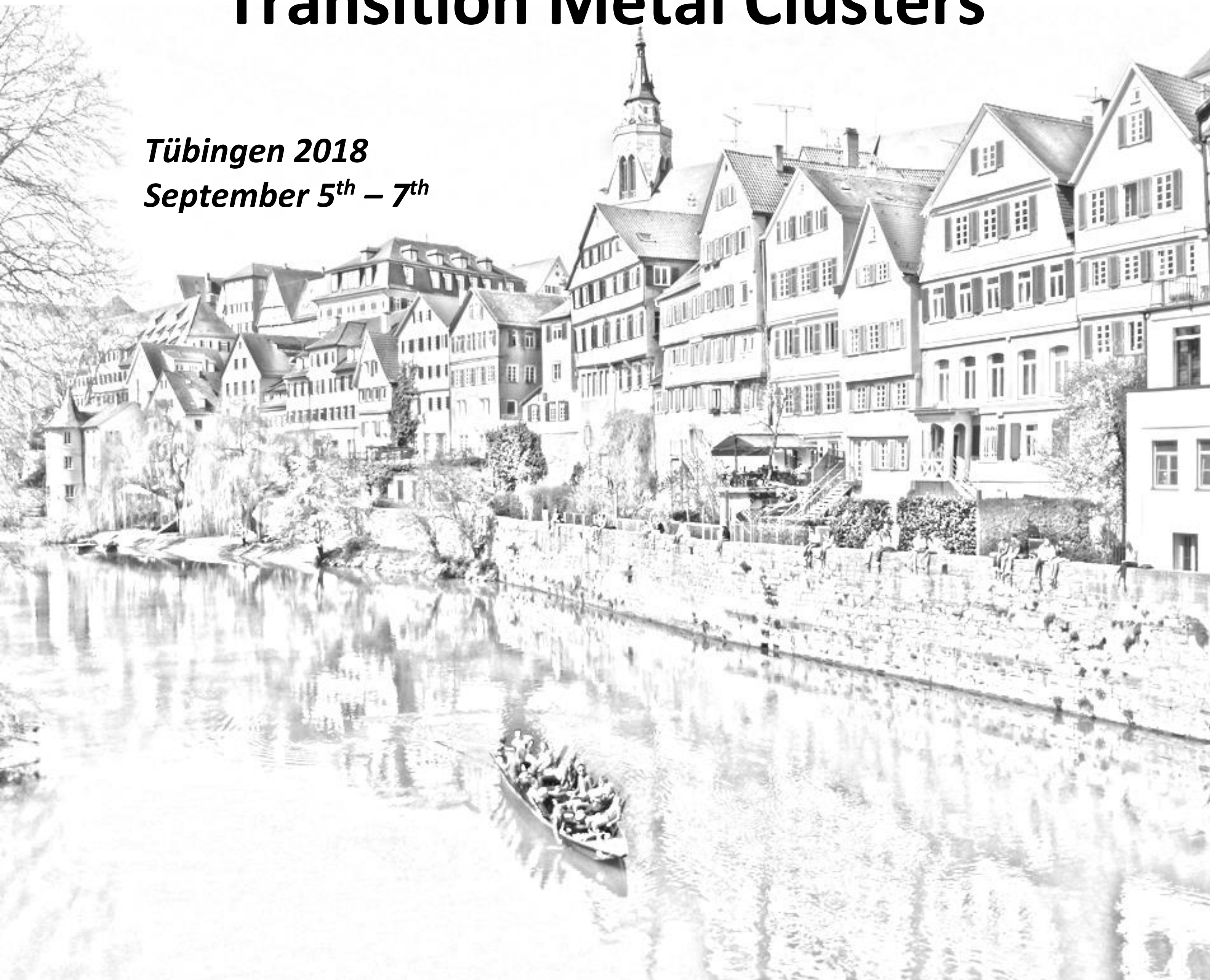
International Workshop on Transition Metal Clusters



Tübingen 2018
September 5th – 7th

IWTMC-2018

VIth International Workshop of Transition Metal Clusters

September 5th, 2018 – September 7th, 2018

held at the Hall of the Museum (1. Floor)

Wilhelmstr. 3, Tübingen (Germany)

Edited by

Prof. H.-Jürgen Meyer

Universität Tübingen

Overview:

Following the format of previous IWTMC workshops held in Rennes (2008), Rostock (2010), Benicassim (2012), Novosibirsk (2014), and Rennes (2016), this VIth IWTMC-2018 is an international forum to present and discuss recent results in cluster chemistry.

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Dear Participants, Dear Colleagues,

welcome to the International Workshop on Transition Metal Clusters (IWTMC) held in the halls of the Museum in the heart of the city of Tübingen!

I am very pleased that you have been able to follow our invitation to attend this VIth workshop and I look forward that you enjoy this meeting by sharing your research interests with expert scientists from several countries.

This workshop was initiated ten years ago as a trilateral meeting on metal cluster chemistry between scientists from France, Germany and Russia. The goal was to bring internationally recognized scientists in cluster chemistry together to discuss latest developments and future perspectives.

Research in cluster chemistry has a long tradition in many countries, most of them are likely represented in this workshop. Today, the word “cluster” can have different meanings. According to the definition of *Cotton* it resembles compounds containing metal-to-metal bonds. In a more general view it describes an ensemble of atoms of intermediate size in the sense of a very large molecule.

Today´s research on cluster chemistry has merged with several other fields thanks to the creativity of researchers, and the properties of such compounds have gained a lot of importance. Topics of the VIth workshop include inorganic and hybrid cluster compounds, cluster functionalization, clusters in biology and medicine, Zintl (related) phases, molecular and supramolecular assemblies, nanomaterials, quantum chemistry, functional surfaces, and several other topics. Some out of these compounds or materials are showing interesting (catalytic, optical, magnetic, or electronic) properties, as emphasized within this workshop by expert scientists from the relevant fields.

Special thanks are addressed to sponsors who have made this meeting possible, and to the local organizing committee and volunteers for their help in organizing this workshop.

Let´s look forward for an inspiring meeting!

H.-J. Meyer

Hans-Jürgen Meyer

Lunch Options

Lunch Options

1. Restaurant Museum

International & regional food,
Wilhelmstraße 3, Ground floor
12:00 – 2:30 pm & 6 - 11 pm

2. Wurstküche

Regional swabian food,
Am Lustnauer Tor 8,
Mon - Thu 11:30 am – 11 pm Fri & Sat 11:30 am - 0:00

3. Stadtpost

BBQ,
Neue Straße 9, 6 pm – late

4. La Torre

Pizza & Pasta,
Neckargasse 22,
Mon - Fri 11 am – 3 pm, 5 pm - 11 pm, Sat- Sun 11 am - 11 pm

5. Neckarmüller

Regional food
Gartenstraße 4,
Mon - Sat 10 am - 11 pm

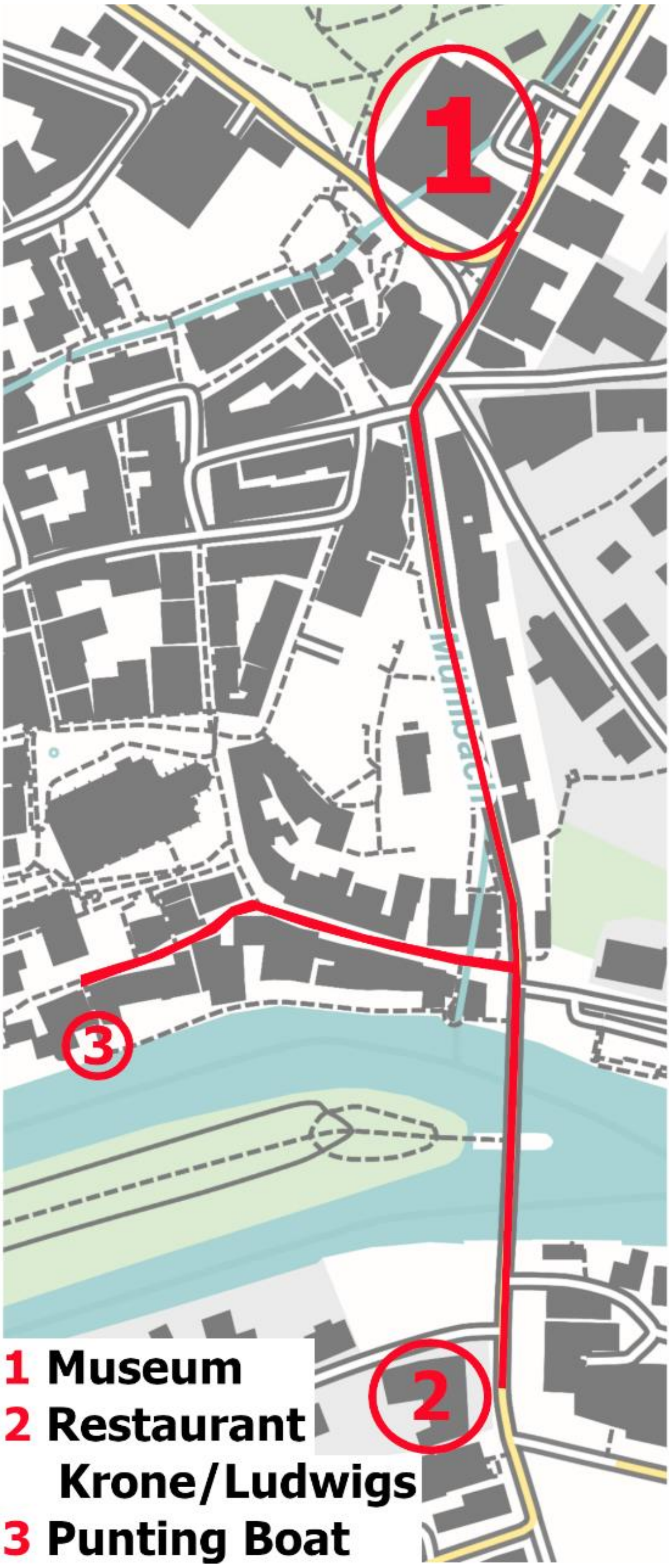
6. Kichererbse

Eastern & arabic vegetarian/vegan food,
Metzgergasse 2,
Mon - Thu & Sat 11 am - 9 pm, **Fri closed**

Old Town

Bars, Pubs, Restaurants, Shops
Yellow area on the map

Conference Dinner and Punting Boat



Conference Dinner and Punting Boat

1. Museum (Conference Location)

Wilhelmstraße 3

2. Restaurant Krone/Ludwigs

Uhlandstraße 1

3. Punting Boat

Bursagasse 2/1

Conference Schedule

Wednesday, September 5th 2018

	H.-Jürgen Meyer
13:00	Welcome and Opening Remarks
Chair	Angela Möller
13:15	**Thomas Fässler**
13:45	**Slavi Sevov**
14:15	**Stephane Jobic**
14:45	Andrei V. Shevelkov
15:05	Sergey N. Konchenko
15:25	Maxim Sokolov
15:45	Silvia Ruggieri
16:00	Coffee-Break
Chair	Rosa Llusar
16:30	**Stephane Cordier**
17:00	Jerome Cuny
17:20	Arthur Huguenot
17:35	Carmelo Prestipino
17:50	Maxim R. Ryzhikov
18:10	Iván Sorribes
18:25	Iuliia Laricheva
18:40	End of Session
19:00	Beer and Pretzels

Thursday, September 6th 2018

Chair	Stephane Jobic
09:00	**Takao Mori**
09:30	**Thomas Jüstel**
10:00	**Katja Heinze**
10:30	Coffee-Break
Chair	Martin Köckerling
11:00	**Vladimir Fedin**
11:30	**Kamil Lang**
12:00	Michael A. Shestopalov
12:30	Lunch-Break
Chair:	Andreas Schnepf
14:00	**Hansgeorg Schnöckel**
14:30	Janet Arras
14:45	**Bryan Eichhorn**
15:15	Tatiana N. Pozmogova
15:30	Yakov Gayfulin
15:45	Alina D. Mironova
16:00	Coffee-Break
Chair	Thomas Fässler
16:30	**Arndt Simon**
17:00	Angela Möller
17:30	**Gerd Meyer**
18:00	**Zhiping Zheng**
18:30	Arndt Simon
19:00	End of Session
20:00	Conference Dinner

Friday, September 7th 2018

Chair	Vladimir Fedin
09:00	**Pierre Braunstein**
09:30	**Stefanie Dehnen**
10:00	**Rosa Llusar**
10:30	Coffee-Break
Chair	Stephane Cordier
11:00	Kaplan Kiraki
11:20	Yuri Mironov
11:50	Clement Falaise
12:10	Mohamed Haouas
12:30	Lunch-Break
Chair	Pierre Braunstein
14:00	**Martin Köckerling**
14:30	Grigore A. Timco
14:50	**Stefano Zacchini**
15:20	Alvaro Munoz-Castro
15:40	End of Session
17:00	Punting Boat

Content

Oral Contributions

Content

Poster Contributions

Oral Contributions

Mixed Metal Clusters in Neat Solids and Isolated from Solution

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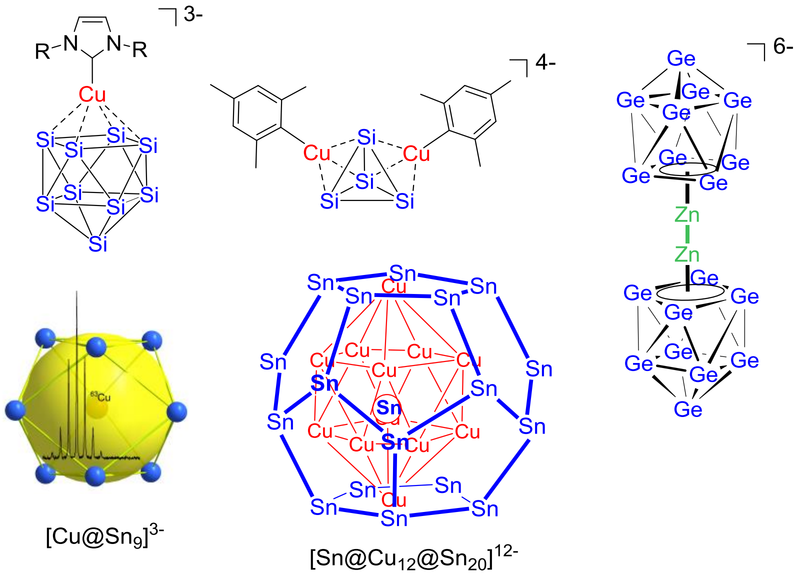
Abstract

Homoatomic deltahedral clusters have been proven to be an excellent source for the targeted synthesis of mixed main-group / transition metal clusters. Examples of discrete mixed-metal clusters occur in intermetallic compounds but can also be synthesized in solution. The versatile chemistry of bare $[E_4]^{4-}$ and $[E_9]^{4-}$ (E = Si to Pb) clusters as well as reactions towards transition metal complexes is discussed, and the possibility of formation of related clusters in intermetallic compounds is presented.

The question on the oxidation state of transition metals in mixed metal clusters is highlighted.



Anionic main-group clusters sprinkled with transition-metal atoms

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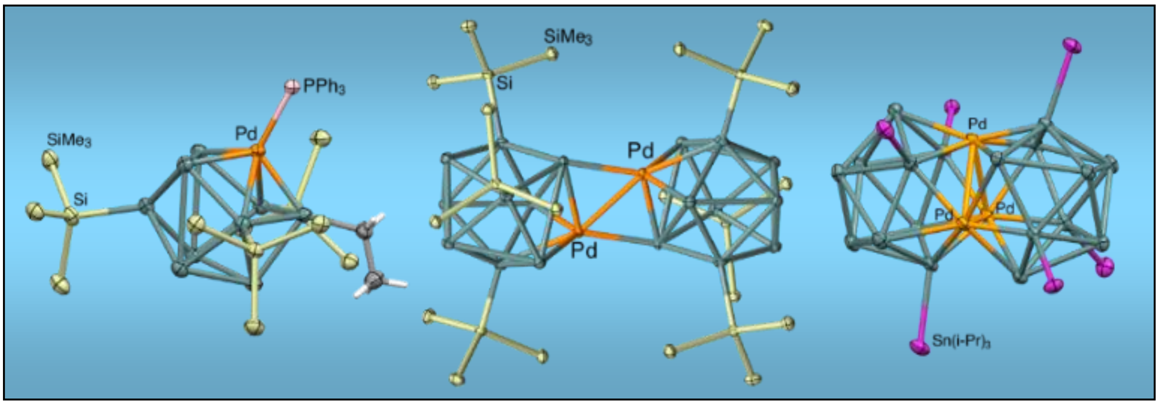
Abstract

My group has explored the solution chemistry of the post-transition metals and semi-metals, i.e. the heavier *p*-elements, in negative oxidation states. Upon electron transfer, many of them form anionic molecules and clusters, often referred to as Zintl ions.[1] Examples of these are the nine-atom deltahedral clusters E_9^{n-} where E = Si, Ge, Sn, Pb (n = 2, 3, 4), Pn_7^{3-} where Pn = P, As, Sb, Bi, as well Bi_2^{2-} dimers and Bi_3^{3-} trimers.[2-5] The talk will focus on the effect of incorporation of one or more transition-metal atoms into functionalized anionic and neutral main-group clusters $Ge_9R_3^-$ and Ge_9R_4, respectively. Thus, we have added a Pd^0-atom as the tenth vertex in the tetra-substituted $Ge_9(Si(SiMe_3)_3)_3Et$ to form the new species $(Ph_3P)\{PdGe_9\}(Si(SiMe_3)_3)_3Et$ shown in the Figure below (left).[6,7] We have also inserted a Pd_2^{2+} dimer between two tri-substituted anionic cluster to form the neutral $(Pd_2)\{Ge_9(Si(SiMe_3)_3)_3\}_2$ where each Pd(I) is a tenth vertex of each cluster (Figure, middle). Lastly, a triangle of Pd-atoms is incorporated between two trisubstituted clusters $Ge_9R_3^-$ to form a twin icosahedron $[Ge_{18}Pd_3R_6]^{2-}$. Interestingly, the six R-substituents are *staggered* (Figure, right) or *eclipsed* when R = Sn^iPr_3 or Si^iPr_3, respectively.[8,9] Using relativistic DFT calculations, we elucidated the reasons for the different positioning of the ligands in the stannyl- and silyl-functionalized species.[9]

Also discussed in the talk will be the effect of adding transition-metal atoms to the anionic Bi_n^{n-} oligomers, namely formation of deltahedral clusters. The thermal treatment of such main-group/transition-metal clusters leads to further aggregation by both oxidation and deligation of the clusters.



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Impact of nanostructuration on the nature of charge carriers in ZnO. Opening to Zn based Metal Organic Frameworks

*Benoit Chavillon[1], Adèle Renaud[1,2], Tengfei Jiang[1], Congcong Shang[1], Martine Bujoli-Doeuff[1], Xavier Rocquefelte[2], Philippe Deniard[1], Eric Faulques[1], Romain Gautier[1], Camille Latouche[1], Eric Gautron[1], Franck Tessier[2], François Cheviré[2], Laurent Cario[1], Stéphane Jobic[1]**

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Abstract

Zinc oxide is considered as a very promising material for optoelectronics. However, to date, the difficulty in producing stable p-type ZnO is the main bottleneck hindering the advent of ZnO-based devices. In that context, nitrogen-doped zinc oxide receives much attention ($O_O^x \rightarrow N_O^{'} + 1h^+$). However, numerous reviews report the controversial character of p-type conductivity in N-doped ZnO, and a recent theoretical contribution explains that N-doping alone cannot lead to p-typeness in Zn-rich ZnO [1]. A few years ago, we reported that the ammonolysis at low temperature of ZnO_2 yields pure wurtzite-type N-doped ZnO nanoparticles with an extraordinarily large amount of Zn vacancies (up to 20%) [2]. Factually, these Zn vacancies segregate at the surface of the nanoparticles, as confirmed by *ab initio* calculations, to form a pseudo core-shell structure made of a dense ZnO sphere coated by a Zn free oxo-hydroxide mono layer [3]. In other terms, oxygen terminated surfaces are privileged over zinc-terminated surfaces for passivation reasons what accounts for the Zn off-stoichiometry observed in ultra-fine powdered samples. Electrochemical and transient spectroscopy studies clearly demonstrated that these N-doped Zn-poor nanoparticles exhibited a p-type conductivity that was conserved, an exceptional fact, over more than 2 years and half under ambient conditions [2]. Our studies concluded that nanostructuration

plays a major role in the inversion between n-type and p-type charge carriers in zinc oxide. This assertion agrees with the observation of a p-type conductivity in undoped ZnO materials with abundant zinc vacancies as reported by Pan et al. [4] that turned out to be nanoparticles and the achievement of a p-type dye sensitized solar cell with a photocathode built upon potassium doped ZnO nanoparticles [5]. Indeed, nanostructuration can be regarded as a methodology to modify the opto-electronic properties of semiconductors. Another way to stabilize p-type charge carrier in ZnO derivative consists in the preparation of metal organic framework materials with both high porosity and an embedded continuous 3D inorganic framework. In that context, we embarked on the synthesis of p-type Zn based MOFs that turn out to be p-type semiconductors [6].

Acknowledgements

The Agence Nationale de la Recherche (ANR) is acknowledged for financial supports (Grants ANR-13-BS08-0010 and ANR-12-PRGE-0016-01).

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Clusterization versus segregation of copper in clathrates of the A-Cu-P(As,Sb) systems

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Abstract

Zintl clathrates are polar intermetallic compounds, in which the charge of an anionic framework is compensated by large cations sitting in cage-like polyhedral voids. Although tetrahedrally-bonded frameworks require sp^3-hybridized p-elements, some d-metals are also known to enter such frameworks, copper being notable for its presence in various types of clathrate compounds. In this work, we focus on the role of copper in Zintl clathrates. We discuss two types of compounds, $A_8Cu_{16}P_{40}$ [1] and $A_7Cu_{44}E_{23}$ [2]. The former type (A = Ba, Eu) displays an orthorhombic superstructure of the type-I clathrate. In its crystal structure, copper atoms are distributed over 8 crystallographic positions in such a way that Cu-Cu contacts are avoided, and P_{12} and P_{18} clusters form instead. The crystal structure of $A_7Cu_{44}E_{23}$ (A = Eu, Sr; E = As, Sb) is of clathrate-like type, with 6/7 of large A-cations residing in oversized 20-vertex cages. Unlike $A_8Cu_{16}P_{40}$, these compounds show segregation of E atoms, whereas copper forms from 4 to 9 Cu-Cu bonds depending on its position in the crystal structure. We will compare crystal and electronic structures, and transport and thermal properties of these compounds, paying special attention to the reasons underlying the difference in their properties.

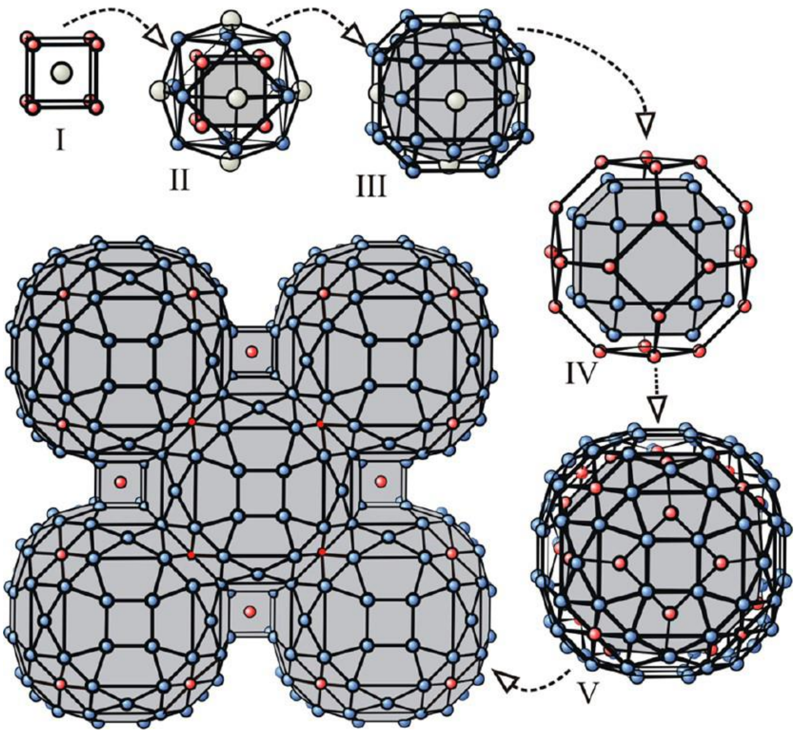

Figure 1: Crystal structure of $A_7Cu_{44}E_{23}$ presented as shells of endohedral clusters.

