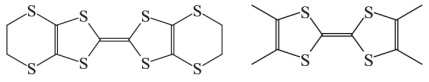
Chemical Physics, Chernogolovka, (Russia). [b]*N.S.Kurnakov Institute of General and Inorganic Chemistry, Moscow, (Russia).* [c]*A.N.Nesmeyanov Institute of Organoelement Compounds, Moscow, (Russia).* [d]*V.N.Karazin Kharkov National University, Kharkov, (Ukraine).* E-mail: koh@icp.ac.ru

Radical cation salts and charge transfer complexes based on tetrathiafulvalene (TTF) and their derivatives constitute a wide class of organic materials with transport properties ranging from insulating to superconducting. The iron group metal bis(1,2-dicarbollide) complexes $[3,3'\text{-M}(1,2\text{-}C_2B_9H_{11})_2]^-$ (M = Fe, Co, Ni) have been proposed as counterions for synthesis of new radical cation-based molecular materials. Substitution of hydrogen atoms in these complexes for various atoms and groups opens practically unlimited perspectives of their modification.

In this report we describe synthesis, crystal structure and electrical conductivity of tetrathiafulvalenium salts of iron bis(dicarbollide) anion $[3,3'\text{-Fe}(1,2\text{-}C_2B_9H_{10})_2]^-$: $(ET)_2[3,3'\text{-Fe}(1,2\text{-}C_2B_9H_{11})_2]$ (**1**) and $(TMTTF)[3,3'\text{-Fe}(1,2\text{-}C_2B_9H_{11})_2]$ (**2**).



The geometry of the $[3,3'\text{-Fe}(1,2\text{-}C_2B_9H_{10})_2]^-$ anion are similar in the salts. The dicarbollide ligands are mutually rotated by 180° producing *transoid* conformation (Fig. 1).

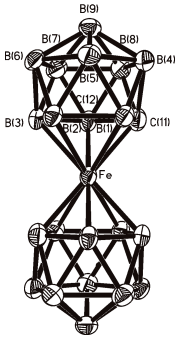


Fig. 1. $[3,3'\text{-Fe}(1,2\text{-}C_2B_9H_{10})_2]^-$ anion in (**1**). Hydrogen atoms omitted for clarity.

Both radical cation salts prepared were found to be semiconductors. The activation energy of (**1**), E_a, was found to be ~0.07 eV, the room temperature conductivity is 1.5×10^{-2} $\Omega^{-1}cm^{-1}$, whereas for (**2**) it is lower than 10^{-10} $\Omega^{-1}cm^{-1}$.

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Keywords: organic conductors, X-ray study, structure-property relationship

MS31.P14

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Crystal structure of human tyrosylprotein sulfotransferase

Yoshirou Kawaguchi,[a] Takamasa Teramoto,[a,b] Yukari Fujikawa,[a] Katsuhisa Kurogi,[c] Masayuki Soejima,[a] Rumi Adachi,[a] Yuichi Nakanishi,[b] Emi Mishiro-Sato,[c] Ming-Cheh Liu,[d] Yoichi Sakakibara,[c] Masahito Suiko,[c] Makoto Kimura,[a,b] Yoshimitsu Kakuta,[a,b] [a]*Laboratory of Structural Biology, Graduate School of Systems Life Sciences, Kyushu University, Hakozaki 6-10-1, Fukuoka 812-8581, (Japan).* [b]*Laboratory of Biochemistry, Department of Bioscience and Biotechnology, Graduate School, Faculty of Agriculture, Kyushu University, Hakozaki 6-10-1, Fukuoka 812-8581, (Japan).* [c]*Food Research Branch, Department of Biochemistry and Applied Biosciences, Faculty of Agriculture, University of Miyazaki, Miyazaki 889-2192, (Japan).* [d]*Department of Pharmacology, College of Pharmacy, The University of Toledo, Toledo, Ohio 43614, (USA).* E-mail: yoshiro1103@gmail.com

