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Nitrogenase: Mechanism and ApplicationsMarkus W. Ribbe¹

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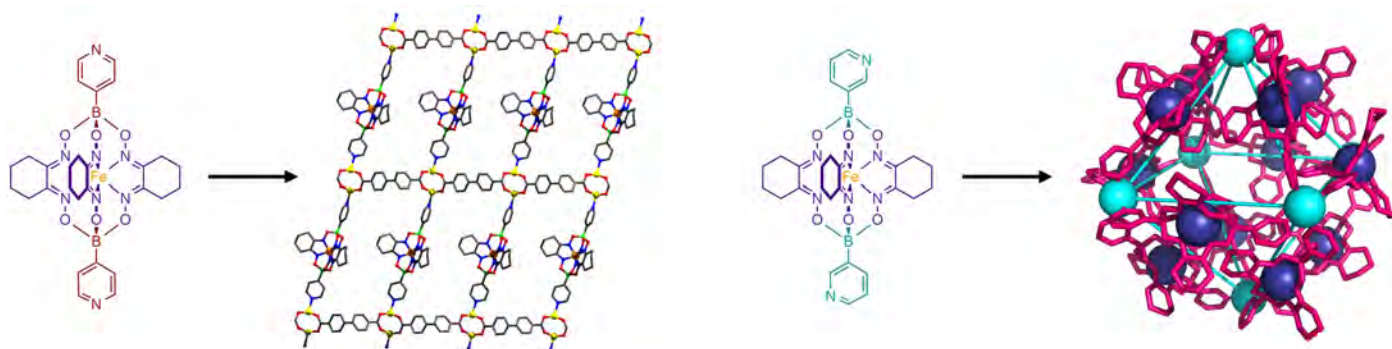
Nitrogenase is highly complex in structure and uniquely versatile in function. It is capable of catalyzing two reactions that parallel two important industrial processes: the reduction of nitrogen (N_2) to ammonia (NH_3), which parallels the Haber-Bosch process in ammonia production; and the reduction of carbon monoxide (CO) to hydrocarbons (C1-C4 alkanes and alkenes), which parallels the Fischer-Tropsch process in carbon fuel production. Despite decades of dedicated research, the biosynthetic and catalytic mechanisms of nitrogenase have remained elusive, largely due to the complexity of the metal centers within this enzyme. Taking a combined genetic, biochemical, spectroscopic and structural approach, we have made progress in piecing together the biosynthetic pathway of nitrogenase, as well as in identifying homologous systems for mechanistic studies of this enzyme. These developments not only afford a better understanding of how nitrogenase is assembled into a functional unit, but also provide a useful platform for future design of nitrogenase-based applications.

Functionalised Clathrochelate Complexes - New Building Blocks for New Supramolecular Structures

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The structure and function of a supramolecular assembly is determined by the building blocks from which it is derived. Consequently, control over the steric, functional and geometric characteristics of these building blocks is an imperative aspect of supramolecular chemistry.¹ We have developed a new family of building blocks based upon boronic acid-capped tris(dioxime) iron(II) clathrochelate complexes and shown these complexes to be extremely versatile scaffolds for the preparation of long, rigid bipyridyl ligands. The length, steric bulk and co-ordination vectors of these metalloligands can be modulated simply by changing the commercial starting materials from which they are synthesised. Clathrochelate-based metalloligands up to 5.4 nm in length and bearing 4-pyridyl groups were initially prepared, and the potential for these complexes as supramolecular building blocks was unveiled through their incorporation into a molecular square and a 3D coordination polymer.² Subsequently, clathrochelate complexes capped by 3-pyridyl groups, in combination with square planar Pd²⁺ ions, were employed in the preparation of octahedral cage compounds.³ The structure-directing role played by the clathrochelate itself is instrumental in this remarkable self-assembly process and enables a single, entropically disfavoured, unprecedented structure to be obtained from an inherently unpredictable 3,3'-bipyridyl building block.