Acknowledgements

We thank Russian Science Foundation for supporting this research under grant #16-12-00004.

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Molecular Polypnictide Clusters of Rare Earths

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Abstract

Solid phases based on or containing rare-earth (Ln) polypnictides are well established owing to their potential application in solar cells or thermoelectric devices. In contrast to them molecular examples of *f*-element polypnictides are really uncommon. In 2009, we have described the first polyphosphide of the rare-earth elements, $[(Cp^*{}_2Sm)_4P_8]$[1]. Later, in 2016, we have synthesized the first *d*/*f*-polyarsenides[2, 3]. All the compounds were obtained using a reductive approach by reacting appropriate pnictogen containing substrate with the corresponding divalent samarium species. The same approach was recently used to prepare new hetero- and homometallic polyarsenides $[(Cp'''Co)_2As_4Sm(\eta^5\text{-}C_5Me_4R)_2]$ (R = Me, ^{n}Pr)[4] and $[\{(DippForm)_2Sm\}_2(\mu,\eta^4{:}\eta^4\text{-}As_4)]$[5]. To access the similar polystibides we have developed two approaches (A and B, Fig. 1) consisting in different routes of Sb activation followed by the reaction with Sm(II) species. Both the approaches result in different intermediates, and finally in $[(Cp^*{}_2Sm)_4Sb_8]$[6].

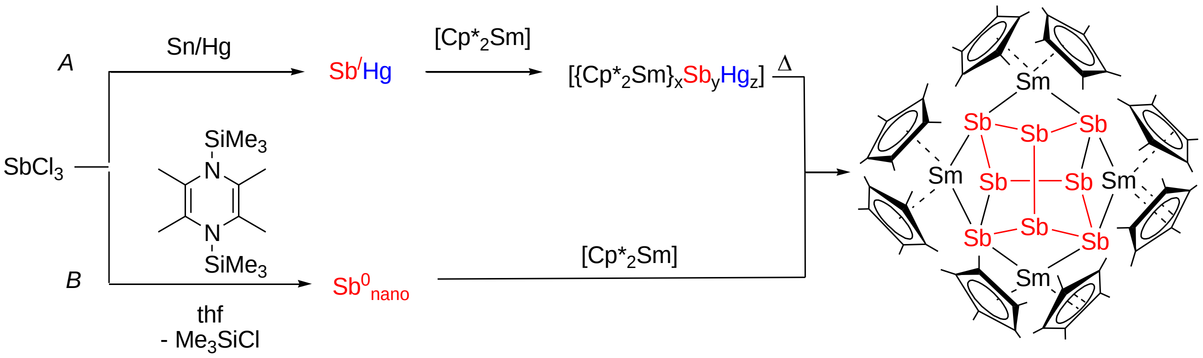

Figure 1: Two routes of Sb activation and its reaction with $[Cp^*{}_2Sm]$.

Acknowledgements

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Octahedral iodide clusters of tantalum

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Abstract

Ta powder reacts with I_2 at 650°C with the formation of Ta_6I_{14} which was originally reported as comproportionation product between TaI_5 and Ta. It belongs to the series of $\{M_6(\mu\text{-}X)_{12}\}$ clusters. Combination of 18 heavy elements in a single cluster unit offers unique possibilities of making new X-ray contrast agents with high radiopacity. Earlier works reported only preparation and structural characterization of Ta_6I_{14}, while its reactivity remained unexplored. In the present study we found that Ta_6I_{14} undergoes aquation with the formation of $[Ta_6I_{12}(H_2O)_6]^{2+}$ (ε (640 nm) = 3230 (l/mol*cm), ε (749 nm) = 2600 (l/mol*cm). Crystal structure was determined for $[Ta_6I_{12}(H_2O)_6](BPh_4)_2$ (Ta-Ta 2.9322(6) Å, Ta-I 2.8104(7) Å, Ta-O 2.3430(5) Å). With DMF, $[Ta_6I_{12}(DMF)_6]I_2$ was isolated (Ta-Ta 2.9500(2) Å, Ta-I 2.8310(4) Å, Ta-O 2.2880(7) Å). In CH_3CN the aqua complex undergoes solvolysis with the formation of $[Ta_6I_{12}(CH_3CN)_6]^{2+}$, while $[Ta_6I_{12}(DMF)_6]^{2+}$ remains intact. Cyclic voltammetry shows that $[Ta_6I_{12}(H_2O)_6]^{2+}$ undergoes two consecutive quasi-reversible one-electron oxidations with the formation of $[Ta_6I_{12}(H_2O)_6]^{4+}$ ($E_{1/2}$ 0.61 and 0.92 V vs. Ag/AgCl). This is in agreement with the similar behavior of corresponding cluster chloride and bromide; what is remarkable, however, is *increasing reluctance* to lose electrons on going from Cl to I (octahedral iodide clusters of Mo and W *are always easier* to oxidize that their bromide and chloride analogues). Reaction of Ta_6I_{14} with Bu_4NI/Ph_4PCl yields $(Ph_4P)_4[Ta_6I_{12}(CN)_6]$ (Ta-Ta 2.9777(4) Å, Ta-I 2.8165(6) Å, Ta-C 2.2730(7) Å). The clusters are diamagnetic. Quantum chemical calculations reproduce well experimental geometry of the aqua complex and cyanide cluster and show essentially Ta-centered nature of both HOMO and LUMO, which are in agreement with diamagnetism. Long-term stability of solutions of $[Ta_6I_{12}(H_2O)_6]^{2+}$ can be greatly enhanced in the presence of polystyrenesulfonate (PSS) which forms nanoparticle associates with the aqua complex in water (ca. 1 cluster per 3 PSS monomeric units). Preliminary experiments (in collaboration with Dr. M. Feliz, Valencia) show modest photocatalytic activity of $[Ta_6I_{12}(H_2O)_6]^{2+}$ in HER reaction.

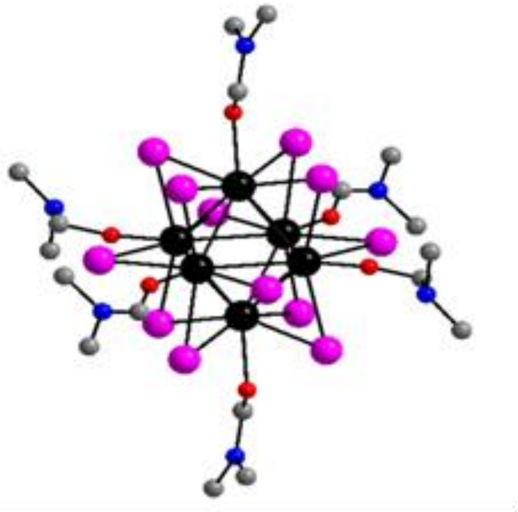

Figure 1: $[Ta_6I_{12}(DMF)_6]^{2+}$ cation in $[Ta_6I_{12}(DMF)_6]I_2$. Hydrogen atoms are omitted.

Acknowledgements

Authors thank Prof. E. Benassi, Dr. P. Abramov and Dr. T. Sukhikh for valuable help.

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Synthesis, characterization and biological activity of some new Rh-Ge carbonyl clusters

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Abstract

The chemistry of homo-[1] and hetero-metallic rhodium carbonyl clusters has been widely investigated in the last decades. Nevertheless, the known examples of rhodium clusters which interstitially host heavier elements than carbon[2] and nitrogen[3] are limited[4]. Therefore, in order to widen the chemistry of hetero-metallic rhodium compounds, we investigated the reaction between the $[Rh_7(CO)_{16}]^{3-}$ cluster precursor and Ge^{2+} and Ge^{4+} salts, which led to the synthesis and characterization of new Rh-Ge carbonyl clusters, namely $[Rh_{13}Ge(CO)_{25}]^{3-}$ and $[Rh_{14}Ge_2(CO)_{30}]^{2-}$, both with germanium atoms interstitially lodged in rhodium metallic frameworks.

Moreover, $[Rh_{13}Ge(CO)_{25}]^{3-}$ in solution under CO atmosphere undergoes a reversible reduction process, forming the icosahedral species $[Rh_{12}Ge(CO)_{27}]^{4-}$(Fig. 1).

These three new Rh carbonyl clusters have been characterised by IR spectroscopy and ESI-MS spectrometry and their molecular structures determined by X-ray diffraction studies.

Cytotoxicity tests of the two new compounds obtained under nitrogen atmosphere have been conducted against a human ovarian cancer cell line (A2780) and its cisplatin-resistant strain (A2780cisR).

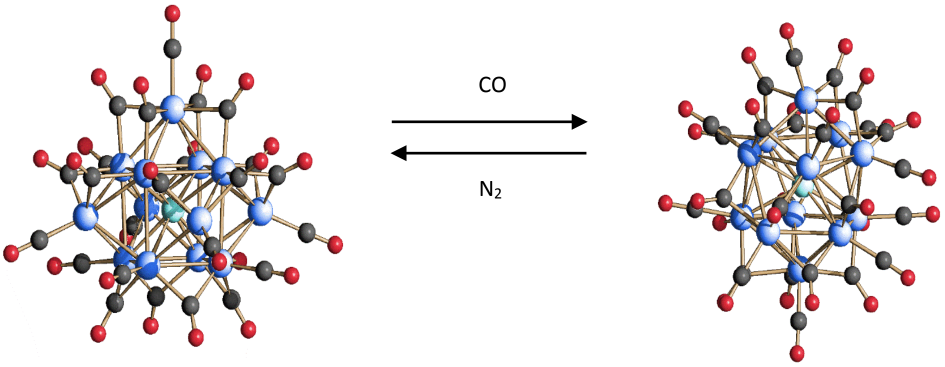

Figure 1: Reversible conversion of $[Rh_{13}Ge(CO)_{25}]^{3-}$ into $[Rh_{12}Ge(CO)_{27}]^{4-}$.

Acknowledgements

We thank the University of Bologna and the EPFL for financial support.

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Crystal chemistry and investigation of physical properties of coordination materials based on octahedral clusters building blocks

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Abstract

$[M_6Q^i_8(CN)^a_6]^{n-}$ cluster units exhibit a wide range of chemical and physico-structural properties that depend on the nature of the metal and that of the ligands. The chemistry of metal clusters is actually widely studied owing to potential applications of cluster compounds in lighting, photodynamic therapy, photocatalysis and energy conversion. The search of new building blocks is of prime importance not only to optimize the properties of final materials for potential applications but also to better understand the relations between electronic counts, crystal structures and physical properties. In this frame, we are actually studying $[Mo_6Q^i_8(CN)^a_6]^{n-}$ cluster units with mixed Br/Q inner ligands (Q = S or Se) and hetero-metallic $[M_6Se^i_8(CN)^a_6]^{n-}$ ($M_6 = Mo_{6-x}Re_x$).

In a first part, the structures, optical and magnetic properties of 3 new cyanides based on $[Mo_6Br^i_6Q^i_2(CN)^a_6]^{n-}$ units (Q = S and Se) will be presented. The structure of $[\{Ni(NH_3)_6\}_4\{Ni_2(NH_3)_8\}][Mo_6Br_6Q_2(CN)_6]_3\cdot 12H_2O$ derived from that of Prussian blue and can be depicted as the association of (i) Ni dimer-based $[Ni_2(NH_3)_8]^{4+}$ cubic complexes, (ii) $[Ni(NH_3)_6]^{2+}$ octahedral complexes, and (iii) $[Mo_6Br^i_6Q^i_2(CN)^a_6]^{4-}$. Antiferromagnetic interactions have been evidenced within the Ni dimer-based structure at low temperature.[1] Cs_x[*trans*-$(Mn^{II}_xMn^{III}_{1-x})(H_2O)_2][Mo_6Br_6Q_2(CN)_6]$ contain 2D square-net-layers built-up from [*trans*-$Mn^{III})(H_2O)_2]$, [*trans*-$Mn^{II})(H_2O)_2]$ and magnetic $[Mo_6Br^i_6Q^i_2(CN)^a_6]^{3-}$ (Q = S, Se) cluster units.[2] The two

oxidation states Mn^{2+} and Mn^{3+} metal cations were confirmed by electron energy loss spectroscopy and by the measurement of magnetic susceptibilities. Structures of $(H_3O)H[\textit{cis}\text{-}Cd(H_2O)_2][Mo_6Br_6Q_2(CN)_6]\cdot H_2O$, owing to the *cis*-position of the two water molecules around the transition metal compared to that of $Cs_x[\textit{trans}\text{-}(Mn^{II}_xMn^{III}_{1-x})(H_2O)_2][Mo_6Br_6Q_2(CN)_6]$, exhibit a close-packed 3D structure based on an interpenetrated framework of cluster-based chains. In particular, it contains infinite chains alternating luminescent $[Mo_6Br^i_6Q^i_2(CN)^a_6]^{4-}$ units and H^+ protons as linkers.

In a second part, we report the control of 3D polymeric structures based on cluster cyanometallate by hydrogen bonding. It was found that interactions of $[Re_3Mo_3Se_8(CN)_6]^{5-}$ cluster anions and Cd^{2+} cations in aqueous ammonia lead to the formation of 1D polymeric compound $\{[Cd(NH_3)_5]_2[Cd(NH_3)_4]_3[Re_3Mo_3Se_8(CN)_6]_2\}\cdot 5H_2O$ (**1**).[3] The addition of KX (X = Cl, Br, I) to the reaction mixture led to the selective formation of the 3D framework compounds $\{[Cd(NH_3)_4]_3[Re_3Mo_3Se_8(CN)_6]\}X$ (**2**-**4** for X = Cl, Br, I, respectively) stabilized by the N-H…X hydrogen bonding. Compounds **2**-**4** demonstrate high thermal stability as well as the ability to reversibly lose ammonia and to be reversibly oxidized in the solid state. This reversible loss is accompanied by reversible purple/grey color change.

Acknowledgements

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Transition Metal Clusters as Building Blocks for Multifunctional Proton-Conducting Materials

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Abstract

Proton-conduction has been identified in a large variety of solid-state compounds: metal-organic frameworks, coordination polymers, polyoxometalates and covalent organic frameworks [1]. In the present contribution, I will present our recent study that demonstrates for the first time that efficient proton-conducting materials can also be synthesized from molybdenum metal clusters. Three compounds will be discussed: $(H)_4[Mo_6Br_6S_2(OH)_6]\cdot 12H_2O$ (1) and $(H)_2[Mo_6X_8(OH)_6]\cdot 12H_2O$ (X = Br (2), Cl (3)). Both compounds are built on a 3D arrangement of $Mo_6L^i_8(OH)^a_6]^{2-/4-}$ cluster units link together by hydroxyl bridges and surrounded by crystallization water molecules (see Fig. 1a). The proton conduction was characterized experimentally at different temperatures and relative humidity and coupled to ab initio molecular dynamics simulations to provide an atomistic scale description of the proton conduction mechanism. We demonstrate that the hydroxyl bridges between the cluster units can promote proton transfer between adjacent oxygen atoms (see Fig. 1b and c) which leads to a Grotthuss-type mechanism through the hydrogen bond network.

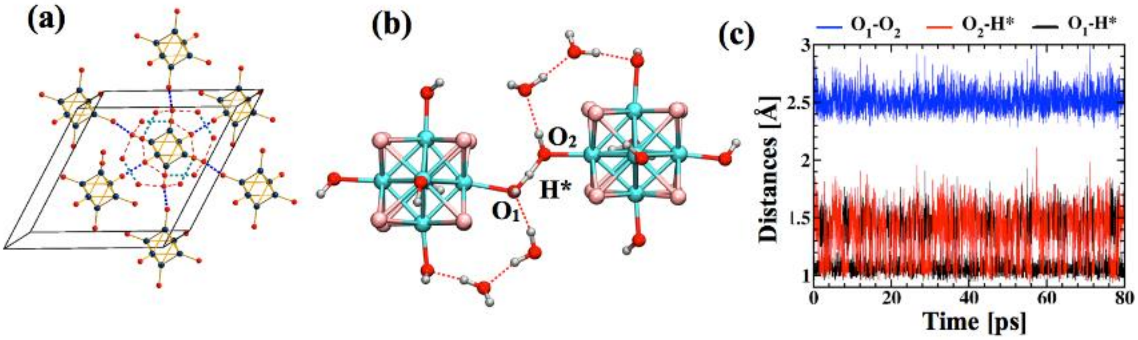

Figure 1: (a) View along the c (a) axis in (1) of the connection between a given $[Mo_6Br_6S_2(OH)_6]^{4-}$ cluster unit and the surrounding six cluster units. (b) and (c) Figure 6: (a) Time evolution of the O_1-H*, H*-O_2 and O_1-O_2 distances along a 300 K AIMD simulation in (2).

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Transport Properties of Molybdenum Sulfide Clusters: Experimental & Theoretical Results

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Abstract

In molybdenum cluster chemistry, the Chevrel phases have been extensively studied mainly because of their superconducting properties. Theses phases consist of a stacking of Mo_6Q_8 (Q = S, Se, Te) units (Mo_6 octahedron inscribed in a pseudo Q_8 cube) and contain channels where additional metal atoms can be inserted. Investigations of their transport properties have shown that they are interesting candidates at high temperature (1000K)[1]. Molybdenum clusters with a nuclearity higher than six can also be obtained. Among them the ternary $Ag_xMo_9Se_{11}$ ($3.4 < x < 3.9$) show outstanding low lattice thermal conductivities that give rise to a rather high value of the dimensionless thermoelectric figure of merit ZT of 0.65 at 800 K for x = 3.8 – 3.9[2,3]. Several additional molybdenum cluster selenides such as $Ag_3In_2Mo_{15}Se_{19}$[4], $Ag_2Tl_2Mo_9Se_{11}$[5] and $Cu_xCs_2Mo_{12}Se_{14}$[6] (x ranging from 0 to 2) have been synthesized. Their crystal structures have been studied by single crystal X-ray diffractions techniques and their transport properties were measured (see Fig. 1). Theoretical calculations were carried out in order to rationalize their structural and physical properties[3-7].

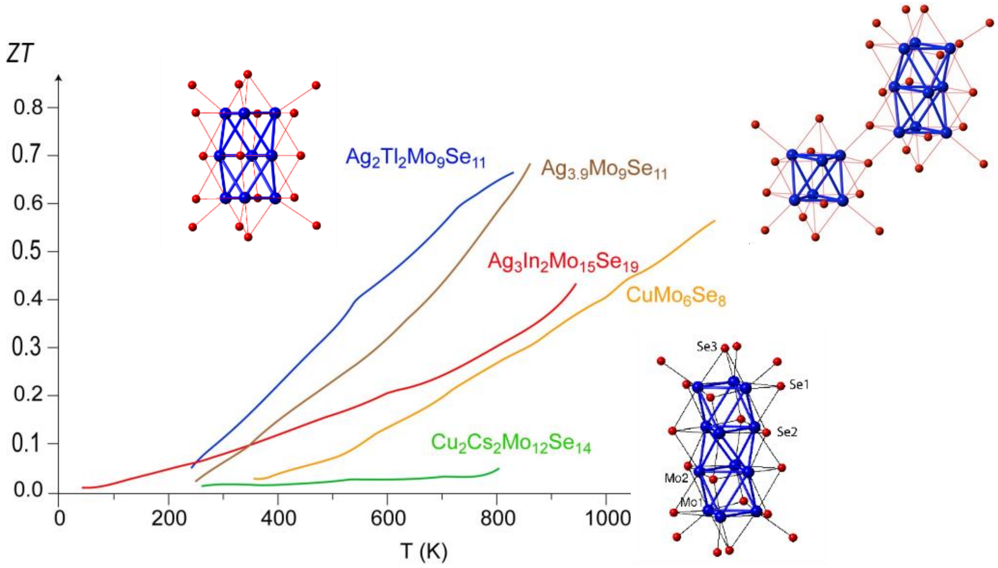

Figure 1: Figure of merit of cluster-based selenides.

Since this family of materials seems to be promising for thermoelectric power generation applications, sulfide molybdenum analogs containing various cluster have been synthesized and characterized. In some cases, transport properties were measured to assess their thermoelectric potential. Band structure calculations were carried out for a better understanding of their structural and physical properties.

Acknowledgements

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In-situ synchrotron powder diffraction study of Chevrel phase electrochemical intercalation

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Abstract

The Chevrel phases (CPs) are molybdenum chalcogenides of formula $M_xMo_6X_8$ (M is a cation and X a chalcogen, S or Se) that represent a large variety of compounds intensively studied for their unusual properties. From 2000 to date, CPs electrochemical properties have drawn a lot of attention as the more performing cathode materials for rechargeable Mg batteries [1]. The CPs intercalation properties have been also recently considered as promising materials for the electrochemical treatment and detection of different metallic cations in liquids [2]. The electrochemical process is based on intercalation/de-intercalation reactions occurring in the host matrix and allows for a selective extraction of the desired metal. In this context the study of multicationic intercalation/deintercalation in CPs is mandatory to understand the electrochemical response in industrials wastes, as produced from electrical and electronic equipment recycling industry. For such reasons coupled synchrotron XRPD and electrochemistry experiment (Figure 1) at the ID-22@ ESRF beamline in mono, bi and tri-cationic electrolytes containing cadmium cation has been performed. This experiment has allow to underline a complex kinetic behavior of CPs intercalation that highlights the difference in cationic migration mechanism in the CPs phases with different stoichiometry and preferential intercalation of Cd^{2+}.

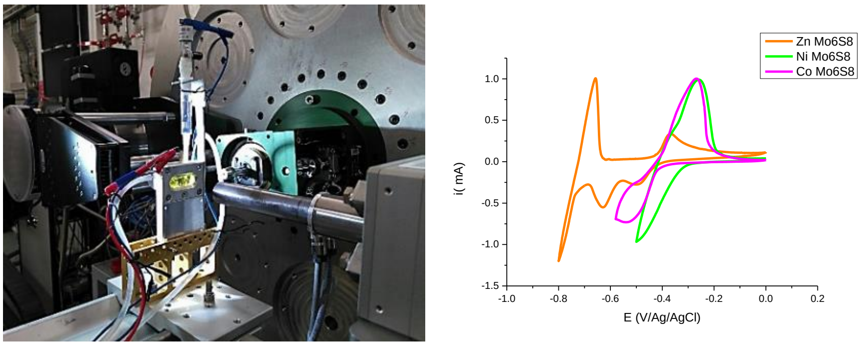

Figure 1: Experimental setup at synchrotron and cyclic voltammetry signals.

Acknowledgements

We deeply thank Catherine Dejoie and Andy Fitch pour technical support during XRD measurements.

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Spin states on metal atoms of M_2bdc_2DABCO metal organic frameworks

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Abstract

Metal-metal interactions in secondary building units of metal organic frameworks can influence on the properties, particularly, paramagnetic species can change type of magnetic ordering. In the work, different possible spin states of M_2bdc_2DABCO [1,2] (M-DMOF, where M=Co, Ni, Cu, Zn) metal organic frameworks are investigated by quantum chemical methods.

