From nuclear fuels to CO_2 functionalization and H_2O splitting catalysis at reactive uranium complexes

Chemistry between phobia and enthusiasm

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RSEQ Real Sociedad Española de Química El Sitio de la Química en España

From nuclear fuels to CO_2 functionalization and H_2O splitting catalysis at reactive uranium complexes – Chemistry between phobia and enthusiasm

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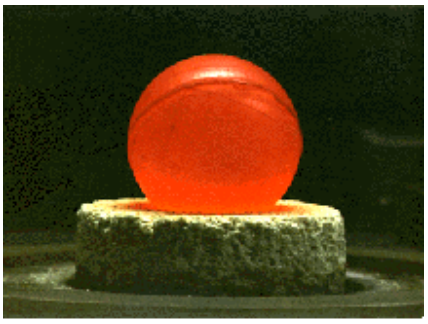
Uranium and, its in traces existing heavier neighbor, plutonium, are the heaviest naturally occurring elements, and they share one common thing with each other: they undeniably have the worst reputation of all elements of the periodic table.



Fusion heat powered red-hot glowing 100 Watt $^{238}PuO_2$ heat source used in the 1970s space missions. The source is about 250 g and about 3 cm in diameter.
Photo: Courtesy of Dr. David L. Clark, LANL

In this lecture, a general introduction is given on how radioactivity of naturally abundant and man-made elements, e.g. in plutonium-powered cardiac pacemakers and satellites, impact our modern life. A brief tour through basic inorganic chemistry shows how pitchblende is transformed into nuclear fuels, how organometallic chemists have discovered the element for basic chemical research, and how this field has sparked new discoveries of current interest ever since. In our efforts to activate small molecules of industrial and biological importance, we have turned our attention to coordinatively unsaturated, reactive uranium coordination complexes. For example, the chelating triazacyclononane (tacn), single N, and arene-anchored tris(aryloxide) ligands, $(ArO)_3tacn^{3-}$, $(ArO)_3N^{3-}$, and $(ArO)_3mes^{3-}$ have provided access to reactive coordination compounds of uranium in oxidation states II, III, IV, V, and VI with tailorable steric and electronic profiles. These complexes display a pronounced selectivity and reactivity in reactions with carbon dioxide, related small heteroallene molecules (COS and CS_2), and H_2O. In this seminar, our work on CO_2 activation, including unprecedented coordination modes, reductive cleavage, insertion, and functionalization reactions is reported. Most recently, the stoichiometric and catalytic "disproportionation" of CO_2 to CO and CO_3^{2-} *via* reductive cleavage of CO_2 was accomplished. The molecular and electronic structure of a new oxidation state in U coordination chemistry is reported; namely U(II), with a $5f^4$ quintet ground state. In K(2.2.2-crypt)[((^{Ad,Me}ArO)$_3$mes)U], the electron-rich U(II) center is supported by δ backbonding.

Finally, a rare U(IV) hydroxo complex, [((^{Ad,Me}ArO)$_3$mes)U(OH)], with a terminal OH functionality was synthesized by selective oxidation of the U(III) complex [((^{Ad,Me}ArO)$_3$mes)U] with H_2O. Comprehensive electrochemical studies revealed that the U(III) complex can be regenerated in a catalytic cycle combining chemical and electrochemical reaction steps to produce H_2 from water. Thus, trivalent [(^{Ad,Me}ArO)$_3$Mes)U] was found to be the first molecular uranium catalyst for electrocatalytic H_2 production. Utilization of [(^{Ad,Me}ArO)$_3$Mes)U] during H_2O electrolysis lowered the overpotential by 0.5 V, increased the steady-state electrolysis current by a factor of 10, and lowered the faradaic resistance of the reaction by three orders of magnitude.

Leading References:

D.P. Halter, F.W. Heinemann, J. Bachmann and K. Meyer in *Nature* **2016**, DOI:10.1038/nature16530.