[1] R. Chakrabarty, P. S. Mukherjee, P. J. Stang, *Chem. Rev.*, **2011**, 111, 6810.

[2] M. D. Wise, A. Ruggi, M. Pascu, R. Scopelliti and K. Severin, *Chem. Sci.*, **2013**, 4, 1658.

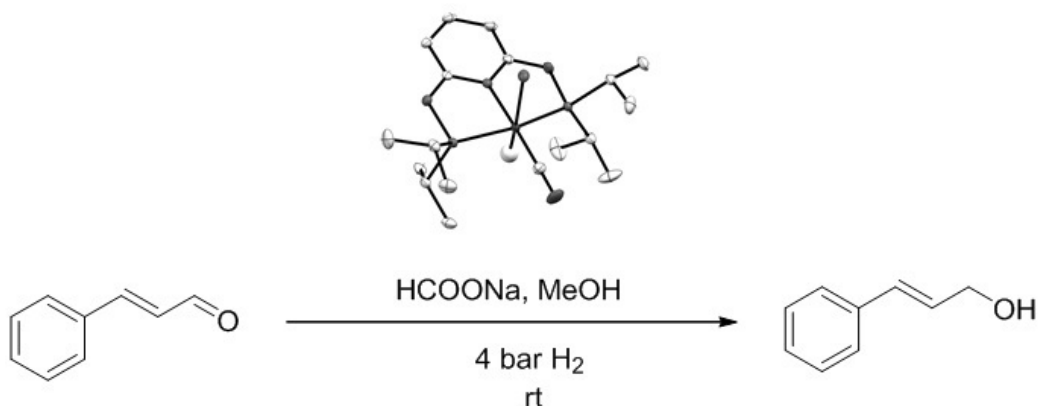
[3] *Manuscript in preparation*

Iron Catalysts for Hydrogenation of Aldehydes: an Alternative to Precious Noble Metals

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Two new and structurally characterized iron-hydride complexes bearing the tridentate PONOP^[1,2] pincer ligand [*i*PrPONOP)FeH(CO)Br] and [*i*PrPONOP)FeH(CO)(CH₃CN)](OTf) are presented. Interestingly, we found that these complexes show high reactivity in the H₂ cleavage and they are efficient catalysts for the homogeneous H₂ hydrogenation of aldehydes in very high yields (up to 95%)^[3,4]. The hydrogenation reactions take place under very mild conditions using only 4 bar of hydrogen pressure and at ambient temperature.



Remarkably, our catalytic systems show a broad functional-group tolerance and a great chemoselectivity towards aldehydes ^[5]. When α,β -unsaturated aldehydes were used as substrates the reduction of the carbonyl group occurred yielding the corresponding allylic alcohols as the only products.

Synthesis, Structure and Reactivity of a Ruthenium Complex with an Unusual P_4Cl_2 Ligand

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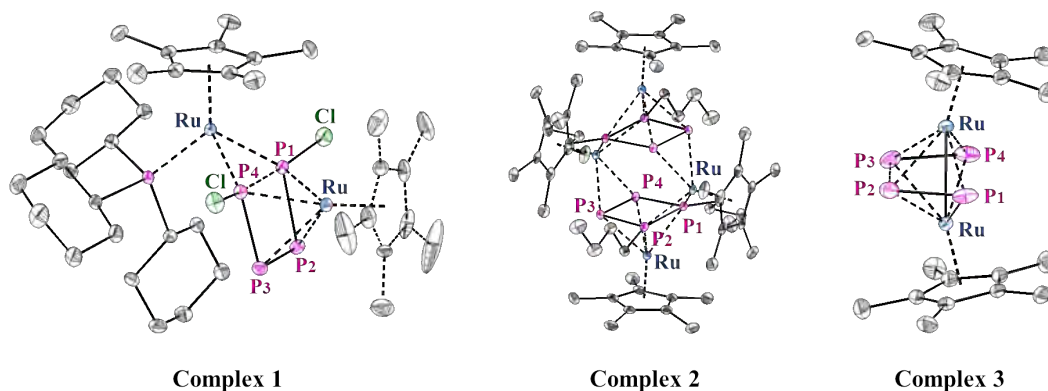
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The need to develop more sustainable routes to convert elemental phosphorus into organophosphorus compounds lead to a widespread interest in the coordination chemistry and transition metal mediated activation of P_4 .^[1] Upon reaction with a transition metal, the tetrahedral P_4 can coordinate as an intact P_4 tetrahedron or rearrange to a P_4 unit of different geometry.