Metal-metal interactions in M-DMOFs with Ni, Cu, and Zn can be characterized as intermediate interactions [3]. In Co-DMOF formation of Co-Co covalent bond is possible in diamagnetic and ferromagnetic states. Co-Co covalent bond was not found in antiferromagnetic state of Co-DMOF. The least stable spin state of Co-DMOF is ferromagnetic (0 eV), diamagnetic (-0.04eV) state is energetically close to ferromagnetic and the most stable is antiferromagnetic (-0.57 eV) state. Spin density analysis shows that in the ferromagnetic and anti-ferromagnetic states unpaired electrons are mainly localized on metal atoms (Fig. 1). There is also a small contribution from oxygen atoms of the bdc ligand and nitrogen atoms of the DABCO linker. Difference between populations of α and β electrons for Co1/Co2 atoms is 2.7/2.7 and 2.6/-2.6 for ferromagnetic and antiferromagnetic states respectively. Thus, each of Co atoms have approximately 3 unpaired electrons with spin $S_{Co}=3/2$. Consequently, Co-DMOF shows the variety of possible spin states, which under the influence of external conditions (like temperature) can switch between each other.

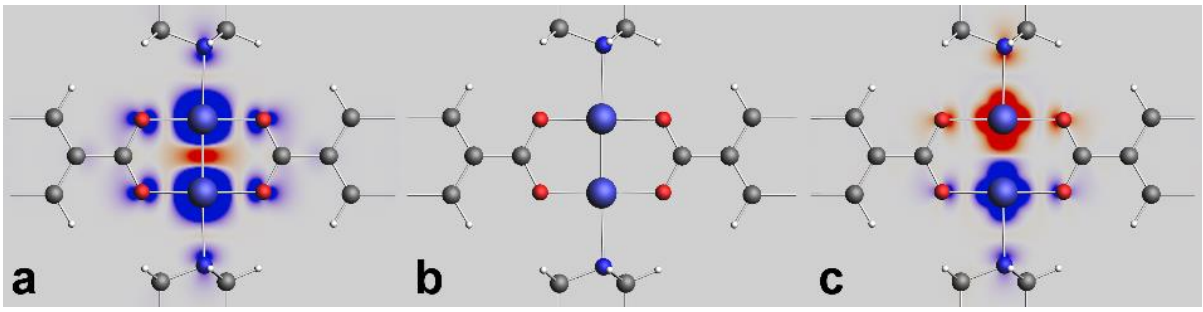

Figure 1: Spin density maps for ferromagnetic (a), diamagnetic (b) and antiferromagnetic ordering (c) in Co-DMOF. Blue and red colours show α- and β-electron excess, respectively.

Acknowledgements

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Cluster-based Nanostructured Metal Sulfides and their Applications in Catalysis

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Abstract

Transition metal sulfides constitute a wide family of materials with many interesting applications in different research areas. In catalysis, MoS_2-based materials promoted by cobalt or nickel have been extensively used as hydrotreating catalysts in petroleum refineries for upgrading crude feed-stocks[1] Nevertheless, the full potential of this family of catalysts, especially their application in selective transformations to get highly valuable organic chemicals, still remains unknown. Herein, it is shown that under modification and adaptation they become in highly active and selective heterogeneous catalysts able to carry out the selective hydrogenation of a desired reacting group while the others remain untouched. The preparation of a series of nanostructured cobalt–molybdenum sulfide based-materials has been accomplished by a one-pot hydrothermal synthesis that furnishes the obtained unsupported catalysts with a high number of actives sites per unit volume. These catalysts have been applied for the chemo- and regioselective hydrogenation of nitroarenes and *N*-heteroarenes allowing for the straightforward and general preparation of functionalized anilines and 1,2,3,4-tetrahydroquinolines with an impressive tolerance to other reducible moieties.[2, 3] An extensive characterization of the prepared nanostructured catalysts reveals their different composition, and how they undergo a continuing evolution during catalysis. Active phases responsible for the outstanding activity, chemo- and regioselectivity of these catalysts have been well established.

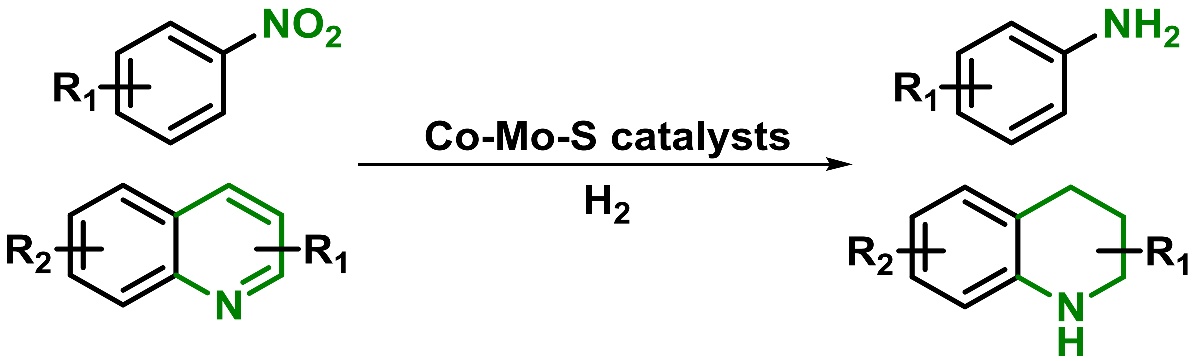

Figure 1: Co-Mo-S-catalyzed chemoselective hydrogenation of nitroarenes and quinoline-based compounds.

Acknowledgements

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Thermoelectric and magnetic properties of inorganic cluster and cage compounds, and novel principles for thermoelectric enhancement

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Abstract

Cluster and cage-like structure compounds have been studied extensively. One notable feature is that they possess strong structure-property relationships, and interesting physical properties have been discovered. In this talk I will focus on thermoelectric and magnetic properties we have been carrying out research on.

Thermoelectrics

Approximately two thirds of all primary energy (oil, coal, natural gas, etc.) being consumed in the world, sadly turns out to be unutilized, with much of the waste being heat. The direct conversion of waste heat to electricity is a large incentive to find viable thermoelectric (TE) materials [1]. One need exists to develop mid to high temperature inorganic TE materials for thermal power plants, steelworks, incinerators, focused solar power, etc. [2].

1.1.1 As a synthesis method we have discovered that small amounts of third elements like C, N, and Si in borides can function as bridging sites, and result in the formation of novel and varied boron cluster structures [3]. This has previously led to the long-awaited n-type counterpart to p-type boron carbide, for example [4]. I will discuss recent results on controlling atom site occupancy which has led to difficult p, n control of these boron cluster compounds [5].

1.1.2 Boron cluster compounds generally possess intrinsic low thermal conductivity, κ, despite their strong bonding and generally high sound velocities. I will discuss the origins of this, of which novel mechanisms like "Symmetry mismatch effect", have been proposed[6].

1.1.3 REB_{66} (RE=rare earth) is known as a boron cluster compound with relatively low thermoelectric performance. In general, among a rare earth series, the Sm and/or Yb and/or Eu compounds are known to sometimes have anomalous properties due to mixed or divalent valency. We grew floating zone (FZ) single crystals of SmB_{66}- and YbB_{66}-type compounds and investigated the physical properties. As a result, compared to other rare earth phases like Y and Er, we observed up to a 30 times enhancement in the power factor $P = \alpha^2\sigma$, where α and σ are the Seebeck coefficient and the electrical conductivity, respectively [7]. Recently there has been found an interesting interplay between magnetism and thermoelectricity [8]. Magnetic measurements indicate mixed valency in SmB_{66}- and YbB_{66}, and the origin of enhancement will be discussed.

1.1.4 Some cage-like structure compounds like skutterudites and clathrates have shown excellent thermoelectric properties. This can be attributed to the so-called "rattling" phenomena, for example, due to rare earth atoms in the voids of the cage structure of skutterudites for example, which are only loosely bound with the cage atoms, and which movement effectively scatters phonons. We have discovered a method to create nano-micropores in these materials, which led to a 100% of figure of merit $ZT=\alpha^2\sigma/\kappa$ enhancement for rare-earth free, so called empty skutterudites of ZT~1.6 [9].

Magnetic properties

Unexpectedly strong magnetic coupling was previously discovered in dilute f-electron insulating borides. This was found to manifest in a wide variety of magnetism such as one-dimensional and dimer-like transitions, two-dimensional spin glasses, and three-dimensional long range ordering which will be described in detail. We have proposed that the boron icosahedra B_{12} cluster is a novel mediator of magnetic interaction [10].

Acknowledgements

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Mn^{4+} Comprising Compounds - From Photosynthesis to Photoluminescence

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Abstract

Mn ions play a key role in photosystem II (PSII) and in many other redox enzymes. It is assumed that a Mn^{4+} comprising [Mn_4Ca] cluster cleaves water in PSII, which is the central reaction in the energy harvesting chain of autotrophic organisms. The high redox potential of Mn^{4+} allows its application in catalysis too and thus Mn ion comprising solid state compounds are amongst others in the focus of R&D activities aiming at the development of novel catalysts, e.g. for fuel cells.

Since the introduction of K_2SiF_6:Mn (PSF) by General Electric, Mn^{4+} doped solid state materials are considered as suitable red emitting luminescent materials for obtaining warm white phosphor converted light emitting diodes (pcLEDs). For lighting applications, particularly in high brightness pcLEDs, the high thermal quenching temperature of the Mn^{4+} photoluminescence is a rather important feature. The thermal quenching temperature $T_{1/2}$ of Mn^{4+} luminescence can be close to that of widely applied LED phosphors, e.g. Ce^{3+} doped garnets or (Ca,Sr)$AlSiN_3$:Eu, but it varies in a wide temperature range as function of the host composition. The origin of such different $T_{1/2}$ values of Mn^{4+} luminescence in different hosts is a hot topic in Mn^{4+} phosphor development for pcLEDs. However, another shortcoming caused by the redox potential of Mn^{4+} comprising phosphors, especially of fluorides, are their low photochemical and thermal stability due to the degradation of the fluoride host. A way to circumvent this bottleneck is the use of Mn^{4+} in an oxide type host. Unfortunately, this red-shifts the photoluminescence towards the 650 to 700 nm range, which is much less suitable

for lighting applications due the low sensitivity of the human eye in this spectral region. Therefore, R&D on Mn^{4+} activated LED phosphors deals with the stabilization of PSF and on the search for novel Mn^{4+} luminescent materials with better thermal as well as photochemical stability.

This work concerns the synthesis, photoluminescence, reflection spectra, and thermal quenching behavior of Mn^{4+} in several oxide or fluoride solid state compounds comprising octahedral sites suitable for the incorporation of Mn^{4+}. It turned out that multi-phonon relaxation from the excited ^2E state to the $^4A_2$ (^4F) ground state of Mn^{4+} does not appear to be the mechanism of thermal quenching. Moreover, no direct correlation between the energy of the emitting Mn^{4+} ^2E state and thermal quenching temperature could be discovered. The thermal quenching temperature $T_{1/2}$ of Mn^{4+} photoluminescence in the studied phosphors correlates with the energy of the $^4T_{2g}$ crystal-field term of Mn^{4+} and/or the O^{2-} - Mn^{4+} charge transfer state (CTS) which can both serve as quenching states for the Mn^{4+} photoluminescence.

Furthermore, this work discusses the relation between the energy of the emitting $Mn_{4+\ 2}E$ state and the chemical nature of the solid state compound, which is of high relevance for the application area aimed at. Beyond the application of Mn^{4+} phosphors in pcLEDs for general lighting, these phosphors found also tremendous interest for horticulture applications recently. Suitable examples are $(K,Rb)_2Ge_4O_9:Mn^{4+}$ and $Y_2Mg_3Ge_3O_{12}:Mn^{4+}$. Particularly, the latter one is of considerable interest for high power pcLEDs due to its very high $T_{1/2}$ value.

Finally, the future role of Mn^{4+} doped compounds for application in horticulture lighting and in catalytically active materials will be illuminated. Some conclusions concerning guidelines for further R&D on Mn^{4+} phosphors will be drawn too.

Understanding and Exploiting the NIR Emissive Molecular Ruby

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Abstract

Emission, especially near-IR emission, from earth-abundant 3d metal complexes is very difficult to achieve.[1,2] If emission is observed, it is often short-lived and of low efficiency.[1,2,3] By using the ddpd ligand (*N*,*N'*-dimethyl-*N*,*N'*-dipyridin-2-ylpyridine-2,6-diamine)[4] with its large N-M-N bite angle[4,5] and its strong σ-donor properties we obtained the chromium(III) complex $[Cr(ddpd)_2]^{3+}$, which, to the best of our knowledge, outperforms every 3d metal complex in that photophysical respect with luminescence quantum yields above 10 % and luminescence lifetimes of almost a millisecond in solution at ambient temperature.[1,2,6] Solvent and ligand deuteration can further boost these values to record quantum yields and lifetimes of 30 % and 2 ms, respectively.[7]

A deeper understanding of the extraordinary photophysical properties of this molecular ruby was achieved through experimental (UV-VIS absorption, steady-state and time-resolved emission spectroscopy, transient absorption spectroscopy) and theoretical methods (DFT, TD-DFT, CASSCF-NEVPT2).[8,9,10]

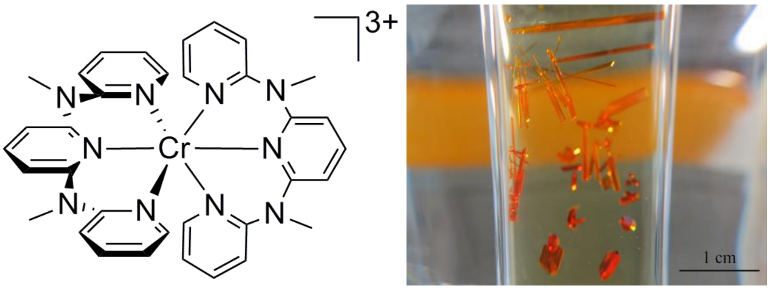

Figure 1: Molecular structure of the molecular ruby and a photograph of single crystals.

The unique chemical and photophysical properties bear the potential for a multitude of sensing and synthetic applications for this and similar compounds. Applications of

$[Cr(ddpd)_2]^{3+}$ in the areas of optical sensing (temperature, pressure, oxygen) and organic photochemical synthesis will be discussed.[9,10,11]

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Multifunctional Metal–Organic Frameworks Based on Redox-Active Rhenium Octahedral Clusters

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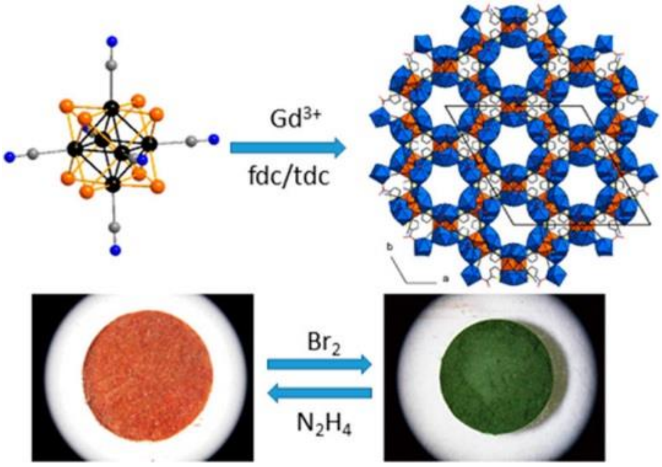
Abstract

Cluster complexes of transition metals have been intensively studied due to their fascinating structures and useful physical properties. Particularly, the octahedral rhenium clusters of $[\{Re_6Q_8\}L_6]$ (Q = S, Se, Te) type display an intensive NIR luminescence, high radiopacity and reversible redox transition which is accompanied by a change in the optical and magnetic properties. Using these features, many perspective materials have been obtained in recent years based on $\{Re_6Q_8\}$ clusters, e.g. luminescent hybrids, liquid crystals and contrast agents[1-3].

Here we report synthesis and investigation of multicomponent MOFs constructed from Gd^{3+} ions, furan-2,5-dicarboxylate (fdc) or thiophene-2,5-dicarboxylate (tdc) and $[Re_6Se_8(CN)_6]^{4-/3-}$ cluster anions. Compounds $[\{Gd(H_2O)_3\}_2(fdc)Re_6Se_8(CN)_6]\cdot nH_2O$ (**1**) and $[\{Gd(H_2O)_3\}_2(tdc)Re_6Se_8(CN)_6]\cdot nH_2O$ (**2**) were synthesized by a self-assembly reaction in aqueous solution[4]. Their structures are based on neutral frameworks and contain large channels with a complex inner surface. Frameworks **1** and **2** demonstrate the excellent CO_2/N_2 and CO_2/CH_4 selectivity, the red luminescence, paramagnetic behavior and an ability to react with oxidizing agents due to the presence of redox-active cluster fragment. The crystalline, permanently porous compounds $[\{Gd(H_2O)_3\}_2(L)Re_6Se_8(CN)_6]Br\cdot nH_2O$ (L = fdc (**3**) or tdc (**4**)) were synthesized by the oxidation of **1** and **2** with bromine. Compounds **3** and **4** are isostructural with **1** and **2** but display different optical and magnetic properties. The reverse reaction, namely the reduction of compounds **3** and **4** frameworks, can easily be carried out using the solution of hydrazine.



Acknowledgements

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Octahedral molybdenum clusters: Light vs. X-rays excitation for photodynamic therapy

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Abstract

Nanomaterials whose function is triggered by external source have emerged as pertinent components for biomedical applications, e.g., in photodynamic therapy (PDT). This method is a promising alternative for the treatment of various malignancies due to its minimally-invasive character. One of potent cytotoxic mediators in PDT is the singlet oxygen, $O_2(^1\Delta_g)$, which is typically generated by energy transfer from the excited triplet states of a photosensitizer (PS) to molecular oxygen. In this respect, octahedral molybdenum clusters (Mo_6) are relevant PSs (Fig. 1) with long-lived triplet states, red-NIR luminescence, and the $O_2(^1\Delta_g)$ productivity in high yields even in their aggregated form in contrast to commonly used organic PSs such as porphyrins[1]. A limiting factor for the use of Mo_6 in PDT is their little absorption in the visible region. Recently, we reported that Mo_6 complexes act as radiosensitizers (RSs) of $O_2(^1\Delta_g)$ after exposure to X-rays[2]. The use of these RSs appears as a promising approach to circumvent the depth penetration limitations of PDT and to enhance radiotherapeutical effects [3]. We delineate photoluminescence and radioluminescence properties of Mo_6 complexes and related nanoparticles, their water stability, singlet oxygen productivity under light and X-ray excitation, as well as, their *in vitro* cellular uptake, cytotoxicity, phototoxicity, and radiotoxicity towards human HeLa and MRC fibroblast cells. The nanoparticles significantly enhance the antiproliferative effect of X-ray radiation *in-vitro*. Our results demonstrate that the Mo_6-based RSs of $O_2(^1\Delta_g)$ have strong potential with respect to the enhancement of the radiotherapy efficacy with exciting opportunities for cancer treatment.

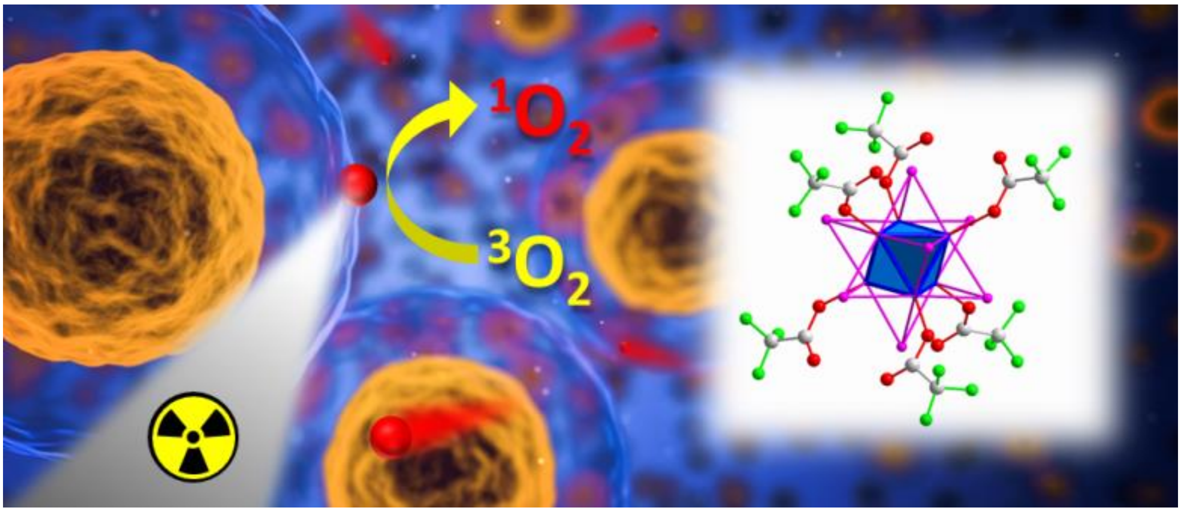

Figure 1: Nanoparticles made of the luminescent Mo_6 significantly enhance the antiproliferative effect of X-ray radiation.

Acknowledgements

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Water-soluble octahedral molybdenum and tungsten clusters with DMSO ligands

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Abstract

Octahedral molybdenum and tungsten clusters of general formula $[M_6X_8L_6]^n$ (where M = Mo, W, X = Cl, Br or I and L are apical organic or inorganic ligands) have become a subject of extensive studies after several exceptionally good luminophores were discovered among these compounds, in particular those of molybdenum. Thanks to intensive emission in red and near-infrared region of spectrum, and concomitant ability to generate singlet oxygen these compounds and materials based on them were considered in a range of various biomedical applications. In the attempt to obtain water-soluble photoluminescent octahedral clusters we have synthesized the first water-soluble tungsten cluster $[\{W_6I_8\}(DMSO)_6](NO_3)_4$ as well as its molybdenum analogue (Fig 1A) and compared their optical properties and kinetics of hydrolysis. Specifically, we demonstrate here that both compounds have similar luminescence, however the hydrolysis half-time at physiological temperatures in aqueous solution of the tungsten compound is 34 h, which is more than that for the molybdenum cluster (52 min).

The higher stability of the tungsten cluster allowed us to undertake the first biological studies on any tungsten octahedral cluster. The study of cytotoxicity of both fresh and aged aqueous

solutions on Hep2 cells showed that dark cytotoxicity of partially or fully hydrolyzed complexes is higher than that for non-hydrolyzed complexes, while the light induced cytotoxicity has an opposite trend. Notably, we found that upon hydrolysis within the cellular media (or even within the cells) the clusters assemble into nanoparticles of not more the 40 nm that retain luminescence and localize within the cells in perinuclear area (Fig. 1B,C). This is the first evidence of the octahedral metal clusters forming nanoparticles.

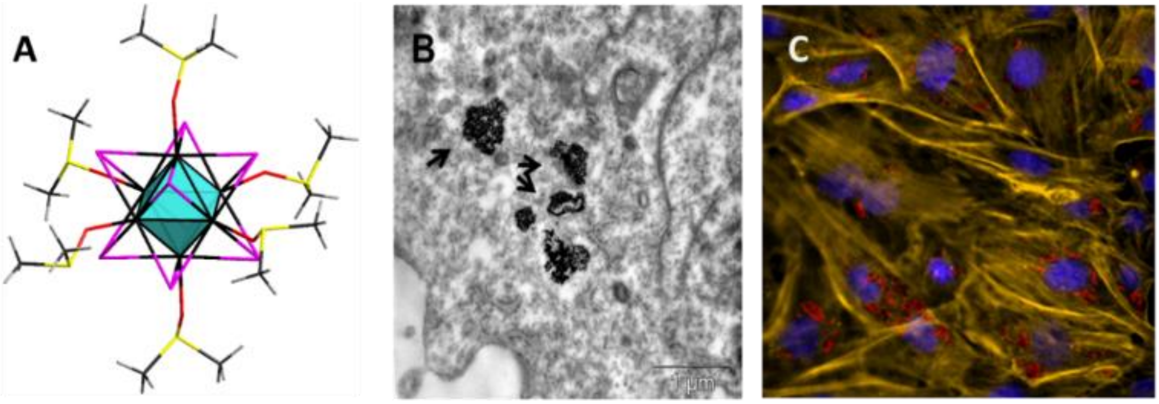

Figure 1: A. The structure of $[M_6I_8(DMSO)_6]^{4+}$ (M=Mo or W); B. Transmission electron microscopy images of ultrathin sections of Hep-2 cells incubated with the tungsten cluster; nanoparticles; C. Fluorescent microscopic images of Hep-2 cells.