H.S. LaPierre, F.W. Heinemann, W. Hieringer and K. Meyer in *Angew. Chem. Int. Ed.* **2014**, *53*, 7158.

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S. Franke, F. W. Heinemann and K. Meyer in *Chem. Sci.* **2014**, *5*, 942.

O. P. Lam, S. Franke, F. W. Heinemann and K. Meyer in *J. Am. Chem. Soc.* **2012**, *134*, 16877.

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A.R. Fox, S.C. Bart, K. Meyer and C.C. Cummins in *Nature* **2008**, *455*, 341.
S.C. Bart, F.W. Heinemann, E. Bill, N.M. Edelstein and K. Meyer in *J. Am. Chem. Soc.* **2008**, *130*, 12536.
I. Castro-Rodriguez and K. Meyer in *J. Am. Chem. Soc.* **2005**, *127*, 11242.
I. Castro-Rodriguez, H. Nakai, L. Zakharov, A.L. Rheingold and K. Meyer in *Science* **2004**, *305*, 1757.

Karsten MEYER (born May 17th, 1968) studied chemistry (October 1989 – 1994) at the Ruhr-University of Bochum (Germany) and received his Diploma in May 1995. Starting in summer 1995, he performed his PhD thesis work under the direction of Professor Karl Wieghardt at the Max-Planck-Institute in Mülheim / Ruhr (Germany) and received his Ph. D. (Dr. rer. nat, *summa cum laude*) in January 1998. He then was awarded a DFG postdoctoral fellowship and, from 1998 to 2000, proceeded to gain research experience in the laboratory of Professor Christopher C. Cummins at the Massachusetts Institute of Technology (MIT, Cambridge, MA, USA). In January 2001, he was appointed to the faculty of the University of California, San Diego (UCSD) as an Assistant Professor and was named an Alfred P. Sloan Fellow in 2004. In 2006 he accepted an offer (C4/W3) to be the Chair of the Institute of Inorganic & General Chemistry at the Friedrich-Alexander-University of Erlangen-Nürnberg, Germany.

Professional Career

Oct. 1989	Study of Chemistry at the Ruhr-University-Bochum in Germany
May 1995	Diploma (Ruhr-University-Bochum)
July 1995	PhD Studies at the Max-Planck-Institute in Mülheim/Ruhr, Germany under the supervision of Prof. Dr. Karl Wieghardt
Jan. 1998	Dissertation (Dr. rer. nat) "Molecular and Electronic Structure of High-Valent Transition-Metal Nitrido Complexes"
Feb. 1998	Postdoctoral Studies at the Max-Planck-Institute Mülheim/Ruhr (Germany)
Oct. 1998	Postdoctoral Studies at the Massachusetts Institute of Technology (MIT) under the direction of Prof. Christopher C. Cummins, USA
Jan. 2001	Assistant Professor at the University of California, San Diego (UCSD), USA
Jan. 2006	University Full Professor (W3/C4) Chair of Inorganic and General Chemistry

Editorial Activities

2005	Volume Editor, Elsevier "Comprehensive Organometallic Chemistry III, Vol. 2"
2009	International Advisory Board, Wiley-VCH "European Journal of Inorganic Chemistry"
2011	International Advisory Board, ACS "Inorganic Chemistry" (2-yr term)
2013	Guest Editor, Wiley-VCH "European Journal of Inorganic Chemistry" Special Issue on "Small Molecule Activation by Reactive Metal Complexes"
2014	International Advisory Board, Taylor & Francis "Journal of Coordination Chemistry"
2014	Associate Editor, ACS "Organometallics"

Awards & Honors

2002	Hellman Fellow, Christ & Warren Hellman Young Faculty Award, USA
2003	Faculty Career Development Award, UC Academic Senate, USA
2004	Alfred P. Sloan Award, USA
2009	Israel Chemical Society, Lifetime Honorary Membership, IL
2009	Visiting Professorship, University of Manchester, UK