Post-translational protein modification by tyrosine sulfation plays an important role in extracellular protein-protein interactions, with implications in immune response, inflammation, hemostasis, and viral infection including that of the human immunodeficiency virus (HIV). The sulfation reaction is catalyzed by the Golgi enzyme called the tyrosylprotein sulfotransferase (TPST). Here we present the first crystal structure of the human TPST (hTPST) complexed with a substrate peptide and a degradation product of the sulfate donor, 3'-phosphoadenosine-5'-phosphosulfate (PAPS). At 1.9Å resolution, the structure shows that the bound substrate peptide forms an L-shaped structure and a short parallel β-sheet with a loop following the PAP-binding site. The central region of the substrate peptide that encompasses the acceptor tyrosine residue interacts specifically with several residues of hTPST2. The anchoring of the central region of the substrate peptide at a fixed distance from the 5'-phosphate of PAP underscores the selectivity of hTPST2 for tyrosine-containing peptide as a substrate. The structural information, in conjunction with the mutational analysis data, provides a molecular basis for substrate-binding and catalysis, and explains how TPST can accommodate a variety of substrate proteins.

Keywords: keyword-1 crystal structure, keyword-2 post-translation

MS31.P15

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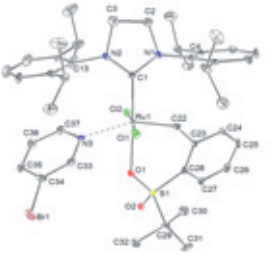
Additional ligand in the ru coordination sphere of hoveyda-type catalysts. Part II

Aleksandra Pazio,[a] Anna Makal,[a] Anna Szadkowska,[b] Karol Grela,[b] Krzysztof Woźniak[a] [a]*Department of Chemistry, University of Warsaw, (Poland).* [b]*Institute of Organic Chemistry, Polish Academy of Science, Warsaw, (Poland).* E-mail: apazio@chem.uw.edu.pl

We report new structures of sulphon and sulphoxide derivatives of a II generation Hoveyda-type catalyst [1]. This catalyst is a one of the most important and effective from all catalysts of the metathesis reaction [2].

Last year we reported, that water molecule was found in the ruthenium coordination sphere of some compounds [3]. This year we present the first structure of the sulphon derivative (Fig. 1), which was possible to obtain only due to the presence of another additional ligand: 3-bromopyridine [4]. We observe that the ruthenium atom is coordinated by oxygen from the sulphon group and thus a 6-membered ring is formed.

We also compare structures of the catalysts containing no additional molecules i.e. the catalyst with water and with 3-bromopyridine. It appears that the 3-bromopyridine moiety interacts with catalyst in the solution, which changes the colour of the solution. This also has a significant influence on the catalyst activity and determines the reaction rate at room temperature. Finally, it does



coordinate the Ru-atom during the crystallization of the product.

[1] (a) J.S. Kingsbury, J.P.A. Harrity, P.J. Bonitatebus, A.H. Hoveyda, *J. Am. Chem. Soc.* **1999**, *121*, 791. (b) S.B. Garber, J.S. Kingsbury, B.L. Gray, A.H. Hoveyda, *J. Am. Chem. Soc.* **2000**, *122*, 8168. (c) S. Gessler, S. Randl, S. Blechert, *Tetrahedron Lett*. **2000**, *41*, 9973. [2] IUPAC Gold Book http://goldbook.iupac.org/M03878.html [PAC, 1994, *66*, 1077 *(Glossary of terms used in physical organic chemistry (IUPAC Recommendations 1994))* on page 1139] (25.05.**2009**). [3] A. Szadkowska, A. Makal, K. Woźniak, R. Kadyrov, K. Grela, *Organometallics* **2009**, *28*, 2693. [4] A. Szadkowska, K. Zukowska, A. Pazio, K. Woźniak, R. Kadyrov, K. Grela, *Organometallics* **2011**, *30*, 1130–1138.