Acknowledgements

This work was supported by the Russian Science Foundation [grant No. 15-15-10006], EPSRC [EP/R006393/1] and Royal society [grant RSG\R1\180123].

Metalloid Clusters of Aluminum, Gallium and Magnesium: A Challenge for Trapping Intermediates during the fundamental Process from the Bulk Metals to their Minerals.

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Abstract

Most elements of the periodic table are metals. Therefore, at a first glance, it seems strange that intermediates during their formation from the minerals and the reverse reaction of the oxidation of the metals are unknown so far. These simple seeming processes of formation and breaking metal–metal bonds, also during the dissolution of base metals in acids, is, besides their fundamental interest, an essential basis for the understanding and development of every metal-based electrochemistry in batteries. However, despite these challenges, it seemed highly utopian to detect intermediates directly during the highly exothermic resp. endothermic reactions between the bulk metals and their minerals: A direct trapping really is and will be a dream for base metals, because these reactions are very fast, e.g. the burning of Al or Mg in air. In order to overcome these problems and to slow down these reactions, we have developed a highly sophisticated technique nearly 30 years ago leading to metal rich clusters containing more metal-metal bonds than metal ligand bonds. The first and most spectacular result was an $Al_{77}R_{20}^{2-}$ cluster containing 57 so called naked Al atoms which are surrounded and protected by 20 AlR moieties, i.e. a slightly oxidized surface. As this cluster was so unusual in comparison to all other clusters known so far, Cotton called this cluster a miracle, a curiosity. We called this kind of clusters metalloid, because the idea of the metal structure is reflected in their atomic arrangement. The Al_{77} cluster was the starting point of an exciting story 21 years ago. Some of the most fundamental examples will be presented.

New Insights into the Compound $Al_5Br_7(thf)_5$

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Abstract

Nearly the complete existing knowledge about aluminium subhalide compounds could be obtained more than 10 years ago.[1] However, since this knowledge is basic chemistry more research in this field is highly demanding. There are known crystal structures of tetrameric Al(I) compounds $\{AlXD\}_4$ [X = Br, I; D = NEt_3, THF, PEt_3],[2] of dimeric Al(II) complexes $\{AlX_2D\}_2$ [X = Cl, Br, I, $Si(SiMe_3)_3$, D = EtOPh, MeOPh, $NMe_2(SiMe_3)$, OEt_2, PEt_3],[3] and of Al(<II) compounds $Al_4X(P^tBu_2)_5$ [X = Cl, Br],[4] $Al_8Br_8(P^tBu_2)_6$,[5] $Al_{12}X_{10}(AlCp^*)_8$ [X = Cl, Br],[6] $[Al_{14}\{N(SiMe_3)_2\}_6I_6Li(OEt_2)_2][Li(OEt_2)_4]$ [7] and $Al_{22}X_{20}D_{12}$ [X = Cl, Br; D = THF, THP].[8] Additionally, 18 years ago $[Al_5Br_6(thf)_6]^+[Al_5Br_8(thf)_4]^-$ was introduced as the first saltlike aluminium subhalide,[9] an analogon of the existing $Ga_5Cl_7(Et_2O)_5$.[10] Herein, we present the missing link between those structures and complement the existing knowledge about the binary, smallest aluminium centered cluster significantly.[11]

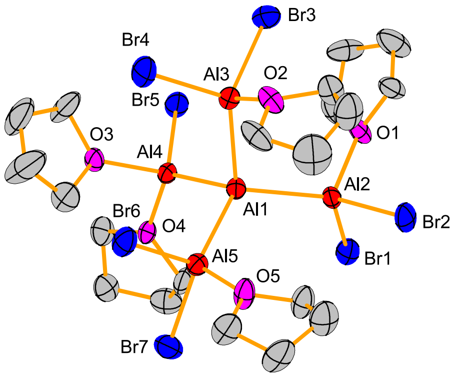

Figure 1: DIAMOND plot (50% displacement ellipsoids) of one enantiomer of the complex $Al_5Br_7(thf)_5$ crystallized from THF/n-pentane in the solid state. Hydrogen atoms have been omitted for clarity. Selected distances (Å) and angles (°): Al1–Al2 2.546(4) [Al1‘–Al2‘ 2.540(4)], Al1–Al3 2.551(4) [Al1‘–Al3‘ 2.537(4)], Al1–Al4 2.532(4) [Al1‘–Al4‘ 2.535(4)], Al1–Al5 2.548(4) [Al1‘–Al5‘ 2.551(4)], Al2–Br1 2.355(3) [Al2‘–Br1‘ 2.376(3)], Al2–Br2 2.371(3) [Al2‘–Br2‘ 2.349(3)], Al3–Br3 2.359(3) [Al3‘–Br3‘ 2.362(3)], Al3–Br4 2.348(3) [Al3‘–Br4‘ 2.371(3)], Al4–Br5 2.357(3) [Al4‘–Br5‘ 2.344(3)], Al5–Br6 2.361(3) [Al5‘–Br6‘ 2.368(3)], Al5–Br7 2.346(3) [Al5‘–Br7‘ 2.347(3)], Al2–Al1–Al3 109.45(13) [Al2‘–Al1‘–Al3‘ 110.24(13)], Al2–Al1–Al4 109.47(14) [Al2‘–Al1‘–Al4‘ 109.56(13)], Al2–Al1–Al5 120.30(13)

[Al2′−Al1′−Al5′ 120.36(13)], Al3−Al1−Al4 101.33(13) [Al3′−Al1′−Al4′ 100.03(13)], Al3−Al1−Al5 108.35(14) [Al3′−Al1′−Al5′ 109.10(13)], Al4−Al1−Al5 106.25(13) [Al4′−Al1′−Al5′ 105.54(13)].

Acknowledgements

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High Symmetry Ligand-Free Inorganic Clusters: Structures, Properties and Reactivities

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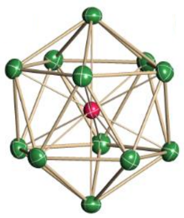
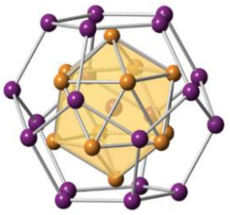
Abstract

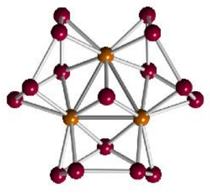
Binary cluster anions comprising transition metals and main group elements are synthesized from reactions between soluble main group polyanions (Zintl ions) and low oxidation state transition metal complexes. While binary transition metal complexes of the halides, oxides and sulfides are ubiquitous, the binary clusters of the pnictides (group 15 elements) and tetralides (group 14 elements) are far less studied and quite different from their group 16 and 17 counterparts. This talk will outline the chemistry of these unusual clusters that often have very high symmetries ($Pt@Pb_{12}^{2-}$ and $As@Ni_{12}@As_{20}^{3-}$ have perfect I_h point symmetry), remarkable dynamic and spectroscopic properties and interesting acid/base behavior ($Ni@Sn_9^{3-}$ is as basic as LDA). The $E@M_{12}@E_{20}^{n-}$ icosahedra (M = Pd, Ni; E = As, Sb; n = +1, -1, -2, -3, -4) have multiple redox states that mimic the fullerenes. Network structures of these clusters will be described.



$Pt@Pb_{12}^{2-}$



$As@Ni_{12}@As_{20}^{3-}$



$Rh_3As_{16}^{3-}$

Octahedral molybdenum cluster doped silica particles – New materials for biomedical applications

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Abstract

Silica is an excellent matrix for a wide range of biomedical applications, due to its high inertness, biocompatibility and versatility of the forms and shapes that can be achieved. For example, silica nanoparticles were successfully used for the cellular delivery of nucleic acids, proteins, drugs against various types of diseases, imaging agents, etc. Many of these applications require, however, multi-step bespoke modification of silica particles by luminescent tags to allow their monitoring using conventional imaging techniques such as confocal microscopy or flow cytometry. In this work we present $(Bu_4N)_2[Mo_6I_8(NO_3)_6]$ as an excellent precursor for one-pot synthesis of intrinsically luminescent and chemically stable silica nano- (50 nm) and mesoparticles (500 nm). We demonstrate that both types of particles are taken well by the larynx carcinoma (Hep2) cells and have low dark toxicity, which is predominantly determined by silica itself and not by the molybdenum cluster. The photoinduced cytotoxicity is, however, determined by the size of the particle with the smaller particles being significantly more cytotoxic due to high surface area. Notably, the particles can be further easily modified to allow attachment of a biological cargo. Specifically, the surface of silica mesoparticles were functionalised with epoxy groups to allow successful grafting and

transduction of a model protein – Green Fluorescent Protein. In summary, molybdenum cluster modified silica offers high potential for applications such as photodynamic therapy, bioimaging, biolabeling, protein transduction or other types of traceable cellular delivery as well as in multimodal theranostic applications.

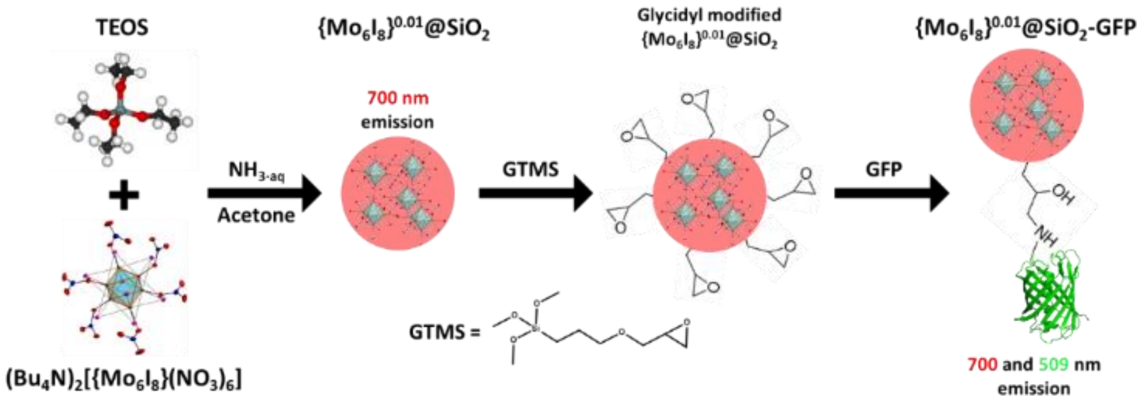

Figure 1: The synthetic procedure of $\{Mo_6I_8\}^{0.01}@SiO_2$-GFP.

Acknowledgements

This work was supported by the Russian Science Foundation [grant No. 18-75-10060], EPSRC grant [EP/R006393/1] and Royal society [grant RSG\R1\180123].

Bioctahedral rhenium cluster complexes: from fundamental chemistry to the functional properties

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Abstract

Chalcogenide clusters of molybdenum, tungsten and rhenium take a special place in the family of cluster compounds because of their extensive and rich chemistry, fascinating structures and useful physical properties. Particularly, the intensive red luminescence of octahedral clusters based on $\{Re_6Q_8\}^{2+}$ (Q = S, Se, Te), $\{Mo_6X_8\}^{4+}$ and $\{W_6X_8\}^{4+}$ (X = Cl, Br, I) cores attract much attention in recent years [1, 2]. During the past decade we have investigated the family of molecular rhenium chalcogenide clusters based on the bioctahedral anions $[Re_{12}(\mu_6\text{-}C)(\mu_3\text{-}S)_{14}(\mu\text{-}L)_3L'_6]^{n-}$. These anions consist of two octahedral cores connected face-to-face by one $\mu_6\text{-}C^{4-}$ and three $\mu\text{-}L^{2-}$ ligands (L = O, S, Se, SO_2 and SO_3). The remaining faces of $\{Re_6\}$ octahedra are capped by $\mu_3\text{-}S^{2-}$ ligands while three outer Re atoms of each $\{Re_6\}$ octahedron coordinate the terminal ligands L′. Bioctahedral clusters display interesting chemistry due to the presence of chemically active inner ligands. It was found that the $\mu\text{-}S^{2-}$ ligands possess a higher chemical activity as compared to $\mu_3\text{-}S^{2-}$ ones and can be selectively oxidized to form the $\mu\text{-}SO_2^{2-}$ groups by reaction of $[Re_{12}CS_{14}(\mu\text{-}S)_3CN_6]^{6-}$ with aqueous H_2O_2. The $\mu\text{-}SO_2^{2-}$ ligands of the $[Re_{12}CS_{14}(\mu\text{-}SO_2)_3(CN)_6]^{6-}$ anion are very active and react with air oxygen forming $\mu\text{-}SO_3^{2-}$ groups [3]. The $\mu\text{-}SO_3^{2-}$ ligands can be reduced by chalcogenide ions yielding $\mu\text{-}SO^{2-}$ and $\mu\text{-}S^{2-}$ ligands, generating a mixture of isotypic cluster anions with common formula $[Re_{12}CS_{14}(\mu\text{-}S/SO/SO_2)_3(CN)_6]^{6-}$. Moreover, selective substitution of $\mu\text{-}SO_2^{2-}$ groups by O^{2-} or Se^{2-} ions has been achieved in relatively soft conditions [4]. Several bioctahedral clusters with $[Re_{12}CS_{14}(\mu\text{-}L)_3]^0$ cores (L = O, Se) were synthesized and investigated. The characteristic bond lengths, spectroscopic characteristics, redox and chemical activity of $[Re_{12}CS_{14}(\mu\text{-}L)_3(CN)_6]^{6-}$ cluster anions change regularly in the row of L = O, S, Se. However, none of the compounds based on bioctahedral clusters with chalcogenide inner ligands showed luminescence.

Now we report the new synthetic approach for obtaining of electron-rich bioctahedral clusters containing inner and terminal halide ligands. It was found that two-step reaction starting from $[Re_{12}CS_{14}(\mu\text{-}S)_3(OH)_6]^{6-}$ anion, HX and Et_4NX (X = Cl, Br) led to formation of new compounds based on $[Re_{12}CS_{14}(\mu\text{-}S)_3X_6]^{8-}$ anions containing 48 cluster valence electrons [5]. Similar reactions starting from $[Re_{12}CS_{14}(\mu\text{-}O)_3(OH)_6]^{6-}$ anion leads to the non-isovalent substitution of inner ligands forming the $[Re_{12}CS_{14}(\mu\text{-}X)_3X_6]^{5-}$ anions. Compounds based on the bioctahedral rhenium clusters with the inner halide ligands were found to be luminescent.

Acknowledgements

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Synthesis and luminescent properties of molybdenum iodide clusters with triazole and aromatic perfluorinated thiolate ligands

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Abstract

Octahedral cluster halide complexes of Mo(II) and W(II), $[\{M_6(\mu_3\text{-}X)_8\}L_6]$ (M = Mo or W; X = Cl, Br or I; *L* = neutral or anionic ligands), are chemically robust constructions with outstanding photophysical properties potentially useful for various applications. In particular, iodide Mo_6 clusters often show superior emission lifetime and quantum yield values [1-3]. We have synthesized new complexes of molybdenum clusters with polyfluoro-substituted thiolate aromatic ligands. Such clusters with extended ligands (Fig. 1), oriented in one direction, can serve as structural blocks in liquid crystals.

$$\mathbf{TBA_2Mo_6I_{14}} \xrightarrow[\mathbf{CH_2Cl_2}]{\mathbf{AgL}} \mathbf{TBA_2Mo_6I_8(L)_6} \quad \mathbf{50\%}$$

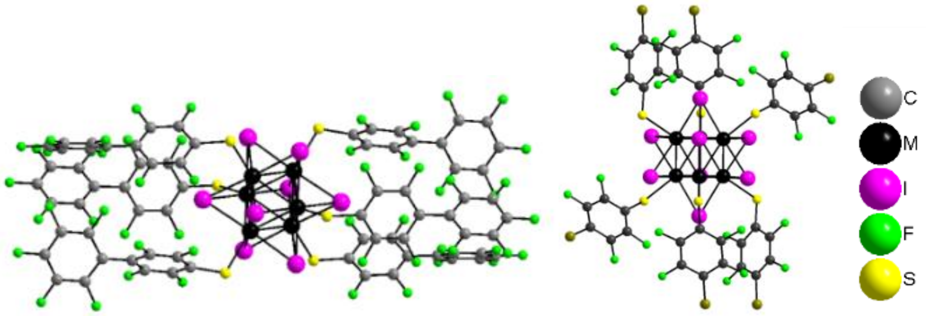

Figure 1: Molybdenum iodide cluster coordinated with perfluorinated thiols.

We have obtained the hexaazide complex of $\{Mo_6I_8\}$ [3] in a new clean reaction of the acetate complex $[Mo_6I_8(CH_3COO)_6]^{2-}$ with Me_3SiN_3 in virtually quantitative yield. Then, by the azide-alkyne cycloaddition reaction, hexa-substituted complexes of molybdenum clusters coordinated with triazolate ligands were synthesized. The scope of the cycloaddition reaction is being explored with other substrates.

$$\mathbf{TBA_2Mo_6I_{14}} \xrightarrow[\text{CH}_2\text{Cl}_2\text{ reflux 48h}]{\text{AgOAc}} \underset{80\%}{\mathbf{TBA_2Mo_6I_8(OAc)_6}} \xrightarrow[\text{CH}_2\text{Cl}_2\text{ reflux 48h}]{(\text{CH}_3)_3\text{SiN}_3} \underset{90\%}{\mathbf{TBA_2Mo_6I_8(N_3)_6}}$$

$$\xrightarrow[\text{boiling in CH3CN 24h}]{\text{acetylene}} \underset{70\%}{\mathbf{TBA_2Mo_6I_8(triazole)_6}}$$

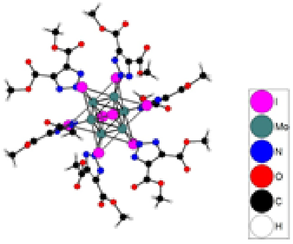

Figure 2: Molybdenum iodide cluster coordinated with a triazolate derived from dimethyl acetylenedicarboxylate.

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Alkali and Alkaline Earth Metal Clusters

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Abstract

Subnitrides of the alkaline earth metals (AE) follow the pattern of alkali metal (A) suboxides which are composed of ionic entities enclosed in structures with purely metallic bonding. An amazingly rich chemistry of A-AE subnitrides was discovered more recently.

Metal clusters normally consist of a metal-metal bonded core and ligands on the outside. To reverse the arrangement of ligands inside and metal atoms outside, such "inverted" clusters are realised with the electropositive alkali and alkaline earth metals in oxides and nitrides, respectively. The characteristic metallic building units are centred by the non-metal atoms O or N as in prototype clusters such as Rb_9O_2, $Cs_{11}O_3$ or $CaBa_{14}N_6$ constituting a plethora of intermetallic compounds with well-defined compositions like $[Rb_9O_2]Rb_3$, $[Cs_{11}O_3]Cs_{10}$ or $[CaBa_{14}N_6]Na_{22}$.

Packing results in extended metal-metal bonding between them. The series Ba_3NNa_x comprises structures with chains of face-sharing Ba_6N octahedra and metallic bonding between the chains (x = 0) or via Na (x = 1 and 5). In the large family of general composition $Ba_{14}CaN_6Na_x$ (x = 7, 8, 14, 17, 21 and 22) the cluster is formed from six face sharing Ba_5CaN octahedra with a central Ca atom and bonded to Na atoms in between. All attempts to incorporate K, Rb or Cs were without success, however, Li participates and adds yet another facet to subnitride chemistry. Whereas so far only the AE atoms coordinate to N, Li can both bind to N as well as form purely metallic substructures. Ba_2LiN is an example of the first kind, its structure being composed of orthogonal rows of edge-sharing Ba_5LiN octahedra. $Ba_{14}LiN_6Na_{14}$ is another example where Li participates in bonding to N by substituting Ca in the isotypic compound. However, whereas the cluster in this compound occurs in a matrix of Na, the purely metallic part of the structure can also contain Li leading to new stoichiometries, e.g. in $Ba_{14}LiN_6Li_4Na_{11}$ or $Ba_{14}LiN_6Li_5Na_{10}$ as well as novel clusters $Ba_{12}Li_8N_6$ in $Li_8Ba_{12}N_6Na_{15}$. Yet, there is evidence for the possibility to substitute Ba by Li, too, in $(Ba,Li)_3N(Li,Na)$, indicating a next step of structural variation.

Due to a unique separation of bonding in space the conduction electrons are confined to the region between the clusters because of the Coulomb repulsion by the charges of the O^{2-} and N^{3-} ions inside the clusters, and space confinement of the conduction electrons leads to a quantum size effect which is measurable in a decreased work function. It is this general structural feature of a "void metal" which makes these materials low energy photoemitters.

Low-dimensional iron containing vanadates

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Abstract

We present reactivity studies on various iron-containing vanadates. The focus will be on structural and electronic properties of magnetic triangular and honeycomb lattices. Investigations by temperature-dependent x-ray diffraction and Mössbauer spectroscopy have been employed to study cooperative effects of the structural phase transition for $BaNa_2Fe[VO_4]_2$[1]. The electronic ground state of Fe^{II} is subject to the Jahn-Teller effect. Here we report the strong dynamics at higher temperatures and a gradual change into the orbital singlet ground state upon lowering the temperature. The latter drives the structural phase transition as a collective axial strain effect. Additionally, we will discuss modifications of the magnetic triangular lattice by (i) chemical substitutions and (ii) ordered defects achieved through internal redox reactions in iron-containing vanadates. For both cases, Mössbauer studies serve as a probe for the electronic ground state of Fe^{II} and Fe^{III} in slightly distorted octahedral environments, namely axial and angular distortions. We will extend our report by commenting on the magnetic order in such triangular and honeycomb lattices. In particular, even in the magnetically ordered state strong fluctuations persist and will be discussed here.

Acknowledgements

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From transition metal atoms sequestered in rare-earth metal clusters to rare-earth rich transition metal polar intermetallics

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Abstract

With endohedral transition metal atoms, *T*, the rare-earth elements, *R*, form clusters of six to eight *R* atoms. These hetero-bi-metallic clusters, $\{TR_r\}$ (r = CN(T) = 6-8), are surrounded by halide ligands, *X*, to build cluster complexes, $\{TR_r\}X_x$. Equal or similar coordination environments are also seen in $\{T_tR_r\}$ polar intermetallics, for example CNs of 8 to 10 in $\{Ru_{11}Lu_{20}\}$. Thus, $\{TR_r\}X_x$ cluster complexes may be understood as a symbiotic arrangement of (polar) intermetallic and salt or, alternatively, ultimate cluster complex condensation produces binary polar intermetallics, $\{T_tR_r\}$.

There is an unknown, presumably large number of even binary polar intermetallics out there that have not been discovered through phase diagram determinations, often subject to inaccurate phase diagram studies. But there are also intermetallics whose synthesis requires more sophisticated routes.

We have discovered a number of examples of “non-existent” intermetallics during our efforts to synthesize new rare-earth cluster halides with endohedral transition metal atoms contributing to the electron count. Two examples are Co_7Pr_{17} and Pt_3Pr_4. These do not exist in the presently known phase diagrams and cannot be synthesized by the traditional, high temperature methods to synthesize intermetallics, e.g. arc melting.