Reacting the unsaturated complex $[RuClCp^*PCy_3]$ where $Cp^* = CpMe_5$, with P_4 , we could isolate a new bimetallic complex of the structure $[RuCp^*(PCy_3)(\mu_2, \eta^{2:4}-P_4Cl_2)RuCp^*]$ (**1**) in 84% yield. Two bonds of the P_4 tetrahedron have been broken and it has been oxidatively inserted into a Ru-Cl bond, resulting in a coordinated planar, dianionic P_4Cl_2 ligand, which has no precedence. The structure shows identical lengths for three of the four P-P bonds, so that the ligand is best described as a butadienyl-like structure, in which the delocalisation of the π -electrons leads to an equilibration of the bond lengths.

The P_4Cl_2 ligand opens up new routes to metal-coordinated organophosphorus compounds, which has been demonstrated by reacting **1** with *n*-butyllithium. This forms the tetrametallic complex $[RuCp^*(\mu_3, \eta^{2:2:4}-P_4^{\eta}Bu_2)RuCp^*]_2$ (**2**), in which the coplanar P_4 units each bear two *n*-butyl groups.

In the presence of magnesium, **1** is quantitatively reduced to a complex of the structure $[RuCp^*(\mu_2, \eta^{2:2}-P_2)_2RuCp^*]$ (**3**), which possesses a Ru-Ru bond and a planar P_4 ligand with an unusual geometry between two $RuCp^*$ units. The structure of the complex as well as the ^{31}P low temperature and solid state NMR spectra bolstered by results from computations including an AIM analysis suggest that the ligand is best described as two weakly bound μ_2, η^2-P_2 units.



[1] (a) M. Peruzzini, L. Gonsalvi, A. Romerosa, *Chem. Soc. Rev.* **2005**, 34, 1038; (b) B. M. Cossairt, N. A. Piro, C. C. Cummins, *Chem. Rev.* **2010**, 110, 4164.

Supported alkene metathesis catalysts: from reaction intermediates to structure activity relationship

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Advances in homogeneous olefin metathesis catalysts in the last 30 years have transformed the way in which a large number of organic molecules are prepared. However, improvements of current heterogeneous catalysts have been relatively limited, since there is a poor understanding of the active sites and reaction intermediates in these systems. Moreover, observation of reaction intermediates would constitute an important step towards a molecular understanding of these systems.

Here we show that the advantages of homogeneous and heterogeneous catalysts can be combined through the controlled functionalization of surfaces via a molecular approach. Using this strategy, we have been able to generate a new series of well-defined silica supported W-based catalysts, based on $^{\circ}\text{SiOW}(=\text{NAr})(=\text{CHR})(\text{X})$ moieties.

We have here focused our approach towards the development of a structure activity relationship for this series, evaluating the influence of both the imido group and the X ligands on the alkene metathesis activity. Among several characterization of these complexes, the observation of metallacyclobutane reaction intermediates with trigonal bipyramid (TBP) and square-based pyramid (SP) geometries in the series allowed probing the σ -donation of the X ligands in situ and establishing structure-activity relationship by relating them to their respective activity.¹ We have identified the relation between the σ -donation of the X ligands and the electronic properties of the imido group required to obtain good catalysts. This approach allowed the generation of highly efficient catalysts with a detailed understanding of the surface sites and reaction intermediates.

