Chemistry–A European Journal

Cover Profile
doi.org/10.1002/chem.202303605

Chemistry Europe
European Chemical Societies Publishing

www.chemeurj.org

Chiral-at-Metal Racemization Unraveled for MX_2(a-chel)$_2$ by Means of a Computational Analysis of MoO_2(acnac)$_2$


George Dhimba


Alfred Muller


Koop Lammertsma

Invited for the cover of this issue are Koop Lammertsma and co-workers at the University of Johannesburg and Vrije Universiteit Amsterdam. The image of the kudu's antlers depicts the isomerization and racemization of the chiral-at-metal complex MoO2(acnac)2 (acnac = β-ketoiminate). Read the full text of the article at 10.1002/chem.202302516.

What is the most significant result of this study?

The three chiral *cis*-MoO_2(acnac)$_2$ isomers are connected by means of DML twists (the kudu's antlers in the cover picture) with each racemizing via a CH twist (horizontal bars). Far less relevant for the isomerizations and racemization are the established Bailar and Ray-Dutt twists for octahedral transition metal complexes. This work could serve as a template to control the barrier heights of the DML and CH twists by substituting the chelates appropriately to ensure chiral integrity for chiral-at-metal catalysis.

What prompted you to investigate this topic/problem?

Chiral-at-metal catalysis is a new field that relies solely on the chirality of the metal center instead of using chiral ligands, as in current asymmetric organometallic catalysis. Eliminating expensive chiral ligands requires chiral integrity of the metal center, which necessitates an understanding of how to control its octahedral coordination sphere with two simple chelates. Since Muetterties' topological studies in the late 1960s, little progress has been made to unravel racemization pathways of transition metal complexes. Our computational study provides a foundation that can be built upon to further advance the field.

What was the inspiration for this cover design?

Chirality is an essential component to life and is often depicted by two hands, left and right. These mirror images are standard in textbooks to reflect enantiomeric carbon centers. Pentacoordinate phosphorus and silicon atoms also display chirality. This study concerns hexacoordinated molybdenum, the chirality of which is readily visualized by the kudu's antlers. As there are three sets of enantiomers, each antler reveals a DML twist to convert one isomer to another, with the two antlers reflecting the enantiomeric relationship. The kudu is a beautiful animal that is prominent in South Africa where this research was conducted.

Chemistry–A European Journal

Cover Profile
doi.org/10.1002/chem.202303605

COVER PROFILE

G. Dhimba, A. Muller, K. Lammertsma*

■■ – ■■

Chiral-at-Metal Racemization Unraveled for MX_2(a-chel)$_2$ by Means of a Computational Analysis of MoO_2(acnac)$_2$

"Eliminating expensive chiral ligands requires chiral integrity of the metal center, which necessitates an understanding of how to control its octahedral coordination sphere with two simple chelates." This and more about the story behind the front cover can be found in the article at 10.1002/chem.202302516).