Flux-growth techniques (salts, ionic liquids, metallic or intermetallic melts, preferably at low temperatures) are more subtle routes to these non-existent intermetallics. These routes are presently explored exhaustively, and a number of new compounds e.g., $Pt_4Sn_6Pr_3$ and $CoSn_3Pr$ (from tin melts) or known compositions with new structures ($Pt_{2-x}Pr_3$) have been discovered.

Acknowledgements

Initial research was supported by the University of Cologne, Cologne, Germany, recent research by the Office of Basic Energy Sciences, Materials Sciences Division, U. S. Department of Energy (DOE). Ames Laboratory is operated for DOE by Iowa State University under contract number DE-AC02-07CH11358.

Giant lanthanide-containing clusters as potential molecular magnetic refrigerants

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Abstract

High-nuclearity lanthanide-containing clusters are of interest for the development of magnetic cooling technologies. In this presentation, we discuss the syntheses and crystal structures of a series of heterometallic Ni(II)-Ln(III) clusters that were obtained from the controlled co-hydrolysis of Ni(II) and Ln(III) ions in the presence of iminodiacetic acid (Figure 1, left). All clusters feature a four-shell metal core structure (Figure 1, middle),[1] much like a Russian *nesting doll* (Figure 1, right);[2] the heterometallic cluster core is encapsulated by the hydrolysis-limiting iminodiacetate ligands. Contrary to the common belief or observation that coordination of different Ln(III) ions varies insignificantly, we found that the cluster nuclearity is sensitively dependent on the nature of the Ln(III) ions used. Specifically, we have obtained a series of clusters whose cores contain 52 Ln ions and a varying number of Ni(II) ions: with the smaller and larger Pr(III), a cluster with a core of $Pr_{52}Ni_{74}$ was obtained, whereas the use of heavier and smaller Dy(III), Ho(III), and Er(III), $Ln_{52}Ni_{44}$ core-containing clusters were produced. For the intermediate Ln(III) ions, clusters of different core structures were obtained even with the same Ln(III) ion.

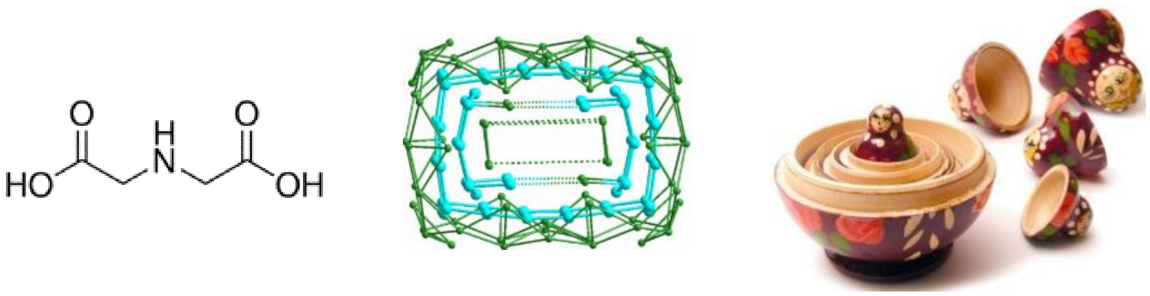

Figure 1: Molecular structure of iminodiacetic acid (left), a representative four-shell cluster core (cyan, Ln; green, Ni), and the image of a Russian nesting doll.

Acknowledgements

We gratefully acknowledge the financial support from the US National Science Foundation and NSFC.

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Historical Clocks and their Restoration

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Abstract

Old clocks and watches are "high tech" products used for centuries. They combine scientific genius with highly developed crafts and artistic design, and they provide deep insight into history and culture. As they have been articles of daily use, corrosion, mechanical wear, careless handling, damage and changing fashions always played a role. There is a great demand for careful restorations in an area of “practical chemistry and physics” using the computer, as well as tools and methods of materials science which to a certain extent can substitute the admirable abilities of the old masters.

A first example will be presented with the work of the huguenot Claudius DuChesne who was forced to escape from France, went to London in 1693 and set up a workshop for sophisticated clocks. One of his musical clocks was delivered to the Prussian court and finally found its way to Dresden. In the course of the restoration a number of surprises turned up including the discovery of an unknown Prussian march. A second example, the famous Baldewein planetary clock (1563-1567) presented in the Zwinger museum in Dresden had been deteriorated in the course of a recent restoration. The reason for the fault could be analyzed and the damage repaired. Last but not least as a third example, the discovery and restoration of a hitherto unknown astronomical pendulum clock, dated 1744, now found its prominent place in the collection of the “Mathematisch-Physikalischen Salon” in the Zwinger in Dresden.

Metallophilic Interactions Metallophilic Interactions Supported by Functional N-Heterocyclic Carbene Ligands

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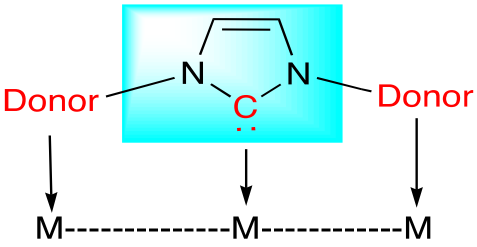
Abstract

N-Heterocyclic carbenes have become ubiquitous ligands in molecular chemistry and their transition metal complexes have attracted a rapidly increasing interest because of their synthetic utility, structural versatility, and catalytic, photophysical and magnetic properties. Their chemical diversity can be considerably enriched by tethering additional donor functions to one or both N-atoms of the heterocycle.[1]



Coordination of all donor atoms to metal centers opens then the possibility to stabilize homo- or heteropolymetallic metal chain complexes.[2] Different synthetic strategies have been applied to the formation of complexes of the coinage metals that display metallophilic d^{10}-d^{10} interactions.[3]

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Structures and Bonding in Multimetallic Cluster Compounds

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Abstract

Intermetalloid clusters, consisting of a main group (semi-)metal shell that embeds one or more transition metal atoms(s), have been actively investigated by many research groups over the past decades, regarding basic properties as well as their potential use as innovative materials.[1,2] Pnictogen trielide or pinctogen tetrelide ions, $[E^{13/14}{}_{x}E^{15}{}_{y}]^{q-}$ ($E^{13/14}$ = Ga, In, Tl; Ge, Sn, Pb; E^{15} = As, Sb, Bi), proved useful synthetic tools for the access of ternary intermetalloid clusters $[M_x@E^{13/14}{}_{y}E^{15}{}_{z}]^{q-}$ by reactions with transition metal (M) compounds.[3] These experiments also allowed first access to corresponding clusters with interstitial lanthanide cations.[4,5] Recently, we extended our studies towards comprehensive exploration of the formation pathways,[6] towards clusters with very unusual geometric and electronic structures,[7-9] and towards intermetalloid clusters embedding actinide ions. While most of the clusters may be understood in terms of (semi-)metal cages that are doped by the interstitial transition metal or lanthanide ions, actinide ions have an even greater impact on the structure and bonding within such species, like $[U@Bi_{12}]^{3-}$ (see Fig. 1), owing to the involvement of f electrons in the bonding.[10]

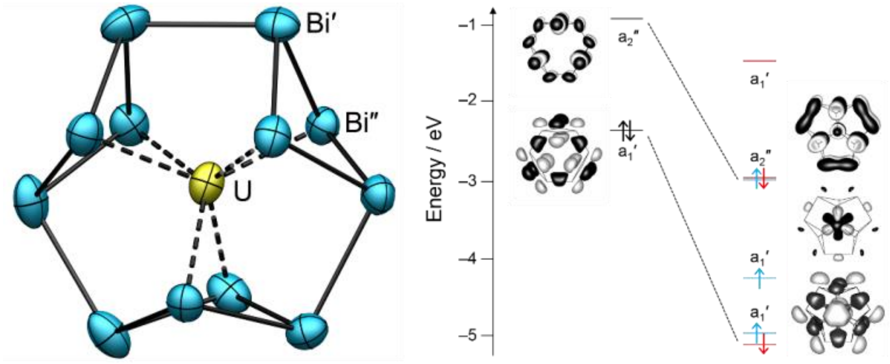

Figure 1: Molecular structure and frontier orbital scheme of the intermetalloid cluster anion $[U@Bi_{12}]^{3-}$.

Acknowledgements

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Molybdenum Sulfide Clusters as an Alternative to Noble Metals for the Catalytic Reduction of Organic Substrates

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Abstract

Molybdenum disulfide, traditionally employed in industry for the hydrodesulfurization (HDS) of fossil fuels, has recently emerged as a low-cost alternative to noble metals as hydrogenation and hydrogen evolution reaction (HER) catalysts.[1] Incomplete cubane-type Mo_3S_4 clusters share structural features with the MoS_2 basal planes, as emphasized in Figure 1, and can serve as molecular analogs of the active sites of this heterogeneous catalyst.

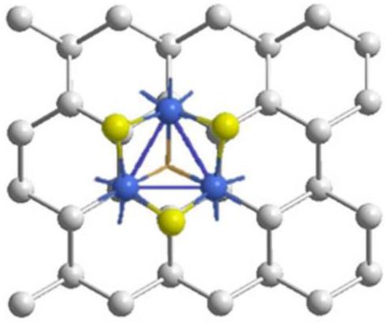

Figure 1: Topological relationship between cuboidal Mo_3S_4 clusters and the basal planes of a MoS_2 monolayer

In this presentation, reactivity aspects of a series of diphosphino, aminophosphino, diamino and diimino trinuclear molybdenum cluster sulfides, relevant to their catalytic applications, will be discussed. The catalytic performance of these complexes in alkynes semihydrogenation and nitroarenes reduction will be analyzed. [2,3] Special emphasis will be given to the mechanistic details of such transformations. For that purpose, DFT theoretical calculations will be combined with kinetic, spectroscopic, electrochemical and structural studies.

Acknowledgements

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Cationic octahedral molybdenum cluster complexes: in-vitro photodynamic and antibacterial activity

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Abstract

The octahedral molybdenum cluster complexes have recently emerged as relevant singlet oxygen, $O_2(^1\Delta_g)$, photosensitizers thanks to attractive chemical and photophysical properties. [1] Upon excitation from the ultra-violet up to the green spectral region, these complexes form long-lived triplet states that are efficiently quenched by oxygen, leading to the formation of $O_2(^1\Delta_g)$ in a high yield up to 92 %.[2] In contrast to commonly used organic photosensitizers such as porphyrins which are losing their sensitizing activity upon aggregation, the Mo_6 cluster complexes remain good $O_2(^1\Delta_g)$ photosensitizers even in the solid state. Generally, the coordination of carboxylate ligands to the $\{Mo_6I_8\}^{4+}$ core provides relatively stable complexes with good light absorption in the visible spectral region, high $O_2(^1\Delta_g)$ productivity, and allows for additional functionalization.[3]

Lately, several Mo_6 cluster-based nanostructured systems were successfully employed in the context of blue-light photodynamic therapy and photo-inactivation of bacteria.[3,4] Still, the use of these complexes in their molecular form for biological applications remains challenging. Herein, we report on the photophysical properties in water solutions of two cationic cluster complexes based on the $\{Mo_6I_8\}^{4+}$ core associated with (4-carboxybutyl)triphenylphosphonium or 4-carboxy-1-methylpyridinium mitochondria-targeting apical ligands (see Fig.1), as well as their photodynamic activity against HeLa and MRC-5 cells under blue-light irradiation and their bacterial photo-inactivation properties against several Gram-negative and Gram-positive bacteria, namely *E. coli*, *P. Aeruginosa, S. Aureus*, and *E. faecalis*. The effect of hydrolysis of the cluster complexes on their photosensitizing ability and on their biological activity are also presented.

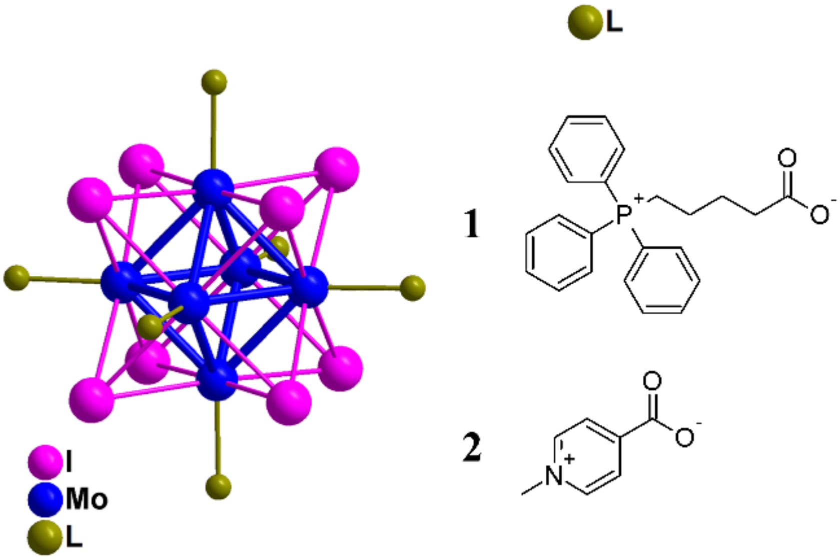

Figure 1: Schematic representation of the molecular structure of the cationic Mo_6 cluster complexes.

Acknowledgements

The work was supported by the Czech Science Foundation (No. 18-05076S).

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Oxides and iodides of metals as precursors of metal cluster complexes: development of new efficient methods for the synthesis of cluster complexes of molybdenum, tungsten and rhenium

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Abstract

Chemistry of cluster compounds is one of the rapidly developing areas of modern coordination chemistry and chemical materials science. For example, the remarkable properties of octahedral cluster complexes of molybdenum, tungsten and rhenium are phosphorescence in the red region accompanied by the generation of singlet oxygen and radiocontrast, which makes such cluster complexes potentially useful as components of various luminescent organic and inorganic materials, as well as solar cells, as sensors, photocatalysts, markers for bioimaging, photosensitizers for photodynamic therapy and radiopaque substances for tomography and angiography. Here we report the synthesis and investigation of cluster compounds starting from the oxides and iodides of molybdenum, tungsten and rhenium as precursor. In the course of the work, the interaction in the systems metal oxide -X-KCN where X = S, Se, Te, P, As, and also in the system metal iodide -X-KCN where X = P, As were studied. For example, it was shown that in the case of the reaction with KCN, a new six-nuclear cluster complex of tungsten namely $[W_6(\mu_4\text{-}O)_2(\mu_3\text{-}CCN)_4(CN)_{14}]^{10-}$ with the unique ligand $(CCN)^{3-}$ is formed. Also, starting from rhenium iodide, number of Re_4 pnictocyanide rhenium cluster complexes was obtained. (Fig. 1)

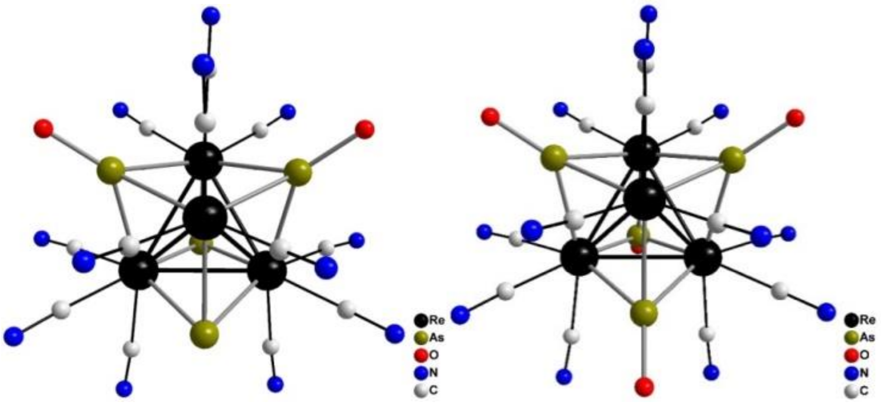

Figure 1: Structures of cluster anions $[\{Re_4As_2(AsO)_2\}(CN)_{12}]^{8-}$ and $[\{Re_4(AsO)_4\}(CN)_{12}]^{8-}$

Acknowledgements

This work was supported by the Russian Science Foundation (project No 18-13-00058)

Designing supramolecular hybrid materials constructed from host-guest inclusion complexes $M_6L^i_8L^a_6@CD_2$ with M= Mo, or W

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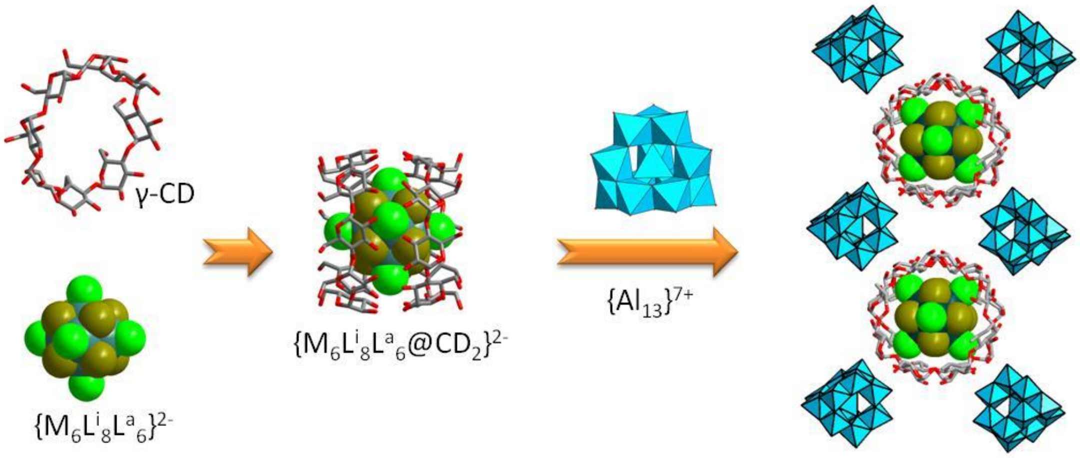
Abstract

Octahedral metal clusters can exhibit a super-chaotropic character (water-structure breaker), involving a strong affinity with hydrophobic and neutral polar surfaces such as some organic macro-cycles. Cyclodextrins (CDs) are water-soluble cyclic oligosaccharides formed of 6 (α-CD), 7 (β-CD) or 8 (γ-CD) glucopyranose units, lining a hydrophobic internal cavity where super-chaotropic ions can be embedded, forming water soluble host-guest complexes. In this communication, we will use the affinity between cyclodextrins and super-chaotropic ions attempt to stabilize polynuclear entities which are normally considered as unstable in water. This underlines that γ-CD host can easily act as a protective layer of the external surface of the polynuclear species against hydrolysis.

We will first discuss about the supramolecular stabilization of highly luminescent clusters $M_6L^i_8L^a_6$ with M = Mo or W. In water, these clusters react with γ-CD producing supramolecular host-guest assemblies. These supramolecular adducts have been systematically crystallized. X-ray diffraction structure analysis reveals the close encapsulation of the octahedral cluster within two γ-CDs. Furthermore, solution studies such as ^{1}H NMR, UV-vis or ESI-MS indicate this host-guest arrangement persists in solution. These encapsulated clusters exhibit a fair hydrolytic stability compare to their derivatives in absence of CDs.

The supramolecular cluster based adducts can be used as an inorganic building blocks to design multi-component well-ordered hybrid systems. The ability to form hierarchically

ordered arrangement will be demonstrated with two examples: 1) a conventional assembly consisting of anionic $M_6L^i_8L^a_6@CD_2$ with cationic aluminium oxo-clusters and 2) an unconventional assembly resulting from the association of two anionic building units ($M_6L^i_8L^a_6@CD_2$ + polyoxometalates). The luminescence properties of the inclusion compounds in solution/solid as well as the multi-components systems will be also discussed.



Supramolecular assemblies of polyoxometalates and metal clusters with cyclodextrins: from inclusion complexes to composite materials

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Abstract

Polyoxometalates (POMs) and octahedral clusters are both inorganic discrete molecular entities built mainly from early transition metal atoms, such as Mo, W, Ta or Re. While POMs are based on metal oxides in their highest oxidation states, octahedral clusters exhibit electron-rich character. Both classes of inorganic systems are relevant for common applications in various fields including medicine, catalysis, and materials science, although they belong to separate chemistries. Thereby, joining POMs and clusters into a single molecular system is expected to generate new innovative area with emerging properties arising from synergetic effects between the two components. Self-assembly strategy based on supramolecular approach through hierarchically-driven molecular recognition would constitute an attractive synthetic method for the design of composite materials.

Recently, cyclodextrins (CDs) showed remarkable ability to form strong sandwich-type inclusion complexes with octahedral clusters, which accommodate deeply the central cavity of the cyclic oligosaccharides [1]. On the other hand, a variety of molecular adducts have also been obtained associating CDs and POMs through weak surface interaction [2-3]. In this communication, we explore the potential of γ-CD to interact with the octahedral clusters $Ta_6Br_{12}(H_2O)_6^{2+}$ and $Re_6Q_8(CN)_6^{4-}$ (Q = S, Se, or Te) as well as the Dawson type POM $P_2W_{18}O_{62}^{6-}$ and the possibility to assemble tantalum or rhenium cluster and Dawson POM into a single

molecular system through mutual interaction with γ-CD (Fig. 1). Stability, reactivity and dynamic behaviors in solution of the resulted complexes have been investigated by a set of complementary methods including multinuclear NMR spectroscopy, ESI-mass spectrometry, and isothermal titration calorimetry. X-ray diffraction analysis is used to determine crystallographic structures and molecular organization in solid state. Interestingly, the host-guest encapsulation phenomenon had led to significant changes in photophysical and redox properties. These results are promising for the elaboration of novel tandem photocatalysts by associating intrinsic properties of each component to reach novel performances through synergetic effect.

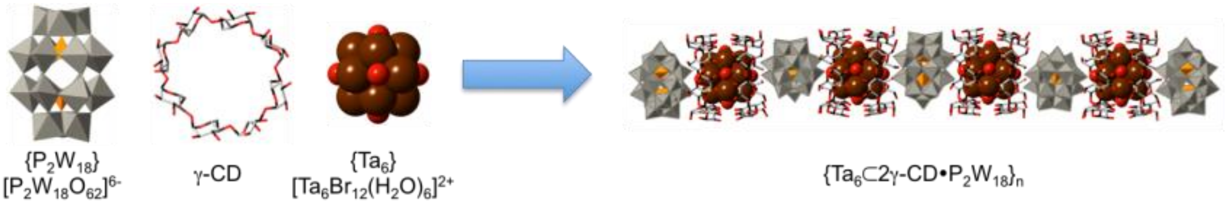

Figure 1: Supramolecular assembly combining Dawson POM $P_2W_{18}O_{62}^{6-}$, γ-cyclodextrin, and tantalum cluster $Ta_6Br_{12}(H_2O)_6^{2+}$.

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Hexanuclear Niobium Cluster Complexes with N- or O-Ligands –Compounds with Nb_6 cluster cations and POM Anions

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Abstract

Cluster compounds with octahedra of metal atoms surrounded by halogenido ligands are known and investigated for a long time.[1] Solution chemical methods allow for ligand exchange reactions, especially of the outer, singly bonded ligands, what gives access to many new compounds with lots of interesting properties. In our efforts to systematically explore the chemistry of hexanuclear niobium cluster compounds, a variety of new compounds was investigated with different N- or O- donor ligands (*L*) under various reaction conditions. Often, compounds of the formula $[Nb_6Cl_{12}^{i}Cl_2^{a}(L)_4]$ with discrete, neutral, and 16-CBEs containing cluster units are obtained. New compounds with *L* = alcohol, amine, amide, azine, amidine, azole, nitrile, phosphane, phosphaneoxide, sulfoxide or water were prepared and characterized. Figure 1 shows exemplarily the structure of the cluster unit with the four cluster-coordinated water molecules being hydrogen-bonded to pyridine molecules in crystals of $[Nb_6Cl_{14}(H_2O)_4]\cdot 9Pyr$. Figure 2 shows the structure of the neutral $[Nb_6Cl_{14}L_4]$ cluster unit with four 4,4'-bipyridine ligands as found in crystals of $[Nb_6Cl_{14}(4,4'\text{-bipy})_4]\cdot 2CH_3CN$. With appropriate preparative procedures, not only four, but all exo-sites are occupied by neutral ligands with the formation of cationic cluster units. Figure 3 shows the structure of a cation-anion pair, which has the charge of the Nb-cluster cation compensated by an anionic polyoxomolybdate anion.