2009	Japanese Society for the Promotion of Science Award (JSPS), JP
2010	Dalton Transactions European Lectureship Award, UK
2010	MBRAUN Lecturer, Pacifichem 2010, Honolulu Hawaii, USA
2011	Fellow of the Royal Society of Chemistry, FRSC, UK
2012	Visiting Professor, Université Paul Sabatier, Toulouse, F
2015	JSPS Professorship "Brain Circulation Project" Nagoya Institute of Technology, JP http://www.nitech.ac.jp/eng/research/partners.html

Publications and Invitations

Karsten Meyer has published 130+ publications in peer-reviewed journals, an H-Index of 41 with a total of approx. 4700 citations, and an average citation per item of 34. The list of publications includes, among others, reports and articles in *Science*, *Nature*, *Nature Communications*, the *Journal of the American Chemical Society* (JACS), and *Angewandte Chemie*. He has given more than 150 invited talks, including opening and plenary lectures, at conferences as well as research and academic institutions worldwide.

Ten Selected Publications

D.P. Halter, F.W. Heinemann, J. Bachmann and K. Meyer*
"Uranium-Mediated Electrocatalytic Production of H_2 form Water"
Nature **2015**, accepted for publication.

A.-C. Schmidt, F.W. Heinemann, W.W. Lukens Jr.* and K. Meyer*
"*Molecular and Electronic Structure of Dinuclear Uranium-di-Oxo Complexes with Diamond Core Structural Motifs*"
J. Am. Chem. Soc. **2014**, *136*, 11980 – 11993.

H.S. La Pierre, A. Scheurer, F.W. Heinemann, W. Hieringer and K. Meyer*
"*Synthesis and Characterization of a Uranium(II) Monoarene Complex Supported by δ Backbonding*"
Angew. Chem. Int. Ed. **2014**, *53*, 7158 – 7162.

F. Scholz, D. Himmel, F.W. Heinemann, P.v.R. Schleyer, K. Meyer* and I. Krossing*
"*Crystal Structure Determination of the Nonclassical 2-Norbornyl Cation*"
Science **2013**, *341*, 62 – 64.

F. Kropp, M.M. Khusniyarov, F.W. Heinemann, K.M. Lancaster, S. DeBeer, E. Bill and K. Meyer*
"*Manganese Nitride Complexes in Oxidation States III, IV, and V: Synthesis and Electronic Structure*"
J. Am. Chem. Soc. **2012**, *134*, 15538 – 15544.

J.J. Scepaniak, C.S. Vogel, M.M. Khusniyarov, F.W. Heinemann, K. Meyer* and J.M. Smith*
"*Synthesis, Structure, and Reactivity of an Iron(V) Nitride*"
Science **2011**, *331*, 1049 – 1052.

S.C. Bart, C. Anthon, F.W. Heinemann, E. Bill, N.M. Edelstein and K. Meyer*
"*Carbon Dioxide Activation with Sterically Pressured Mid- and High-Valent Uranium Complexes*"
J. Am. Chem. Soc. **2008**, *130*, 12536 – 12546.

A.R. Fox, S.C. Bart, K. Meyer and C.C. Cummins
"*Towards Uranium Catalysts*"
Nature **2008**, *455*, 341 – 349.

C. Vogel, F. W. Heinemann, J. Sutter, C. Anthon and K. Meyer*
"*An Iron Nitride Complex*"
Angew. Chem. Int. Ed. **2008**, *47*, 2681 – 2684.

I. Castro-Rodriguez, H. Nakai, L. N. Zakharov, A.L. Rheingold and K. Meyer*
"*A Linear, O-Coordinated* η^1*-*CO_2 *Bound to Uranium*"
Science **2004**, *305*, 1757 – 1759.

For a complete and up-to-date list of publications, please see:
http://www.inorganic-chemistry.net/kmpages/publications.html