The synthesis, detailed characterization of the surface species through advanced spectroscopic methods (solid-state NMR, XAS) and the catalytic properties of these catalysts will be presented.

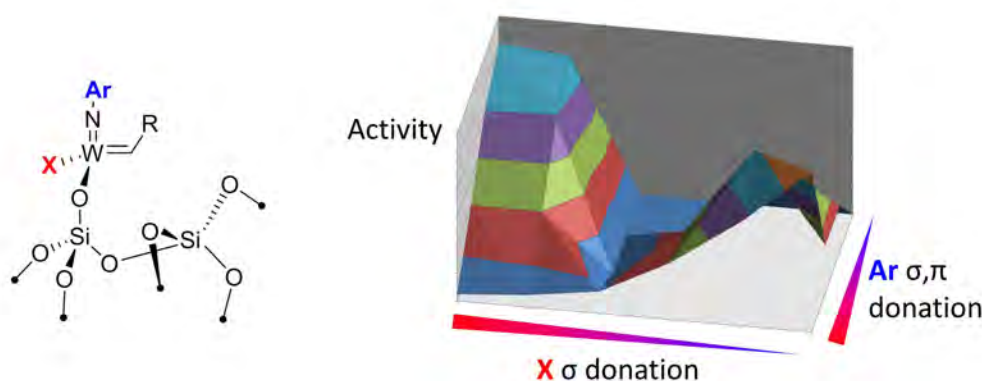


Figure 1. Influence of electronic properties of Ar groups and X ligands on the alkene metathesis activity.

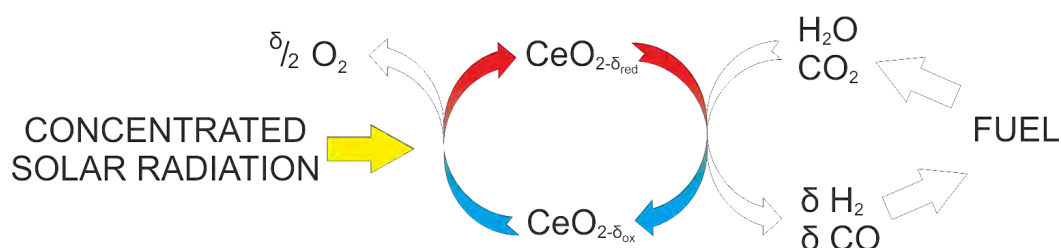
(1) Mougel, V.; Copéret, C. *Chem. Sci.* **2014**, 5, 2475-2481.

Performance and in situ characterization of ceria-based non-stoichiometric oxides for the conversion of solar energy using two-step thermochemical cycles

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Thermochemical cycles driven by concentrated solar radiation as source of high temperature heat are promising processes for the conversion of solar energy and its storage in chemical bonds [1]. Oxygen storage materials such as ceria-based nonstoichiometric oxides are of great interest as reactive intermediates for the production of H₂ from H₂O and/or CO from CO₂ in a two-step redox cycle (figure 1). Typical temperatures are 1773 K for the reduction step and 1073 K for the oxidation step.



For improved energy efficiency, a redox material that provides a higher non-stoichiometry δ at higher pressure and lower temperatures than pure ceria is needed [2]. Introducing dopants into the fluorite-type ceria lattice strongly affects thermodynamic properties, the kinetics of the oxidation step as well as the stability and recyclability of the resulting redox materials. The water-splitting performance of Hf and Cr doped materials was measured in a comparative study.

To determine structural changes that occur under the extreme conditions in a solar thermochemical reactor, in situ XAS measurements were performed from RT to 1773.

The quantitative determination of the electronic structure of Ce and dopants provides insight into the relation between structure and solar fuel production.

[1] Chueh W.C., Falter C., Abbott M., Scipio D., Furler P., Haile S.M., Steinfeld, A. Science 2010, 330 1797-801.

[2] Ermanoski, I., Miller, J. E., Allendorf, M. D. Physical Chemistry Chemical Physics (2014), 16, 8418-8427.