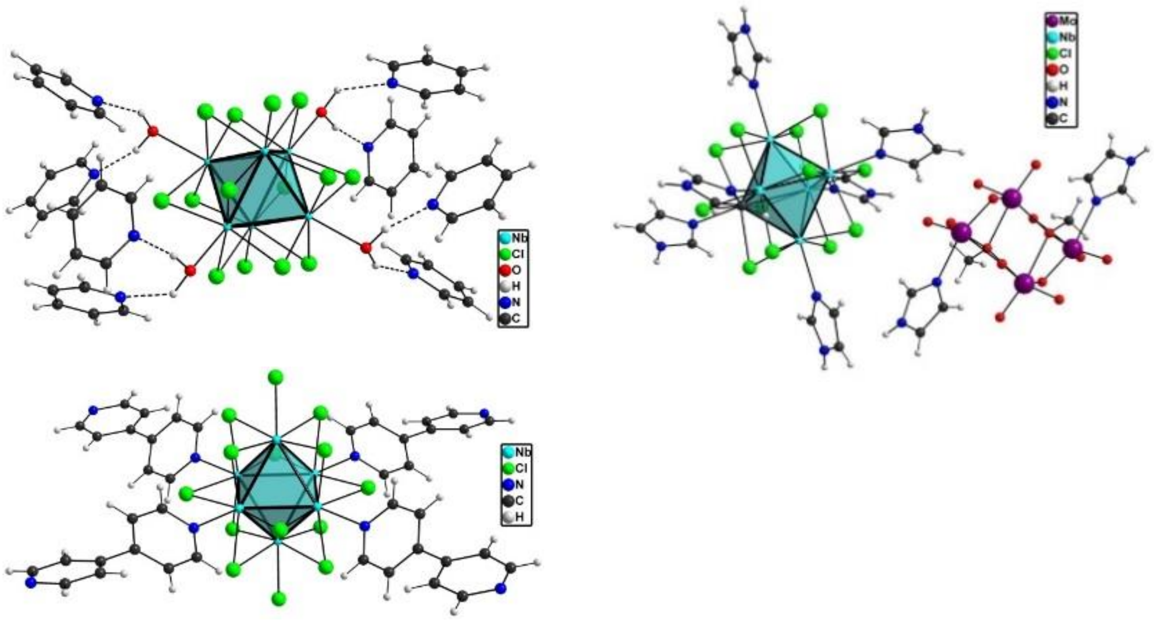

Figure 1. Structure of the neutral 16CBE cluster complex $[Nb_6Cl_{14}(H_2O)_4]$ with H-bonded (dashed lines) pyridine molecules **(top left)**. Structure of the $[Nb_6Cl_{14}(4,4'\text{-bipy})_4]$ cluster, in crystals of $[Nb_6Cl_{14}(4,4'\text{-bipy})_4]\cdot 2CH_3CN$ **(bottom left)**. Structure of the Nb_6-cluster cation – Mo-POM-anion salt in crystals of $[Nb_6Cl_{12}(1H\text{-Imi})_6][Mo_4O_{12}(OCH_3)_2(1H\text{-Imi})_2]\cdot 2CH_3OH$ (1H-Imi = 1H-imidazole) **(top right)**.

Acknowledgements

Financial support from the DFG through the SPP 1708 is gratefully acknowledged.

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Heterometallic Rotaxanes and their Supramolecular Assemblies

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Abstract

Hybrid organic-inorganic rotaxanes consist of an organic template about which a cyclic coordination compound or metal ring can be grown. They differ from metallocrowns and other metal rings in that the design of the organic template, or thread, is such that bulky groups or stoppers are included to prevent the thread leaving the ring.[1] Previously we have shown that we can make supramolecular assemblies of hybrid organic-inorganic [n]-rotaxanes where the components of hybrid organic-inorganic rotaxane are the heterometallic octanuclear metallic wheels based on chromium(III) fluoride-carboxylate bridged $[Cr_7M^{II}F_8(O_2C^tBu)_{16}]^-$ rings and the axle is an organic thread which act also as a template for formation of the heterometallic ring about this axle.[2] This route has allowed us to make hybrid organic–inorganic [2]- and [3]-rotaxanes. Using functionalised 'stoppers' on the axles we can produce hybrid organic–inorganic [2]- and [3]-rotaxanes that can act as ligands. Then these polymetallic rotaxane-ligands can be used as building blocks (modules) for construction of various supramoleculal assemblies.[3] Recently we have examined creating hybrid organic-inorganic rotaxanes featuring a new type of metallic wheels based on titanium(IV) oxo-carboxylate bridged $[Ti_7M^{III}O_8(O_2C^tBu)_{16}]^-$ rings.

Here we present the designed supramolecular architectures obtained by linking hybrid organic–inorganic [2]- and [3]rotaxanes into various [n]-rotaxanes (where n= 4 - 24).

The ability to grow isostructural but different heterometallic rings around similar threads has also allowed us to make a hetero-heterometallic-hybrid [3]-rotaxane $\{[Ti_7Fe][Cr_7Ni]\}$ (Figure 1).

As the rings have been proposed as qubits for QIP, the strategy provides a possible route towards scalable molecular electron spin devices for QIP.

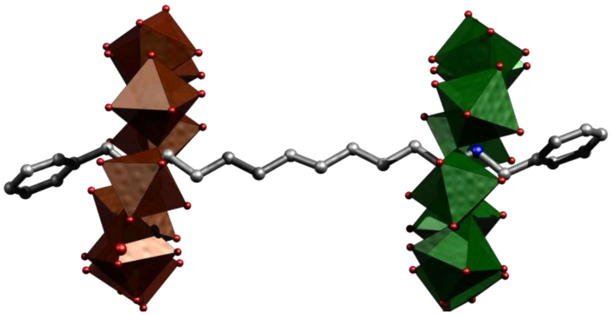

Figure 1: [3]-Rotaxane $\{[(PhCH_2NH_2)_2(CH_2)_{10}]\ [Ti_7FeO_8(O_2C^tBu)_{16}]\ [Cr_7NiF_8(O_2C^tBu)_{16}]\}$.

Acknowledgements

This work was supported by the University of Manchester and the National EPR Facility.

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Molecular Metal Carbonyl Nanoclusters

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Abstract

A renewed interest for molecular (atomically precise) metal nanoclusters has recently appeared because of their relevance to nanochemistry, nanotechnologies and nanoscience.[1] At the subnanometer scale (0.5-3 nm) typical of molecular (atomically precise) metal nanoclusters, there is not a direct relationship between the size of the nanocluster and its structure and properties. Indeed, within this ultra-small size regime these no longer relies on the size but rather on the geometric structure and surface ligands of the cluster. This is the realm of molecular clusters which has been pioneered, among the others, by the work of Chini and Longoni.[2] In this respect, molecular clusters of increasing sizes may be viewed as snapshots along the way from small metal containing molecules, to metal nanoclusters and ultra-small metal nanoparticles. Within this context, the interest of molecular cluster chemists has moved along the years from smaller to larger clusters. Thus, there is nowadays an overlap between the chemistry of larger molecular metal clusters and ultrasmall metal nanoparticles (Figure). In this presentation, some recent developments of the chemistry of molecular metal carbonyl nanoclusters will be discussed in the above mentioned framework. In particular, molecular metal carbonyl clusters containing hydride ligands will be used as an example to discuss some structural, chemical, spectroscopic and electrochemical aspects of molecular (atomically precise) metal nanoclusters.[3]

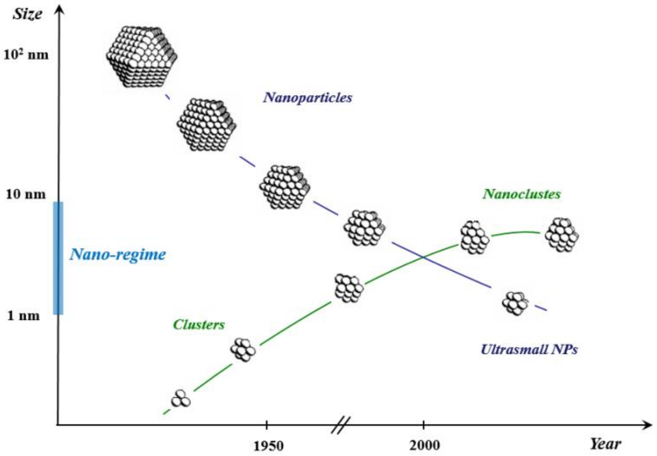

Figure 1: From small molecular clusters and large metal nanoparticles to molecular nanoclusters and ultrasmall NPs.

Acknowledgements

I dedicate this presentation to Professor Giuliano Longoni in occasion of his 75th birthday and in recognition of his fundamental contributions to metal carbonyl cluster chemistry. I heartily thank him for his inspirational leadership, friendship and continuing encouragement to carry out this wonderful journey in the chemistry of molecular carbonyl clusters.

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Concentric Bond and Intercluster Bonding, Useful Concepts in the Formation of Multilayered Structures

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Abstract

The seminal concept of chemical bond[1] dates back from more than a century ago, being the central conception in the formation of molecular structures from individual atoms. Interestingly, such notion of chemical bond involves the interaction between orbitals of separated nuclei, with different origin. Herein, we introduce the concept of Concentric Bond, involving the interaction of orbitals which remain coincident to a common origin. This new chemical bond concept, is introduced along the superatom concept (SAC)[2], which further rationalize the bonding in clusters composed by several structural layers. We will apply this concept to the full-shell icosahedral clusters, $[Au_{13}(dppm)_6Cl_2]^{3+}$ and $[Au_{55}(PPh_3)_{12}Cl_6]^-$ (**1**) both landmark species characterized in the beginning of the 80's, depicting two and three structural shells, respectively.[3] Their electronic structure can be ascribed as $1S^21P^6$ and $1S^21P^61D^{10}2S^22P^61F^{14}1G^{10}$, according to SAC,[2] unraveling the nature of each electronic shell as bonding, non-bonding and antibonding combinations between the different structural layers. For 1, its Au_{55} core can be described as a combination of $Au@Au_{12}@Au_{42}$ structural layers (Fig. 1), which in turn leads to the overall 1S, 2S and 3S levels, resulting from the combination of concentric S-type (atomic and superatomic) functions, which denotes an overall bonding, non-bonding and antibonding interaction between the respective shells (Fig. 1). The same is observed for P-type (Fig. 1), and related shells. Moreover, the intercluster bonding is also discussed, showing single, double, and aromatic bonds, in addition to hypothetical example for a triple bond.[4]

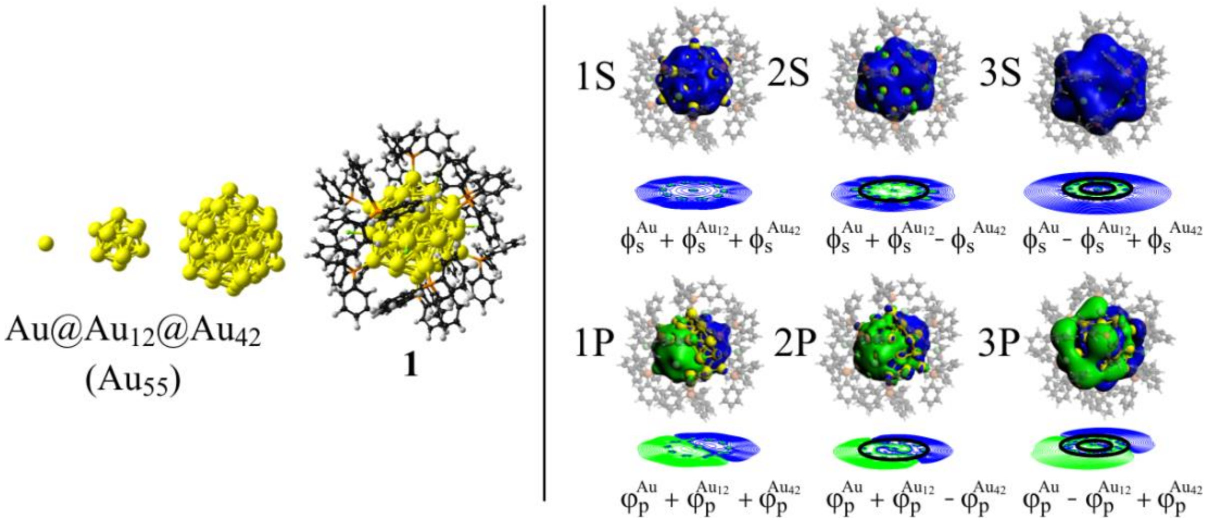

Figure 1: Multilayer architecture of the Au_{55} core from **1**, leading to the combination of different concentric orbital functions (φ) from Au, Au_{12} and Au_{42}. Radial nodes denoted as black circles in the contourplots.

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This work was supported by FONDECYT 1180683.

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Poster Contributions

Heteroleptic Chini-Type Platinum Clusters: Synthesis and Characterization of Phosphine Derivatives of $[Pt_{3n}(CO)_{6n}]^{2-}$ (n = 2– 4)

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Abstract

After the seminal work of Chini and Longoni,[1] $[Pt_{3n}(CO)_{6n}]^{2-}$ (n = 1-8) clusters have represented a milestone in the chemistry of molecular clusters and metal carbonyls. These Chini clusters are composed of a stack of triangular Pt_3-units and can interconvert by simple redox reactions.[2] The ability of the higher nuclearity oligomers (n = 5-8) to self-assemble into continuous chains behaving as molecular metal wires has been recently demonstrated.[3] Moreover, they can be used as catalysts, as well as precursors of catalysts, nanoparticles and nanowires. In the last year, the functionalization of Chini clusters with phosphine ligands via CO substitution was investigated and led to the formation of heteroleptic Chini-type clusters.[4,5] Herein, we report the synthesis and characterization of new phosphine derivates of $[Pt_{3n}(CO)_{6n}]^{2-}$ (n = 2– 4), such as $[Pt_{12}(CO)_{20}(PTA)_4]^{2-}$ (Fig. 1) (PTA = 1,3,5-triaza-7-phosphaadamantane). The presence of PTA ligands confers water solubility to Chini clusters, and their cytotoxicity against human ovarian cancer cell lines has been evaluated. Moreover, the reaction of $[Pt_6(CO)_{12}]^{2-}$ with bis(diphenylphosphino)methane (dppm) results in $[Pt_6(CO)_{10}(dppm)]^{2-}$ which undergoes to oxidative oligomerization affording the higher

nuclearity Chini-type clusters $[Pt_{12}(CO)_{20}(dppm)_2]^{2-}$ (fig. 2), $[Pt_{18}(CO)_{30}(dppm)_3]^{2-}$ and $[Pt_{24}(CO)_{40}(dppm)_4]^{2-}$. This process may be reversed by reduction under CO atmosphere.[6]

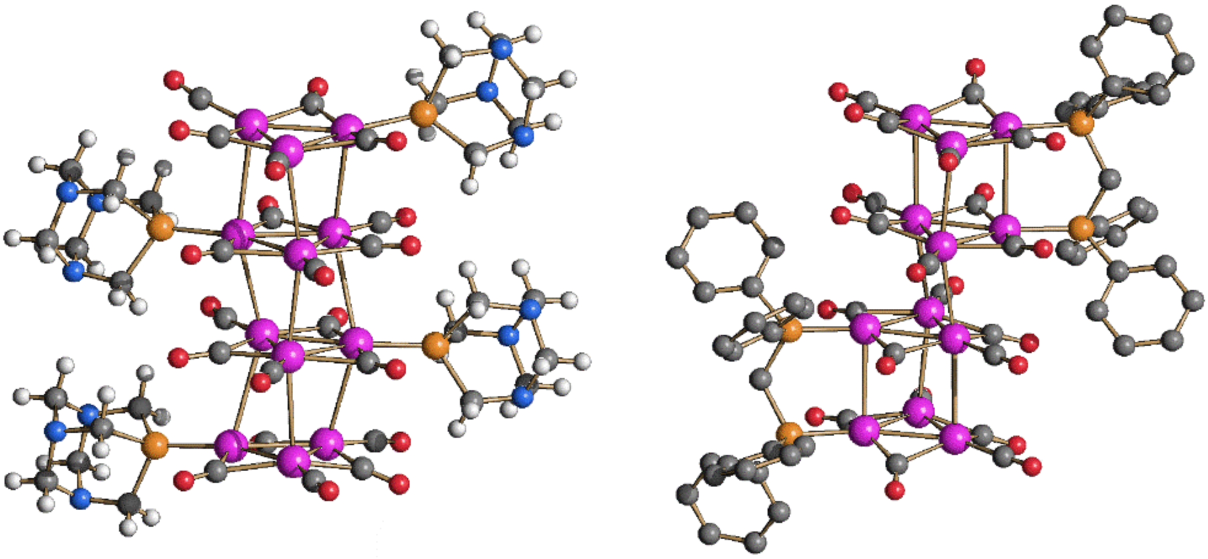

Figure 1: Molecular structure of $[Pt_{12}(CO)_{20}(PTA)_4]^{2-}$ (colour legend: Pt purple, P orange, N blue, O red, C grey, H white) **(left)**. Molecular structure of $[Pt_{12}(CO)_{20}(dppm)_2]^{2-}$ (colour legend: Pt, purple; P, orange; C, grey, O, red) **(right)**.

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Synthesis and Reactivity of New Cp-Stabilized Rare-Earth Metal Clusters

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Abstract

Ever since its discovery in 1978, the Tebbe reagent $Cp_2Ti[(\mu_2\text{-}CH_2)(\mu\text{-}Cl)AlMe_2]$ has been an inspiration to organometallic chemists.[1] It is the classic example of a heterobimetallic methylidene complex stabilized by a Lewis acid. In comparison to well-established transition metal carbene complexes, the application of these concepts on rare-earth metal chemistry presents a particular challenge.[2] As for the Tebbe reagent, the use of strong Lewis acids is an elegant and convenient method to stabilize such compounds and structural motifs like $(L)Ln(III)(CH_2)_x(AlMe_2R)_y$ with L being a monoanionic ligand have been accomplished.[3] Also, Lewis-acid free homometallic rare-earth metal compounds $(L)_3Ln_3(\mu_3\text{-}CH_2)(\mu_3\text{-}X)(\mu_2\text{-}X)_3$ have been accessed, wherein X represents methyl[4] or halogenido[5] moieties. Herein, we present the synthesis of Ln half-sandwich cluster compounds via partial alkyl/halogenido ligand exchange and the effect of the metal ion size on the cluster nuclearity. Subsequent donor-induced tetramethylaluminate cleavage leads to the formation of new homometallic rare-earth metal methylidene complexes. Reactivity studies with carbonylic substrates revealed $CH_2^{2-} \leftrightarrow O^{2-}$ exchange and hence reactivities reminiscent of the Tebbe methylidene transfer reagent.

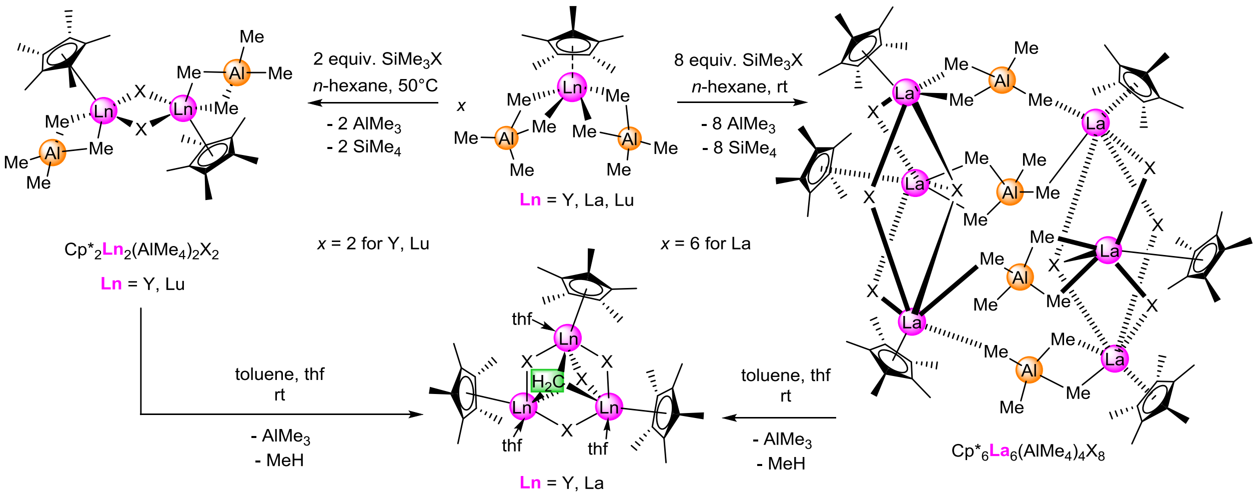

Figure 1: Reaction of mild halogenido transfer reagents with rare-earth metal bis(tetramethylaluminate) complexes (X = Cl, Br, I).

Acknowledgements

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Tungsten trioxide as a convenient precursor for metal cluster complexes

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Abstract

Tungsten trioxide has been found to be a new simple precursor for the synthesis of tungsten cluster compounds based on a new type of cluster units as well as known before. Unpredictably, fully deprotonated form of acetonitrile, anion CCN^{3-}, has been experimentally realized in a new type of anionic bitetrahedral tungsten cluster complex $[\{W^6(\mu_4\text{-}O)_2(\mu_3\text{-}CCN)_4\}(CN)_{16}]^{10-}$ (Fig. 1) as a μ_3-briged ligand coordinated to W_3 face of the W_6 metallocluster. CCN^{3-} ligand was derived from cyanide ion in a one-pot reaction between WO_3 and KCN under relatively moderate conditions. Likewise, similar cluster complex, $[\{W_6(\mu_4\text{-}O)_2(\mu_3\text{-}As)_4\}(CN)_{16}]^{10-}$, with $\mu_3\text{-}As_{3-}$ instead of $\mu_3\text{-}CCN^{3-}$ has been synthesized by the reaction between WO_3, As and KCN. However, the reaction between WO_3, P and KCN led to formation of the complex $[\{W_6(\mu_4\text{-}O)_2(\mu_3\text{-}CCN)_4\}(CN)_{16}]^{10-}$; the presence of phosphorus in the reaction system only increased the yield of the compound but did not lead to formation of a cluster complex with P as a ligand. Both complexes $[\{W_6(\mu_4\text{-}O)_2(\mu_3\text{-}CCN)_4\}(CN)_{16}]^{10-}$ and $[\{W_6(\mu_4\text{-}O)_2(\mu_3\text{-}As)_4\}(CN)_{16}]^{10-}$ represent an unprecedentedly electron-poor W_6 clusters with only 14 Cluster Valence Electrons on 11 metal–metal bonds. The molecular structure of these two complexes was revealed by X-ray single-crystal diffraction and confirmed by elemental analysis as well as by mass-spectrometry. Presence of CCN^{3-} ligands was additionally confirmed by ^{13}C NMR, while $\mu_4\text{-}O^{2-}$ ligand was evidenced by ^{17}O NMR spectroscopy. Also, it has been found that a high-temperature reaction between WO_3 and KCN in the presence of S, Se or Te leads to the formation of well-known W_4 cluster complexes, $[\{W_4Q_4\}(CN)_{12}]^{n-}$ (Q = S, Se or Te), with a high yield in one step.