Keywords: crystal structure analysis, metalloorganic catalysts, metathesis

MS31.P16

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Aluminium hydroxide molecular derivatives. Stabilization and structural characterization

Mª Teresa Muñoz, Yamileth Kadir, Marta E. G. Mosquera, Tomás Cuenca, Carmen Urbaneja. *Inorganic Chemistry Department, Universidad de Alcalá, Alcalá de Henares, Madrid (Spain).* E-mail: martaeg.mosquera@uah.es

Group 13 elements attracts wide attention not only because of its rich chemistry, but also due to the important applications that those elements exhibit in areas as diverse as organic synthesis, electronic materials, structural materials and catalysis.[1] In particular, aluminium derivatives play an essential role in a vast array of catalytic reactions. As an example, aluminoxanes acting as co-catalysts constitute a key part in the Ziegler-Natta olefin polymerization processes being one of the more important activators in industrial processes.[2] As well, aluminium alkoxide complexes have shown to be very active catalysts in ring opening polymerization reactions.[3]

Aluminoxanes are derivatives of general formula [AlRO]n or [$R_2AlOAlR_2$], and can be considered as intermediates in the hydrolysis of organometallic aluminium compounds to aluminium oxide. It is possible to prepare them by the controlled reaction of aluminium alkyl derivatives with water or O-donor reactive species. [4]. Many controlled hydrolysis studies have been done and during these investigations some aluminoxane species could be isolated, by using bulkier groups than methyl [5]. However, none of these prepared species are co-catalysts as efficient as methylaluminoxane (MAO) for olefin polymerization. As such, design and synthesis of new aluminium derivatives able to behave as co-catalyst is still an open challenge.

In this context, we have prepared a series of alkyl and hydride derivatives of aluminium with functionalized aryloxide groups. We have carried out controlled hydrolysis on these species. These studies have allowed us to isolate new species such as the molecular hydroxide compound shown in figure 1.

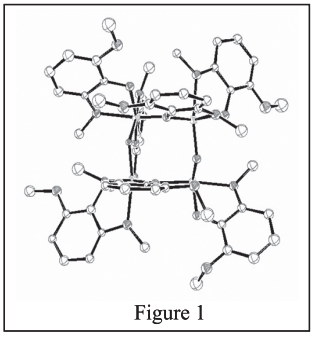

Figure 1

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Keywords: aluminum, catalysis, polymerization

MS31.P17

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Structural effects of amphiphilic dendritic organocatalysts in aldol reactions

Chui-Man Lo,[a,b] Hak-Fun Chow,[a] [a]*Department of Chemistry and Center of Novel Functional Molecules, The Chinese University of Hong Kong, Shatin, (Hong Kong SAR).* [b]*School of Science & Technology, The Open University of Hong Kong, 30 Good Shepherd Street, Homantin, Kowloon, (Hong Kong SAR).* E-mail: cmlo@ouhk.edu.hk

Three series of surfactant-like chiral amphiphilic dendritic organocatalysts containing an optically active polar proline-derived core and one or two nonpolar hydrocarbon dendrons were prepared. These dendritic organocatalysts were employed in the asymmetric aldol additions in oil-in-water emulsions to reveal the effects of dendron size and branching on the catalytic properties.[1] The incorporation of larger hydrophobic dendrons [2] has the advantages of promoting emulsion formation in water, improving the reaction enantioselectivity, decreasing catalyst loading (to 1 mol %), and facilitating catalyst recovery after the reactions.

Inside the hydrophobic pocket, the reaction proceeds in a concentrated organic phase generated by the organic substrates and the surfactant-like organocatalyst inside the emulsion droplets. The structural effects of the size and shape of the surfactant appendages were found to have different results on the micelle formation efficiency and the catalyst properties in the asymmetric aldol reactions. In general, the larger dendrons tended to lower catalyst reactivity due to their increasing steric blocking effect. However, some astonishing observations were found in some of the G1 and G2 dendritic organocatalysts, wherein an increase in the steric bulkiness and branching of the dendron resulted in better catalyst reactivity. It was also found that higher product yields and enantioselectivities were obtained in the aldol reactions when the aromatic aldehyde contains an electron-withdrawing substituent.

The catalysts could be recycled and reused five times in the asymmetric aldol reactions without significant drop in product yields and enantioselectivities. In addition, cross product contamination was not found when the recovered G3 catalyst was subsequently used in another reaction involving different substrates.