

FA4-MS34-T03

When Crystallography meets Kinetics. A study of Rhenium(III) tricarboxylates. Hendrik G. Visser, Andreas Roodt, Alice Brink, Gerdus Kemp, Marietjie Schutte *Department of Chemistry, University of the Free State, P.O. Box 339, Bloemfontein 9300, South Africa.*
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Our interest is to develop methods to incorporate ^{99m}Tc and $^{186/188}\text{Re}$ into biomolecules for potential use as diagnostic and/or therapeutic agents in radiopharmacy. Currently, the synthesis of new radiopharmaceuticals is accomplished with a hit-and-run approach, which can only be changed by a good understanding of the basic chemistry of the specific synthons involved. This study focuses on the thermodynamic and kinetic properties of H_2O substitution in $[\text{Re}(\text{CO})_3(\text{L}-\text{L}')(\text{OH}_2)]^{n+}$ ($\text{L}-\text{L}' = \text{N}, \text{N}', \text{N}, \text{O}$ and O, O ligands and $n = 0, -1$) in the adoption of a typical [2+1] approach [1]. The labilising effect of the bidentate ligands on $\text{Re}-\text{OH}_2$ bond distances in both solid and solution states is illustrated by an extended range of crystal structures obtained from X-ray studies, coupled with IR and kinetic data [2 – 4]. A range of eight crystal structures on model pharmaceutical complexes, as well as the implications on the reactivity and biomolecular uptake, will be discussed in this presentation.

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Keywords: rhenium, kinetics, radiopharmacy

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Unprecedented isomerism of new stable monomeric lead(II) dithiolate $\text{Pb}(\text{SCH}_2\text{CH}_2\text{NMe}_2)_2$. Victor N. Khrustalev. *Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Russia.*
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Herein we report on the comprehensive structural characterisation of new stable monomeric dithiolate $\text{Pb}(\text{SCH}_2\text{CH}_2\text{NMe}_2)_2$ (**1**). Structure and dynamic behaviour of **1** have been studied by multi-nuclear NMR, IR and Raman spectroscopy in solution as well as variable-temperature Raman spectroscopy and X-ray diffraction analysis in the solid-state. Unprecedentedly, compound **1** displays the unusual “flip-flop” process in solution and the reversible pseudorotation of the five-membered rings in the solid-state. The enantiomerically pure solid **1** implies that the mechanism of the “flip-flop” process in solution of **1** may be different from that in solutions of its oxy-analogues $\text{Ge}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_2$ (**2**) and $\text{Sn}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_2$ (**3**) [1]. Apparently, in contrast to **2** and **3**, compound **1** does not form the two enantiomers during the “flip-flop” process, because the spontaneous separation of the enantiomers participating in the “flip-flop” equilibrium was not observed till now. Despite of that the cleavage energies of the two $\text{M}-\text{N}$ coordination bonds in **1**, **2** and **3** are very close (23.5, 21.2 and 29.5 kcal/mol, respectively), this fact could be possibly determined by the larger transformation barrier between the two enantiomers of **1** in comparison to those for **2** and **3**, which depends, in particular, on the size and character of the stereochemically active lone pair of metal atom. The

reversible pseudorotation of the five-membered rings in **1** occurring in the solid-state is explained by the change of conformational degree of freedom upon the thermal change of the unit cell parameters of the crystal. DFT calculations reveal the very small difference in energy of the two conformers - symmetrical and asymmetrical observed in the crystal, which explains the conformational transition between them even in the solid-state. Nevertheless, the predominance of the symmetrical conformer is clearly pronounced that is the driving force of the conformational isomerism.

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Keywords: lead(II) compounds, „flip-flop“ dynamic process, reversible pseudorotation in the solid-state

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Multistep Bidentate Ligand Coordination at Hafnium(IV). J. Augustinus Viljoen, Hendrik G. Visser, Andreas Roodt. *Department of Chemistry, University of the Free State, Bloemfontein, 9300, South Africa.*
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Hafnium and zirconium show extremely similar chemical properties and occur together in nature, and zircon, a zirconium silicate mineral (ZrSiO_4), is the primary source of all hafnium. Zirconium and hafnium are contained in zircon at a ratio of about 50 to 1 [1], and the separation of these metals is very difficult due to the similarities in chemical behaviour [2]. The aim of this study was to investigate the chelating behaviour of hafnium with different organic bidentate ligands e.g. trifluoroacetylacetone (tfaaH), hexa-fluoroacetylacetone (hfaaH) and 8-hydroxyquinoline (OxH) and the characterization of the new compounds obtained from this by means of single crystal X-ray crystallography and UV/Vis spectroscopy. Any small differences in solution behaviour, whether it being reaction mechanism, solubility, coordination modes, equilibrium behaviour, etc., could possibly be exploited in developing novel separation techniques for the two metals. The structures of three new complexes, namely the $[\text{Hf}(\text{tfaa})_4]$ [3], $[\text{Hf}(\text{OH})(\text{hfaa})_3]_2$ [4] and $[\text{Hf}(\text{Ox})_4]$ [5] were determined. This enabled the identification of products for kinetic studies and increased the available pool of these rare compounds in literature. The crystallographic characterization of all these complexes will be presented. As part of the kinetic investigation the formation of the above complexes, i.e., the stepwise reactions between HfCl_4 and OxH ligands were followed by means of stopped-flow and UV/Vis spectroscopy. A total of five reactions were observed for the stepwise coordination of OxH to the tetrachlorido hafnium(IV) complex.

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