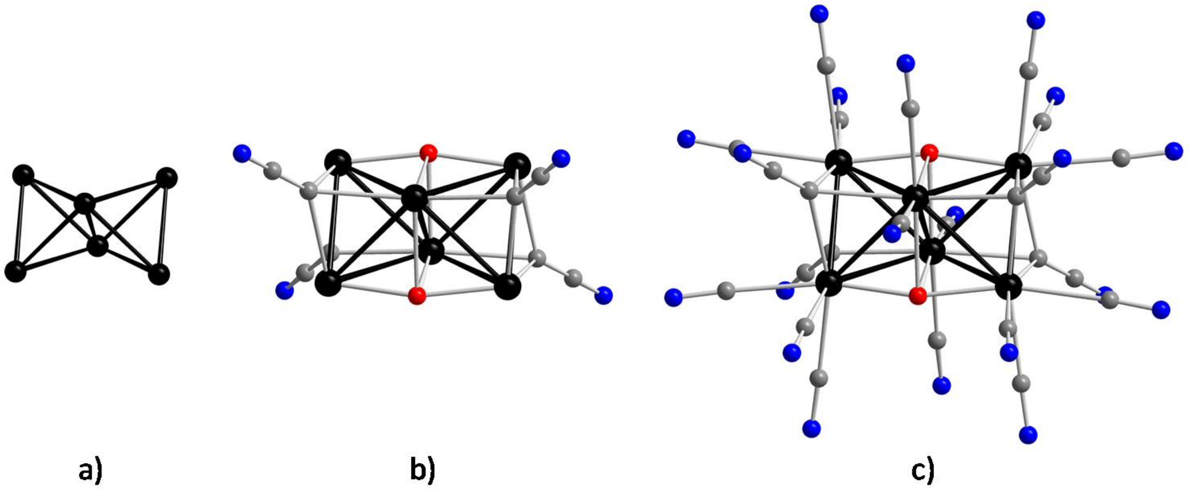

Figure 1: Detailed structure of the cluster complex $[\{W_6(\mu_4\text{-}O)2(\mu_3\text{-}CCN)_4\}(CN)_{16}]^{10-}$: a) bitetrahedral metallocluster W_6; b) cluster core $\{W_6(\mu_4\text{-}O)_2(\mu_3\text{-}CCN)_4\}^{6+}$; c) whole cluster complex $[\{W_6(\mu_4\text{-}O)_2(\mu_3\text{-}CCN)_4\}(CN)_{16}]^{10-}$.

Acknowledgements

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Homometallic Monocyclopentadienyl Rare-Earth Metal Halogenido Clusters: Synthesis and Characterization

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Abstract

Metal cluster compounds display unique coordination modes and can act as useful models for studying reactivities of heterogeneous catalysts. [1] Overall, the bonding in rare-earth metal ligand clusters is highly polarized and selective shielding by ancillary ligands is a deciding factor, when the synthesis is performed in nonaquaeous solvents. [2] A facile synthesis route for salt-like clusters is the halogenido for methyl exchange reaction. For example, the reaction of half-sandwich rare-earth metal complexes $Cp^{*}Ln(AlMe_4)_2$ with halogenido transfer reagents Me_3SiX (X = I) and Me_3GeX (X = Cl, Br) led to the aggregation of mixed ligand clusters as large as $[Cp^{*}_6La_6Cl_8(AlMe_4)_4]$. [3]

In this work, we present the synthesis and characterization of homometallic salt-like rare-earth metal clusters via complete alkyl/halogenido exchange. The reaction of $(Me_3SiC_5H_4)La(AlMe_4)_2$ with various halogenido transfer reagents resulted in the formation of salt-like clusters of distinct nuclearity, depending on the halogenido ion size.

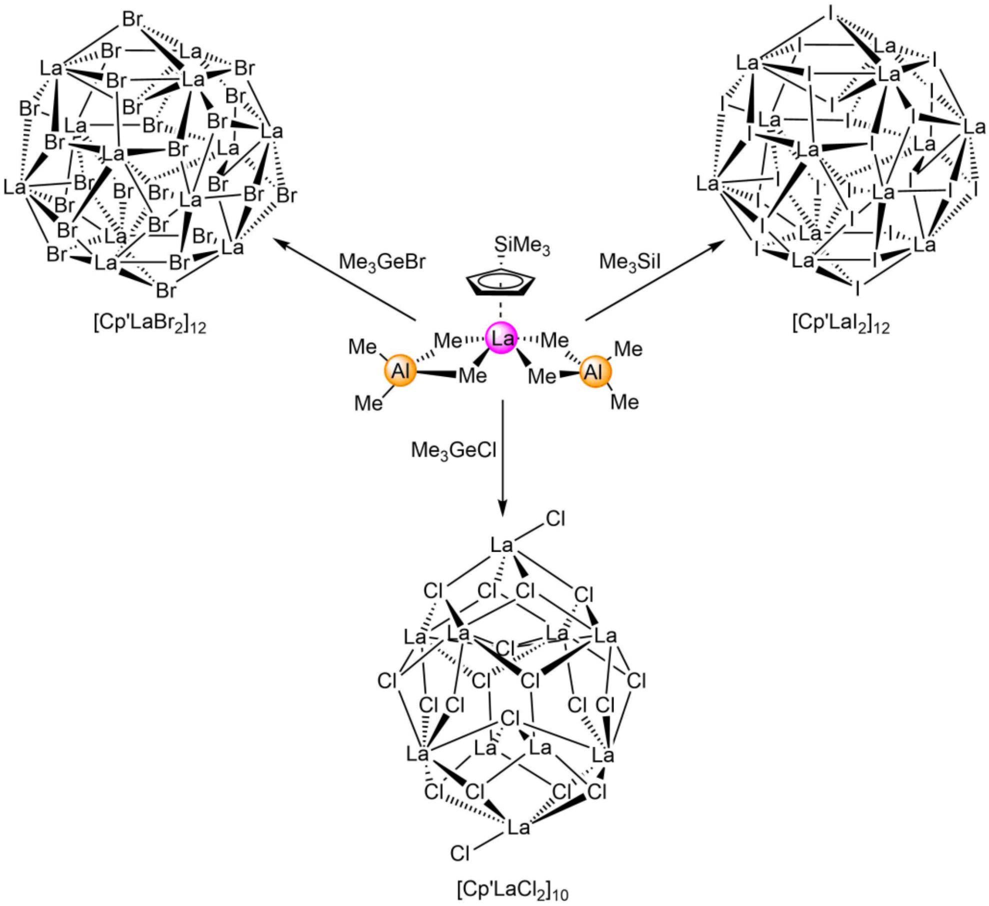

Figure 1: Reactivity of halogenating reagents toward Cp-stabilized rare-earth metal bis(tetramethylaluminate) complexes ($CpSiMe_3$ ligands omitted for clarity)

Acknowledgements

We are grateful to the German Science Foundation for financial support
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Alkaline kryptates of ternary tungsten iodides

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Abstract

Tungsten iodide clusters of the type $A_2[M_6I_{14}]$ (M = W, Mo; A = alkaline) have been studied for their photophysical properties and as precursors for ligand substituted tungsten iodide clusters which then partially show remarkable quantum yields and singlet oxygen generation. The photophysical properties of such clusters can be modified in different ways: by exchanging the terminal iodide atoms[1,2], substituting metal atoms of the cluster core[3] or varying the cation. To get more information on the influence of the cation in compounds of the type $A_2[W_6I_{14}]$ – which are stable in moist air – those compounds were brought to reaction with the kryptate *Kryptofix 222* ($C_{18}H_{36}N_2O_6$). Departing from the reaction of the corresponding ternary tungsten iodide $A_2[W_6I_{14}]$ with *Kryptofix 222* the compounds were obtained as orange to light brown powders. In this work we present the syntheses, crystal structures and luminescence properties of the series of $(C_{18}H_{36}N_2O_6A)_2[W_6I_{14}]$ with A = Na, K, Rb and Cs.

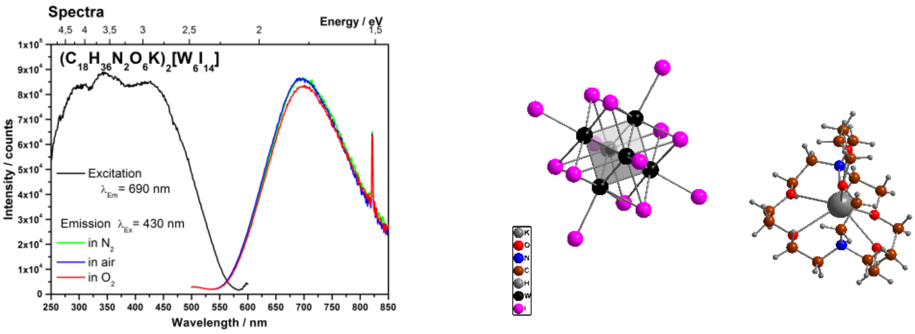

Figure 1. Excitation and emission spectra of solid $(C_{18}H_{36}N_2O_6K)_2[W_6I_{14}]$ under various atmospheres (left). Structure fragments of W_6I_{14} and $C_{18}H_{36}N_2O_6K$ from the crystal structure (right).

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Water-soluble rhenium clusters with triazoles

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Abstract

Octahedral metal cluster complexes are very promising candidates for different biomedical application due to their superb properties such as luminescence with high quantum yield and emission lifetimes and X-ray contrast due to heavy elements in cluster core. However, at the same time, these clusters usually are not water-soluble or not stable in water solution at physiological pH. Thus our work mainly focused on rising this property of octahedral rhenium cluster complexes with formula $[\{Re_6Q_8\}L_6]$ (Q = S, Se, L = organic ligand). Previously it was shown that such clusters with ^{1}H-benzotrialoze (BTA) were soluble in water and very promising to act as cyto- and phototoxic agent for cancer therapy [1]. We expanded this series by changing BTA to 1,2,3-triazole and 1,2,4-triazole and study their physicochemical and biological properties.

In this presentation we will talk about the synthesis of new cluster compounds with triazole ligands $Na_4[\{Re_6Q_8\}(1,2,n\text{-trz})_6]$ (Q = S, Se, 1,2,n-trz = 1,2,3- or 1,2,4-triazole). We carried out already proven for such systems synthesis in the melt of the ligand in a glass tube at 200ºC. Compound obtained were characterized by different methods like elemental analysis, IR- and NMR-spectroscopy, mass- and energy dispersive spectroscopy, etc. Also, we obtained crystals for complexes with 1,2,3-triazole which were characterized by X-ray diffraction analysis. Luminescent properties of compounds obtained were studied and photophysical characteristics were better than one of the previously described complexes with BTA.

We investigated biological properties for obtained clusters. Cytotoxicity, cellular uptake and localization were estimated using MTT test, flow cytometry and confocal microscopy respectively. It was shown that rhenium clusters with triazoles are less cytotoxic than complexes with BTA.

Acknowledgements

This work was supported by the Russian Science Foundation (Grant 15-15-10006).

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Synthesis and luminescence of the new ligand exchanged cluster compound $(^{n}Bu_4N)_2[Mo_6I_8(CH_3SO_3)_6]$

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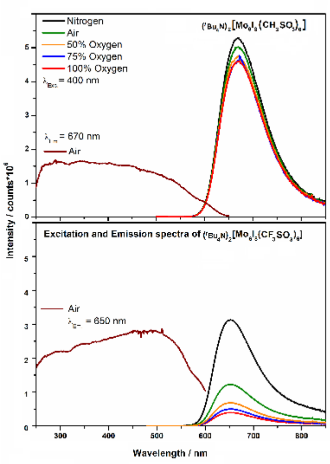
Abstract

Metal cluster complexes of the type $[M_6X_8L_6]^{2-}$ of the early transition metals (M = Mo, W, Re) with X = halide and/or chalcogenide show extraordinary luminescence properties (phosphorescence) and furthermore luminescence quenching in the presence of oxygen. [1][2] These properties can be - to some degree - manipulated by variation of the outer ligands (L), of inorganic or organic nature. Yet, the mechanism of the energy transfer from excited the cluster compound to ground state oxygen and especially the influence of the ligand to that process is not fully clarified. In this work we describe a new molybdenum iodide cluster with methane sulfonate as ligands $(^{n}Bu_4N)_2[M_6I_8(CH_3SO_3)_6]$ and compare its properties with those of the triflate $(^{n}Bu_4N)_2[M_6I_8(CF_3SO_3)_6$ compound.[1] The synthesis follows the well described reaction between $(^{n}Bu_4N)_2[M_6I_{14}]$ and $AgCH_3SO_3$ in acetone, where AgI is precipitated.[1-4]

Luminescence studies in the solid state show strong phosphorescence, yet a low quenching rate (10%) in oxygen atmosphere. In comparison, the analogous $({}^{n}Bu_4N)_2[M_6I_8(CF_3SO_3)_6$ exhibits a weaker luminescence but a stronger quenching rate (88%) in oxygen atmosphere. [3] The drastic change in their luminescence and quenching behavior (Δ = 78%) generated by a small change in the ligand backbone is interesting and not yet pointed out even in similar studies[4] and subject of further investigations.



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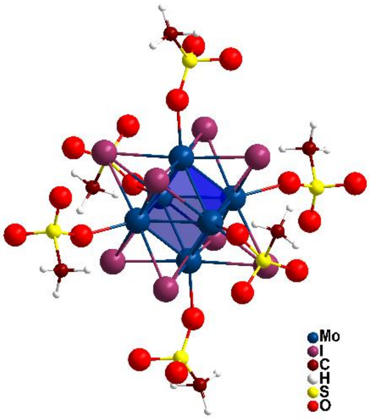

$Rb_{10}Mo_{39}S_{43}$, Last Member of the $Rb_{2n}(Mo_9S_{11})(Mo_{6n}S_{6n+2})$ Series? Synthesis, Crystal and Electronic Structures, and Electrical Properties.

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Abstract

The study of materials with metallic clusters is one of the main topics developed in solid chemistry in the world for more than 40 years (Profs. Corbett., McCarley, Simon, Swennson, Torardi, McCarroll ...). The term cluster was first used by FA Cotton in the early 1960s [1]. It refers to an aggregate of metal atoms (two or more) connected to each other by metal-metal bonds of length close to those found in the metal itself, and which is isolated from its neighbors by its ligand environment. These aggregates or clusters are encountered in many fields such as organic, bioorganic, inorganic and solid-state chemistry. In inorganic solid state chemistry, the most fascinating element is the molybdenum which form 25 different types of clusters the nuclearities of which goes from 3 to 36 to date. Among the latter clusters, the most encountered is the octahedral Mo_6 occurring, for example, in the ternary molybdenum chalcogenides $M_xMo_6X_8$ (M = Ag, Sn, Ca, Sr, Ba, Sn, Pb, 3d elements, rare-earths; X = S, Se, Te, and x ranging from 0 to 4) known as Chevrel phases and discovered in the early 70’s. Subsequently, larger clusters such as Mo_9, Mo_{12}, Mo_{15}, Mo_{18}, Mo_{21}, Mo_{24}, Mo_{30} and Mo_{36} were obtained by the one-dimensional *trans*-face sharing of nMo_6 octahedra (n = 2, 3, 4, 5, 6, 7, 8, 10 and 12) in more than 40 different structural types. From these clusters, we synthesized several families of compounds containing, for example, even-membered clusters ($M_{2n-2}Mo_{6n}X_{6n+2}$ series; M = Rb, Cs; X = S, Se, Te; n = 1 to 6) or odd-membered ($M_{2n-1}Mo_{6n+3}X_{6n+5}$ series; M = Rb, Cs; X = S, Se, Te; n = 2 and 3), as well as families containing mixtures of even- and odd-membered clusters (series $Rb_{2n}(Mo_9S_{11})(Mo_{6n}S_{6n+2})$ (n= 1 to 4) [2]). All members of the latter family crystallize in *R*-3*c* space group with Z=6 in the hexagonal setting. Their crystal structures consist of an equal mixture of Mo_9S_{11} and $Mo_{6n}S_{6n+2}$ (n=1 to 4) cluster units interconnected through Mo-S bonds. The Rb^+ cations occupy large voids between

the different cluster units. Electrical resistivity measurements carried out on single-crystals showed that the four members are superconducting with critical temperatures ranging from 4.2 K to 10.9 K. An interesting feature of their electrical behaviour is the upturn of the resistivity just before the superconducting transition that increases with *n* that clearly shows that the $Rb_{2n}(Mo_9S_{11})(Mo_{6n}S_{6n+2})$ compounds are near at a metal-insulator boundary. We will present the crystal structure and electrical resistivity measurements of the fifth member of the $Rb_{2n}(Mo_9S_{11})(Mo_{6n}S_{6n+2})$ family: $Rb_{10}Mo_{39}S_{43}$. This new compound presents unusual lattice parameters that result from the coexistence of the two high nuclearity clusters Mo_9 and Mo_{30}. Semiconducting properties were measured for this new compound. The electronic structure of the $Rb_{2n}(Mo_9S_{11})(Mo_{6n}S_{6n+2})$ series (n = 1 to 5) have been studied in order understand the structural and physical properties of these compounds, that may exhibit interesting thermoelectric properties because of their unique complex crystal structure

Acknowledgements

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Three-center sulfur mechanism of the catalytic semihydrogenation of alkynes using a Mo_3S_4 cluster

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Abstract

The $[Mo_3S_4Cl_3(dmen)_3]BF_4$ diamino cluster has been proved to be an appropriate catalyst for the selective hydrogenation of nitroarenes.[1] In this work its catalytic activity has been examined in the semi hydrogenation of alkynes. Based on extensive experimental and computational results, we propose an unprecedented mechanism in which only the three bridging sulphur atoms are the active sites to achieve this transformation.[2] The process occurs with the addition of the alkyne molecule to two adjacent sulphur centres to form a dithiolene intermediate and the subsequent hydrogen activation involves the third sulphur centre in cooperation with one of the dithiolene carbon atoms to produce the alkene product, as represented in Figure 1.

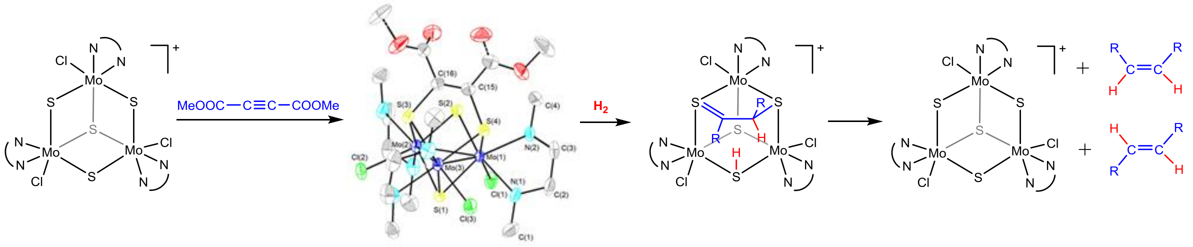

Figure 1: Proposed mechanism for the semi hydrogenation of dmad alkyne.

$[Mo_3S_4Cl_3(dmen)_3(dmad)]BF_4$ dithiolene adduct could be experimentally isolated and its structure determined by X-ray crystallography. In addition, isolation of this intermediate allowed us to study its redox properties. All results regarding the optimization of the catalytic reaction as well as the mechanistic study will be presented.

Acknowledgements

Financial support from the Spanish Ministerio de Economía y Competitividad and FEDER funds of the EU (Grants CTQ2015-65207-P, CTQ2015-65707-C2-2-P, and CTQ2015-71470-REDT), Generalitat Valenciana (PrometeoII/2014/022) and Universitat Jaume I (UJI-A2016-05) is gratefully acknowledged.

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A ternary tungsten iodide having a remarkable quantum yield

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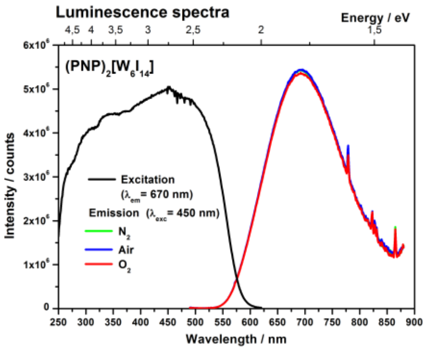
Abstract

Ligand substituted tungsten clusters of the type $A_2[M_6I_8L_6]$ M = W and L = ligand have been studied because of their remarkable photophysical properties.[1] The problem and bottleneck in the synthesis of this compounds is to obtain the starting materials in high yields and quantity. $Cs_2[W_6I_{14}]$ is prepared from W_3I_{12} in the presence of CsI.[2] Afterwards, it is possible to exchange the Cs ions for organic cations like TBA^+ or other cations. Till now a faster route to soluble $A_2[W_6I_{14}]$ compounds which can be produced in high quantities is still missing. Based on the findings of Schäfer et al[3] we have attempted to prepare iodine-rich tungsten iodides. These compounds have potential as precursors for solution reactions. Herein we use the new compound W_6I_{22}, whose crystal structure will be the subject of an upcoming publication. The binary tungsten iodine W_6I_{22} is closing the gap. Departing from this compound we are reporting a high yield synthesis of $A_2[M_6I_{14}]$ with the organic cations *A* = PNP (Bis(triphenylphosphine)iminium) and PPh_4 (tetraphenylphosphonium) and their luminescence properties.



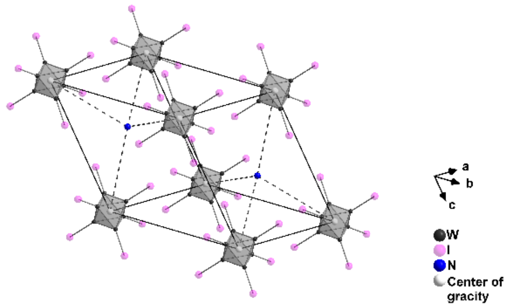


Figure1. Emission spectra of solid $(PNP)_2[W_6I_{14}]$ under various atmospheres (left). Unit cell of $(PNP)_2[W_6I_{14}]$ with nitrogen as center of gravity of the PNP^+ cations.

Table 1. Quantum yields of the purified cluster compounds $A_2[W_6I_{14}]$ with A = TBA, PPh_4, PNP under air and inert conditions.

Compound	Quantum yields	
	Air	Argon
$(TBA)_2[W_6I_{14}]$	16 %	16 %
$(PPh_4)_2[W_6I_{14}]$	16 %	16 %
$(PNP)_2[W_6I_{14}]$	42 %	42 %

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$Au_{108}S_{24}(PPh_3)_{16}$ vs. $Au_{70}S_{20}(PPh_3)_{12}$: A comparison

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Abstract

The interest in colloidal gold nanoparticles is still unabated. In 1857 Michael Faraday reported about his experiments with solutions of colloidal gold.[1] About 150 years later Brust et al. described how to stabilize such colloidal solutions with the help of thiols.[2] It took another 20 years until Kornberg et al. synthesized and characterized the huge metalloid gold cluster Au_{102}(*p*-MBA)$_{44}$ (*p*-MBA = *p*-mercaptobenzoic acid) via x-ray analysis.[3] Since then, a lot of such gold clusters stabilized by thioligands have been synthesized and characterized.[4]

We present the recently obtained metalloid gold clusters $Au_{108}S_{24}(PPh_3)_{16}$[5] (**1**) and $Au_{70}S_{20}(PPh_3)_{12}$[6] (**2**) (figure 1), which show significant differences from the yet described cluster compounds in this field of research.

