

MS43-P17 An Imidazolium-Substituted Pd₃-Cycloheptatrienyl-Sandwich Complex Alexander Pöthig,^a Kevser Mantas-Öktem,^a Karl Öfele,^a Bettina Bechlars,^a Wolfgang A. Herrmann,^a Fritz. E. Kühn,^{aa} *Chair of Inorganic Chemistry /Molecular Catalysis, Catalysis Research Center, Technische Universität München, Ernst-Otto-Fischer-Straße 1, D-85747 Garching, Germany*
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Cycloheptatrienylidene (CHT)-palladium complexes can react with N-donor molecules, showing two different reaction pathways – Nucleophilic attack at the CHT-ligand or coordination to the metal center. A series of single crystal X-ray structures of the resulting products are presented, including an imidazolium-substituted tripalladium-CHT sandwich complex. The latter possesses a Pd₃-moiety, which is nearly coplanar to each CHT-ring and η¹-coordinated to each one of three bromine atoms. The Pd-Pd distances are within a range of 2.732 Å to 2.783 Å and the distance between the Pd₃- and CHT-plane is 2.100 Å and 2.095 Å, respectively. This structural motif has been reported only once with unsubstituted CHT-rings, indicating a formal oxidation state of Pd(I). [1]

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MS43-P18 Coordination and separation chemistry of hafnium oxinato complexes. J. Augustinus Viljoen, Hendrik. G. Visser and Andreas Roodt, *Department of Chemistry, University of the Free State, Bloemfontein 9300, South Africa*
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Hafnium and zirconium metals and alloys have wide application in the nuclear industry because of their unique thermal neutron absorption cross-sections (NAC), mechanical strength and resistance to corrosion associated with nuclear reactors operating at elevated temperatures. Due to lanthanide contractions [1], zirconium and hafnium are very similar in chemistry and usually occur together. The separation of hafnium and zirconium is very difficult because these two elements are so similar in terms of their chemistry. One could almost go so far as to describe these elements as chemical twins. The only other major chemical difference between hafnium and zirconium is their *density* (zirconium being about half as dense as hafnium) and *neutron-capture cross-section* [2] (hafnium about 600 times that of zirconium).

The aim of this study was to investigate the chelating behaviour of tetrachlorido hafnium(IV) (HfCl₄) with different 8-hydroxyquinoline derivatives (OxH) and the characterization of the new compounds obtained from this by means of single crystal X-ray crystallography. 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 seven new complexes, namely the [Hf(Ox)₄] [3], [Hf(5-Cl(Ox))₄], [Hf(5,7-diCl(Ox))₄], [Hf(5,7-diBr(Ox))₄], [Hf(5,7-diI(Ox))₄], [Hf(5,7-diMe(Ox))₄] [4] and [Hf(5-Cl,7-I(Ox))₄] 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 discussed in this presentation.

As part of the study, preliminary separation investigations of the above complexes *via* liquid-liquid extraction were undertaken. It was determined that it is possible to extract freshly synthesized Hf and Zr oxinato complexes from a DMF solution into a dichloromethane (DCM) solution. Selected results from some of these preliminary extraction experiments will be presented.

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[4] Viljoen, J. A., Visser, H. G. and Roodt, A., (2011) *Acta Cryst.*, **E67**, m1428-m1429.

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