The surprising lability of homoleptic and heteroleptic bis-(2,2':6',2''-terpyridine) chromium(III) complexes

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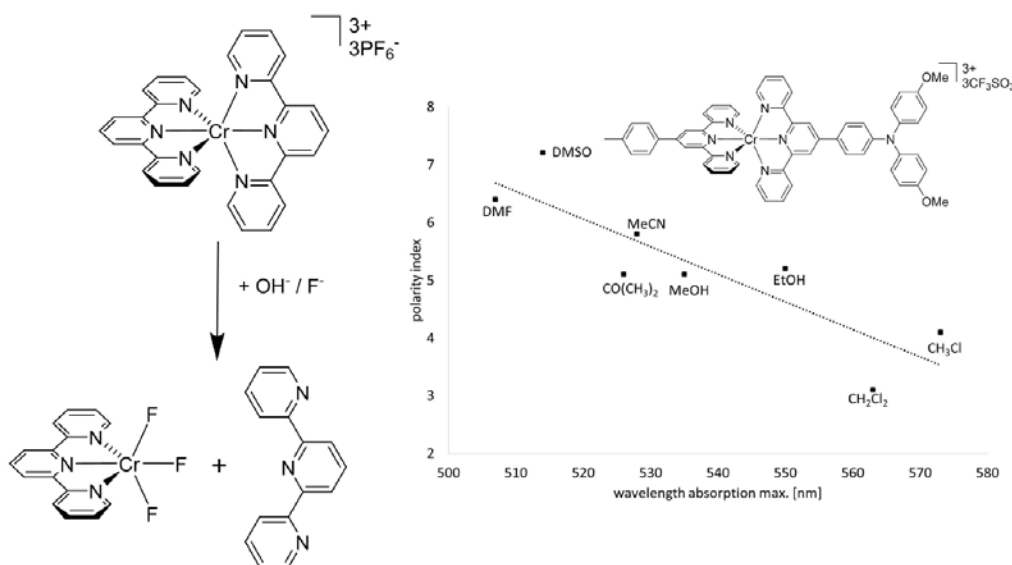
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Since chromium is relatively abundant in the Earth's crust and therefore also cheap, bis-(2,2':6',2''-terpyridine) chromium(III) complexes could be an alternative to scarce metals like ruthenium or iridium for DSC (Dye-sensitized Solar Cell) or LEC (Light Emitting Electrochemical Cell) applications.

We present a new strategy for the synthesis of a series of ionic homoleptic and heteroleptic bis-(2,2':6',2''-terpyridine) chromium(III) complexes. 2,2':6',2''-Terpyridines (= tpy) and derivatives thereof act as tridentate ligands. The heteroleptic complexes could be confirmed by X-ray structures.^[1]

The described complexes are substantially unstable in a basic environment and in the presence of fluoride anions, despite chromium(III) usually being considered to be kinetically inert. This decay can be monitored by a decolouration of the solution and the residue could be determined as $[\text{Cr}(\text{tpy})(\text{X})_3]$ ($\text{X} = \text{OH}^-$ or F^-) and free ligand (figure left).^[1]

Complexes with the 4-([2,2':6',2''-terpyridin]-4'-yl)-N,N-diphenylaniline ligand tend to show a negative solvatochromic effect, where the colour of the solutions varies from red to purple (figure right).



