature on ligand noninnocence.

What other topics are you working on at the moment?

The synthesis of gold corroles got us hooked on 5d metallocorroles, which are unique *size-mismatched* complexes. We were drawn by the sheer challenge of squeezing a large atom, such as osmium or platinum, into the tight central cavity of a corrole. Fortunately, Dr. Abraham Alemayehu, a senior researcher in my laboratory, and Rune Einrem, an enterprising undergraduate, were more than equal to the task so now we have an extensive library of these complexes. There are strong indications that the complexes will prove useful—in photodynamic therapy, photocatalytic water-splitting, organic solar cell—to name only a few potential applications. But it's worth remembering what got us to this point—simply being curious and trying things out in the lab.