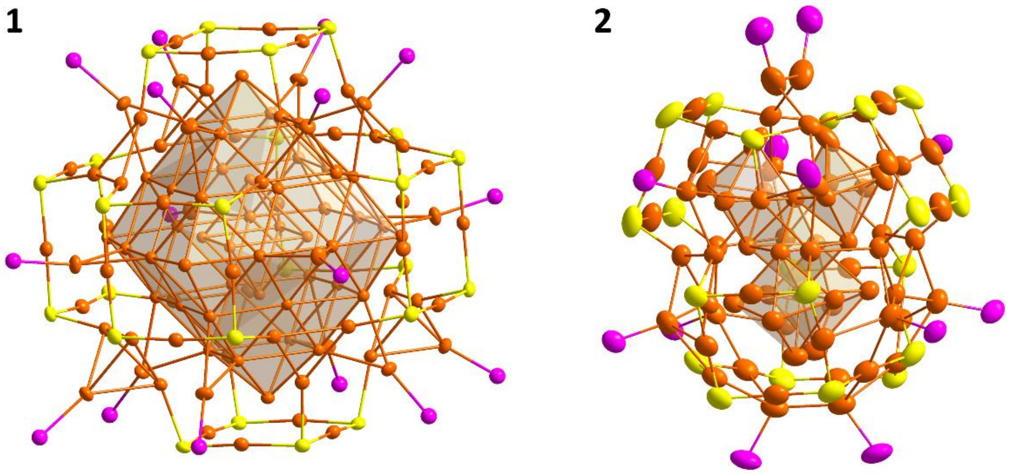

Figure. 1: Molecular structure of **1** and **2** in the solid state. All non-hydrogen atoms are shown with thermal ellipsoids set at 50 % probability. The phenyl groups are omitted for clarity. Au orange, S yellow, P violet.

1 and 2 show unknown structural motifs for big metalloid gold clusters and share some structural re-semblances. Both clusters can be described via a core-shell-structure. The shell consists of Au_4S_4 ring motifs and contains additional gold and sulphur atoms. However, the Au_4S_4 ring motifs are not distributed arbitrarily on the shell surface. They correspond with the symmetry of the core which leads to an octahedral arrangement in the case of 1 and a distorted tetrahedral arrangement in the case of 2. The cluster cores of 1 and 2 also show resemblances to the solid-state structure of elemental gold.

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$Ge_{14}Br_8(PEt_3)_4$: The first Subhalide Cluster of Germanium

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Abstract

Metalloid clusters are ideal model compounds to study the area between molecules and the solid state of the corresponding element.[1] There are different approaches to synthesize metalloid clusters. One of them is the disproportionation reaction of subhalides like E(I)X (E= Ge, Sn; X = Cl, Br), which are obtained via a preparative co-condensation reaction.[2] The halides are then substituted with bulky substituents to kinetically stabilize intermediates on the way to elemental Ge/Sn. Until now it was completely unknown by which unsubstituted intermediates such a disproportionation reaction of group 14 subhalides proceeds.

With $Ge_{14}Br_8(PEt_3)_4$ (**1**) we present the first structurally characterized subhalide cluster of germanium (Fig. 1). Starting from a Ge(I)Br solution in toluene/PEt_3, we obtain red distorted octahedral crystals of **1** after some workup procedures out of a thf extract. **1** is a binary halide cluster, which lies in between Ge(I)Br and elemental germanium and consequently provides insight into the complex mechanism of the disproportionation reaction. Quantum chemical calculations show, that within the cluster core a classical bonding situation is realized with only 2e-2c bonds.[3]

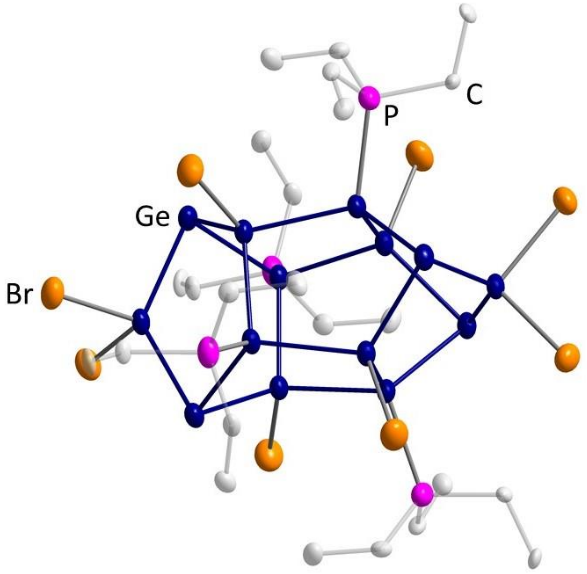

Figure 1: Molecular structure of **1** in the solid state. All non-hydrogen atoms are shown with thermal ellipsoids set to 50 % probability. The hydrogen atoms are omitted for clarity.

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Coordination polymers based on rhenium octahedral clusters $[Re_6Q_8(CN)_6]^{4-}$ and cationic complexes of Ln^{3+} and Bi^{3+}

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Abstract

In the last few decades there has been an intensive development of chemistry of coordination polymers. The most convenient and widespread route for obtaining coordination polymers is their self-assembly in a solution from pre-synthesized building blocks. Among a wide variety of building blocks potentially convenient for the synthesis of coordination polymers, there a wide class of cluster complexes of transition metals. In particular, octahedral cluster rhenium complexes $[Re_6Q_8(CN)_6]^{4-}$ (S, Se, Te) can serve as a building block for the synthesis of coordination polymers with different dimensionality. These clusters are the structural analogs of ferrocyanide $[Fe(CN)_6]^{4-}$, but with significantly larger volume. The presence of interesting physical properties of $[Re_6Q_8(CN)_6]^{4-}$ complexes such as an intensive red luminescence, as well as the possibility of reversible oxidation, accompanied by a change in color, magnetic properties and luminescence, make them interesting for obtaining of functional coordination polymers[1]. Here we report a series of coordination polymers based on cluster anions $[Re_6Q_8(CN)_6]^{4-/3-}$ and cationic complexes of Ln^{3+} and Bi^{3+} with various organic ligands. Among the compounds obtained both layered compounds and porous compound with framework structures are presented. A special attention will be paid to compounds with general formula $[\{Ln(H_2O)_3\}_2(L)Re_6Se_8(CN)_6]\cdot nH_2O$ (L = 2,5-furandicarboxylic acid, 2,5-thiophenedicarboxylic acid or 2,5-selenophenedicarboxylic acid). All compounds from this series demonstrate high CO_2/N_2 and CO_2/CH_4 selectivity, luminescence, paramagnetic behavior and capable to reversible oxidation with accompanied by changing of color, magnetic and optical properties[2].

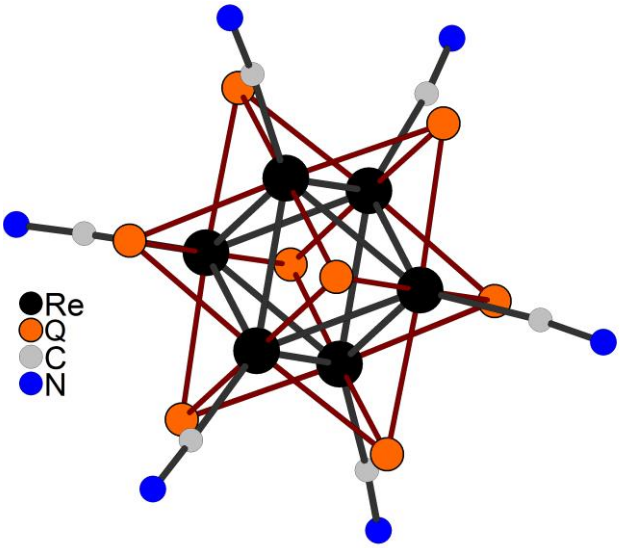

Figure 1: Structure of $[Re_6Q_8(CN)_6]^{4-}$ (Q = S, Se, Te).

Acknowledgements

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Snap-Shots of a Reduction Pathway: A journey through ternary lead chlorido tungstates by thermal scanning

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Abstract

Chemical reduction as part of a redox reaction is an important field of applied chemistry. Usually a reduction should be fast and most efficient. Generally, the reduction of tungsten hexachloride has been explored in many ways, departing from classical[1], and continuing with less-common reduction agents, such as elemental P[2,3] and Bi[4,5]. These elements are reported as reducing agents for the preparation of W_6Cl_{12}.[6] Recently, intermediate phases such as W_6PCl_{17} and $W_4(PCl)Cl_{10}$[3], or $(BiCl)[W_6Cl_{14}]$ and $(BiCl_2)[W_6Cl_{13}]$[5] have been shown to appear in these systems. Later on, a more essential approach of the progressive reduction has been studied for the reduction of WCl_6 with transition metal powders M = Mn[7], Fe[8,9], Co[10], Cu[11] based on the detection and characterization of intermediate phases by combined thermal scanning analysis (DSC, Fig. 1) and structural (XRD) characterization. Reactions in these systems appear quite complex due to a significant number of intermediate stages, of which some occur in a small temperature interval. Reactions with transition metals have revealed a unique pattern including a reductive intercalation (of transition metal) followed by an exsolution (of transition metal chloride). A characteristic feature of most structures is a closest packing of chloride ions, as already present in the structure of WCl_6, which in the process of reduction, is successively intercalated with transition metal ions under simultaneous clustering (reduction) of tungsten ions, forming binuclear, trigonal, and finally octahedral tungsten clusters.

Herein a detailed analysis of the reduction sequence of tungsten hexachloride with lead powder is presented. The aim of this investigation is to make our reduction studies more complete, by demonstrating a reduction sequence in which we use a metal which is not expected to occupy octahedral interstices of a closest packed halide arrangement, as has been obtained in the reduction with (3d) transition metals. Intermediate compounds along the way

of the reduction of W^{6+} to W^{2+} were detected, prepared by solid-state synthesis, and structurally characterized by X-ray diffraction techniques. Five new compounds, namely $Pb_{0.5}WCl_6$, PbW_2Cl_{10}, $Pb_{1.5}[W_3Cl_{13}]$, $Pb_2Cl[W_3Cl_{13}]$, and $Pb[W_6Cl_{14}]$ are discovered to be formed with increasing temperature, and structurally characterized within this study. The analysis of the reduction pathway is meant to get a higher understanding on the metallothermic reduction process and intercalation chemistry in solid state.

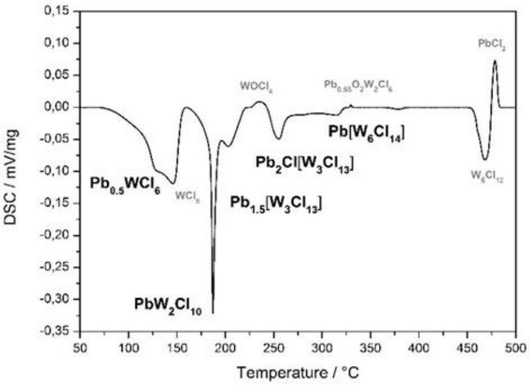

Figure 1. Thermal (DSC) effects (exothermic ↓ and endothermic ↑) obtained during the reduction of β-WCl_6 with lead powder.

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$Ge_6Fp_6Cl_2$ and Ge_6Fp_6 (Fp= $[Fe(C_5H_5)(CO)_2]$): Two cluster compounds of germanium stabilized by transition-metal based ligands

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Abstract

The synthesis of nanoscaled clusters of group 14 metals is a challenging task. However, such compounds are getting more and more interesting as the size of modules in computers is reaching the nanometer range. For the future, it will be very important to be able to synthesize nanoscale compounds with well-defined structures and properties. There are several synthetic routes used to synthesize cluster compounds of germanium in which in all cases sterically demanding ligands such as $-N(SiMe_3)_2$, $-Si(SiMe_3)_3$ or -2,6-$i$$Pr_2$-$C_6H_3$ play an important role in kinetic stabilization. In some cases transition-metal based ligands replace those silyl- or aryl-ligands. Huttner et al. were able to synthesize the octahedral cluster-compound $[Ge_6(Cr(CO)_5)_6]^{2-}$.[1] There are two examples for metalloid cluster compounds of germanium stabilized by transition-metal based ligands only by Schnepf et al..[2],[3] One of them, $[Ge_{12}Fp_8(Fe(C_5H_5)CO)_2]$, is already containing the Fp-ligand.

Here, we present the first neutral germanium-cage compound Ge_6Fp_6 (**1**) stabilized by transition-metal based ligands only and its twice oxidized form $Ge_6Fp_6Cl_2$ (**2**).

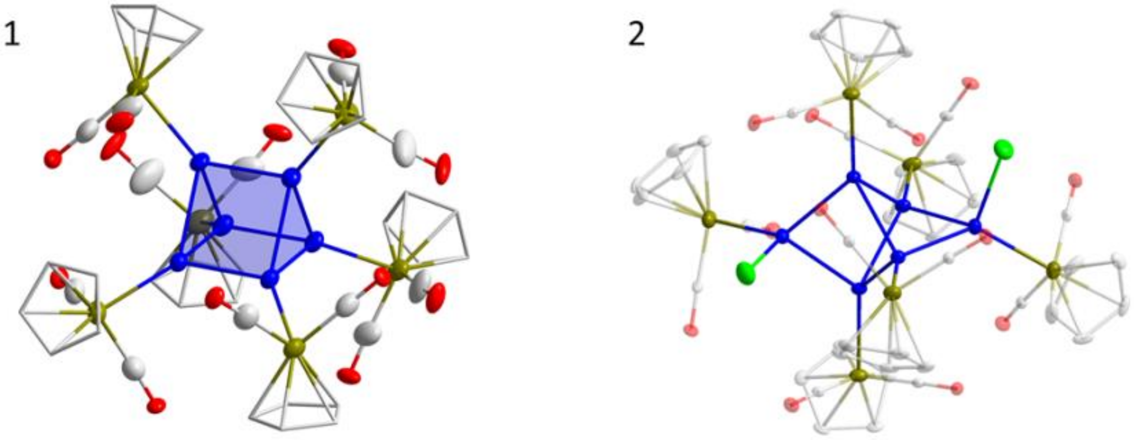

Figure 1: Molecular structure of **1** and **2** in the solid state. All non-hydrogen atoms are shown with thermal ellipsoid sets at 50 % probability. Ge blue, Fe gold, C grey, O red.

1 and **2** were obtained from the reaction of the alkali-metal salt KFp with $GeCl_2$·Dioxan. Both compounds show already known structure motifs.[4],[5] However, the special electronic properties of the Fp-ligand lead to slightly new arrangements of the germanium atoms in the cluster cores.

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Structural flexibility of Zn-SBU in $Zn_2(bdc)_2$DABCO

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Abstract

Breathable Metal Organic Frameworks (MOFs) are characterized by flexible (dynamic) behavior of the structure in response to external physical and chemical factors (temperature, pressure, mechanical and optical effects, etc.). The dynamic behavior of the MOFs includes the movement of organic and inorganic building blocks and the displacement of structural sublattices relative to each other. Nevertheless, the question about simultaneous existence of different isomorphic forms of building blocks in MOF structures remains open. The classic example is the Zn-DMOF ($Zn_2(bdc)_2$DABCO bdc=1,4-benzenedicarboxylate) which shows a remarkable degree of flexibility[1,2]. In Zn-DMOF, the structure of the DABCO molecule can be represented by three isomorphic structures, one of which has D_{3h} symmetry; two others are left and right-twisted conformers with D_3 symmetry [3]. Zinc based Secondary Building Unit (Zn-SBU = $\{Zn_2(O_2C\text{-})_4\}$) also has several isomorphic forms characterized by D_{4h}, D_{2D}, C_2 and D_4 (left and right twisted forms) symmetries. An interesting feature of the structural properties of Zn-DMOF is the existence of a weak splitting of structural positions for oxygen atoms in Zn-SBU above 130 K[1,2]. This splitting disappears as the temperature decreases because of the phase transition associated with the ordering of the bdc^{2-}[2]. However, the mechanism for the appearance of split positions for oxygen atoms remains unclear.

We showed that the structure of Zn-SBU can be represented by the simultaneous existence of an isomorphic form with symmetry D_{4h} and a conformer with symmetry D_4 in the study of non-periodic and periodic model systems. Therefore, the split positions of oxygen atoms in Zn-SBU are due to the existence of a conformer with the symmetry D_4 twisted to the left D_4(S) and to the right D_4(R).

Acknowledgements

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Polynuclear iodobismuthate complexes with I_2 linkers: crystal and electronic structure and properties

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Abstract

Complex bismuth (III) halides have a wide variety of anionic substructures and in combination with organic or inorganic cations form an ever-expanding family of compounds. In these compounds, the anionic substructures' assembling occurs as a result of $\{BiX_6\}$ octahedral sharing by vertex, edges or faces, resulting in polynuclear anions involving from 2 to 10 octahedra or one-dimensional infinite anionic chains. It is assumed that the nature of the cation is one of the fundamental factors affecting the process of the octahedral condensation and the final iodobismuthate anions nuclearity. However, among many other factors influencing the iodobismuthates anionic substructure organization is the interstitial Br_2 or I_2 molecules acting as bridges. In this case, Br_2/I_2 moieties combine Bi/X anions into extended architectures by alternating shorter covalent and longer secondary bonds [1].

Herein we report on the synthesis, crystal and electronic structure, and properties of several new bismuth polyiodides: $(NH_4)_7Bi_3I_{16}(I_2)_{0.5}\cdot4.5H_2O$, $K_{18}Bi_8I_{42}(I_2)_{0.5}\cdot14H_2O$, $[PDA(BiI_4)_2\cdot I_2]$ (PDA = phenylenediammonium, $[NH_3C_6H_4NH_3]^{2+}$) and $[(C_5NH_{10}OH)_3Bi_2I_9\cdot I_2]$ ($C_5NH_{10}OH$ = 3-hydroxypiperidinium) in which I_2 molecules serve as additional linkers for increasing the anionic substructure dimensionality. It is shown that in the presence of interstitial I_2 linkers the number of octahedra condensed in anionic substructures changes, and the possibility of combining several polynuclear fragments in the same crystal structure appears. The bonding within iodobismuthate clusters and interstitial I_2 moiety was analysed using electronic structure calculations.

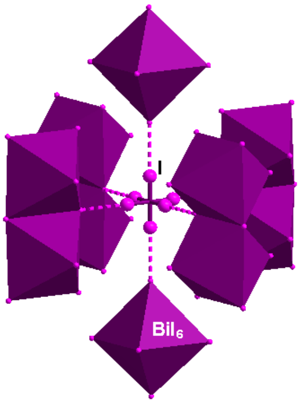

Figure. 1: A group of BiI_6 octahedra around I_2 units that have three alternative orientations in the crystal structure of $K_{18}Bi_8I_{42}(I_2)_{0.5}·14H_2O$

Acknowledgements

The research has been supported by the Russian Ministry of Education and Science, contract No. 378RFMEFI61316X0053 (14.613.21.0053).

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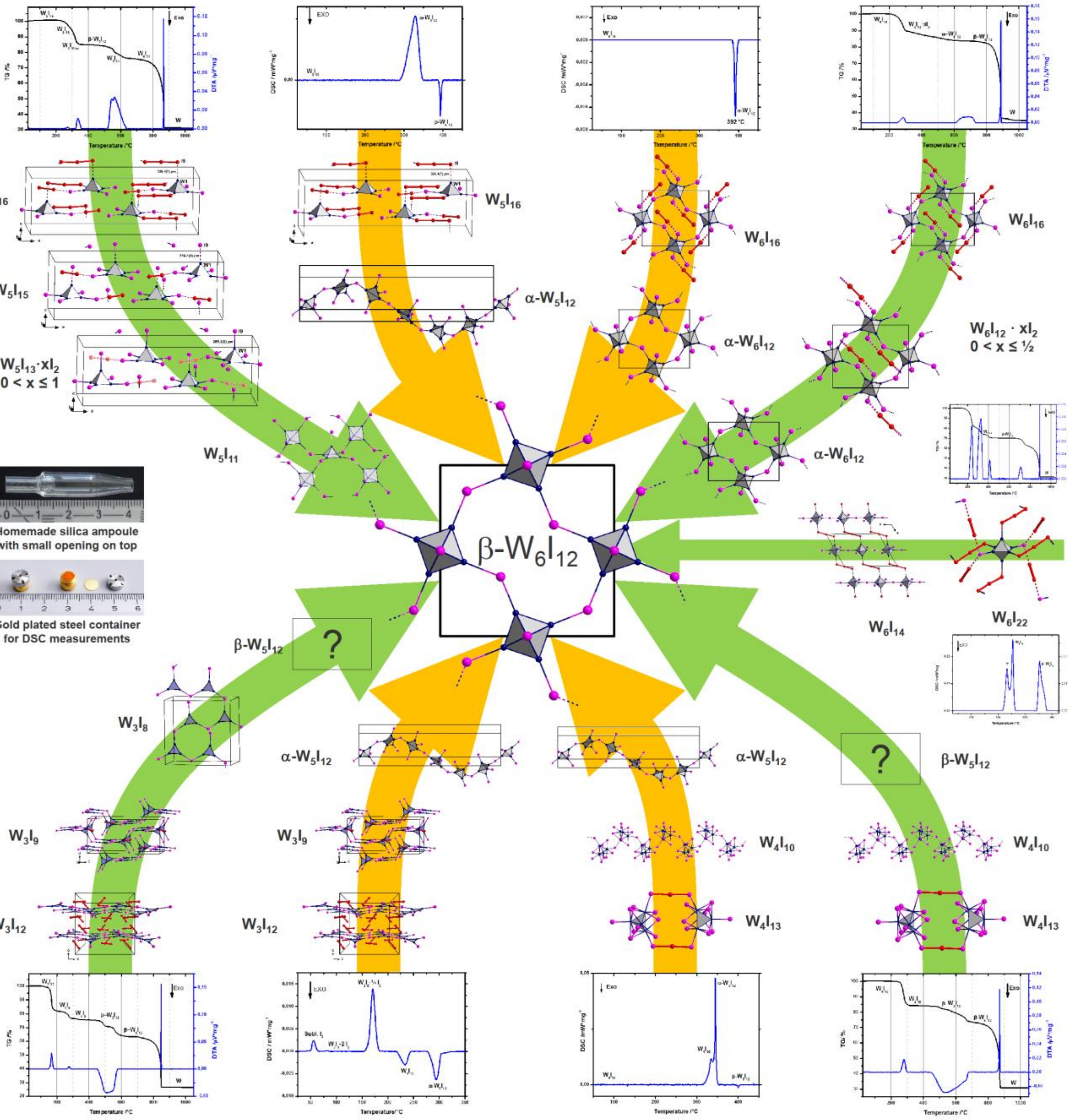
Pandora's Box of Tungsten Iodides: All reaction roads tend to β-W_6I_{12}

Recently a halide exchange reaction for the synthesis of tungsten iodides was developed by us[1]. The main product of this reaction, departing from WCl_6 with SiI_4, is $W_3I_8 \cdot 2I_2$. The discovery of this reaction opened Pandora´s Box of tungsten iodides and resulted in a plethora of new binary tungsten iodides. Thermal transformation reactions of tungsten iodides are strongly dependent on the (iodine) pressure in the system. Therefore, these reactions were investigated by means of DTA-TG measurements in home-made silica ampoules having a small opening on top allowing for low iodine pressures, and in sealed gold-plated DSC steel autoclaves for high iodine pressures (shown below on the left side). The most stable tungsten iodide showing up in all these reactions is β-W_6I_{12}, which is thermally stable up to around 850 °C before decomposing into elementary tungsten and iodine.



Homemade silica ampoule with small opening on top

Gold plated steel container for DSC measurements

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Tungsten Iodides shown: Review-Article: Pandora´s Box of Tungsten Iodides (In preparation)

DSC Measurements. Samples were enclosed into gold plated (5 µm) steel autoclaves (Volume 100 µl, BFT 94, Bächler Feintech AG, Switzerland, Figure 40) under dry argon atmosphere (glove box). Samples were heated and cooled with a rate of 2 °C/min in a differential scanning calorimeter (DSC 204 F1 Phoenix, Fa. Netzsch).

DTA/TG Measurements. Samples were filled into homemade SiO2 containers with a small (Ø 3 mm) opening on top of the container (Figure 41). Samples were heated and cooled with a rate of 2 °C/min with an argon flow of 120 ml/min in a differential thermal analysis system (STA 449F3 Jupiter, Fa. Netzsch).

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