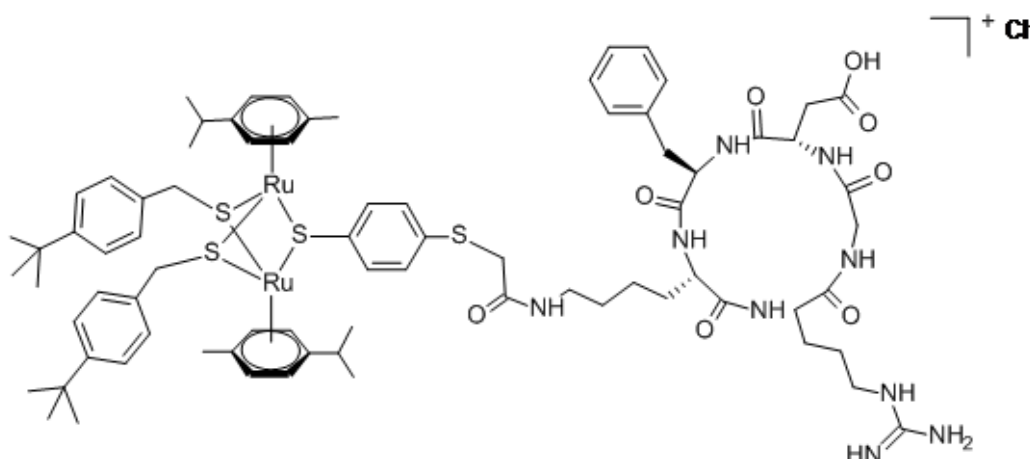
[1] Edwin C. Constable, Catherine E. Housecroft, Markus Neuburger, Jonas Schönle, Jennifer A. Zampese, *Dalton Trans.*, **2014**, 7227–7235.

Peptide Conjugates of Dinuclear Arene Ruthenium Trithiolato Complexes

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We have recently synthesized series of highly cytotoxic thiophenolato-bridged dinuclear *p*-cymene ruthenium complexes of the general formula $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr}^i)_2\text{Ru}_2(\text{SR})_3]^+$ (R being an aliphatic or aromatic substituent), the IC₅₀ values being in the nanomolar range [1]. However, the *in vitro* selectivity between healthy and cancer cells remains low, which could be related to their limited solubility in physiological media.



In order to improve the *in vitro* selectivity towards cancer cells, a new series of ruthenium complexes was obtained by appending selected peptides to one of the thiol groups. The synthesis, characterization and their *in vitro* cytotoxicity towards ovarian cancer cell lines will be presented. The complexes were obtained by conjugating two different thiolato-bridged *p*-cymene Ru-complexes and three selected polypeptides: octaarginine, which is known for its ability to penetrate cell membranes [2], octalysine, and one cyclo-pentapeptide, cyclo-[Lys~Arg~Gly~Asp~Phe], which has been reported to selectively target the $\alpha_v\beta_3$ integrin, overexpressed in many types of cancer cells [3].

[1] Federico Giannini, Julien Furrer, Anne-Flore Ibao, Georg Süss-Fink, Bruno Therrien, Olivier Zava, Mathurin Baquie, Paul J. Dyson, Peter Štěpnicka, *J. Biol. Inorg. Chem.*, **2012**, 17, 951-960.

[2] Swati Biswas, Pranali P. Deshpande, Federico Perche, Namita S. Dodwadkar, Shailendra D. Sane, Vladimir P. Torchilin, *Cancer Letters*, **2013**, 335, 191-200.

[3] Min H. Lee, Jin Y. Kim, Ji H. Han, Sankarprasad Bhuniya, Jonathan L. Sessler, Chulhun Kang, Jong S. Kim, *J. Am. Chem. Soc.*, **2012**, 134, 12668-12674.

Antimicrobial metal-containing Schiff base complexes

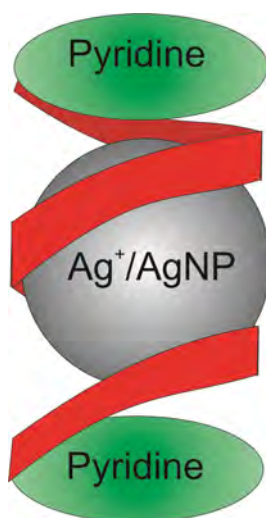
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Schiff base complexes were widely studied due to their catalytic properties in various fields^[1] and partly for their biological activity^[2]. The utilisation of copper (II)^[3] and silver (I)^[4] can introduce antimicrobial properties to these structures or enhance them. That way, new fields of applications are provided, like in medicine. Compared to classical *Schiff* bases, the synthesis of dual *N,N*-donor *Schiff* bases is facile too, and the resulting products contain several coordination sides for diverse metal ions.

Applying these unique advantages, we developed several non-toxic and antibacterial *Schiff* base metal complexes. Our ligand systems are based on functionalized pyridine end-capped imine linker units which differ in the nature of the linker chain, such as ethylene glycols or alkyl chains (*Figure 1*). Substitution on the pyridine rings offer the possibility to attach oligomers or polymer chains which can work e.g. as handles. By applying, for example, mechanical force, like ultra-sonication, the metal ions can be released by an external trigger and used for catalysis or in medicine, where its antimicrobial properties are required.

Figure 1: General structure of the utilized *Schiff* base complexes.



[1] K. C. Gupta, A. K. Sutar, *Coord. Chem. Rev.*, **2008**, 252, 1420.

[2] J. McGinley et al.; *Polyhedron*, **2013**, 55, 169.

[3] J. O`Gorman, H. Humphreys, *Journal of Hospital Infection*, **2012**, 81, 217.

[4] S. Eckhard, P. S. Brunetto, J. Gagnon, M. Priebe, B. Giese, K. M. Fromm, *Chem. Rev.*, **2013**, 113, 4708.

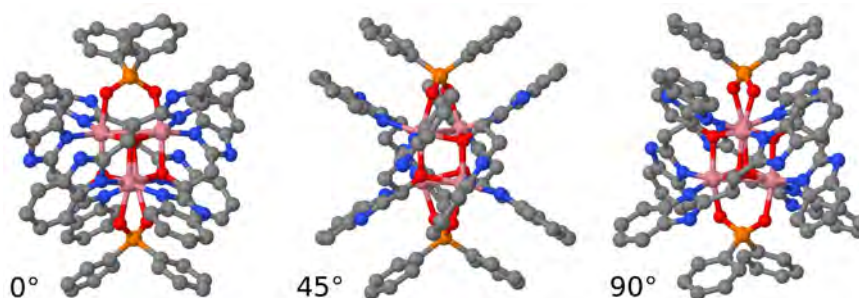
Aspects of the vibrational optical activity (VOA) of tetranuclear Cobalt transition metal complexes

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Chiral transition metal complexes have played a crucial role in the fields of electronic optical activity spectroscopy and rapidly gained interest also in their vibrational homologues. Vibrational optical activity (VOA) provides detailed structural information of chiral molecules, clusters and nanoparticles. The advantage for vibrational circular dichroism (VCD) and Raman optical activity (ROA) is the enhancement of the very weak optical activity signals through the coupling of the strong electronic with the weak vibrational magnetic-dipole moments¹. Apart from this aspect, the high symmetry of transition metal complexes facilitates the analysis of the underlying vibrational behavior. The usually strong colors of these nano-objects, on the other hand, represent an obstacle for ROA measurements when the wavelength of the exciting light is in the visible domain.

We spectroscopically investigated tetranuclear Cobalt quadruple helicates² with two achiral and four chiral ligands by VCD and ROA. Strong enhancement of the optical activity has been observed. The detected bands in the spectra have been theoretically explored with the aim to distinguish between their origin from the overall structural chirality and intrinsic chirality of the ligands. In both cases, VCD and ROA, the calculated intensities arise from a combination of vibrational and electronic molecular properties. To have profound, yet user-friendly insight into these calculated quantities we used PyVib2³.



[1] Nafie, L. a. (2011). *Vibrational Optical Activity*. Chichester, UK: John Wiley Sons, Ltd.

[2] Deville, C., Spyratou, A., Aguirre-Etcheverry, P., Besnard, C., Williams, A. F. (2012). Enantioselective synthesis of tetranuclear quadruple helicates. *Inorganic chemistry*, 51(16), 8667-9.

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X-ray structures of an octameric RNA duplex in the presence of six different divalent and trivalent metal ions reveal a particular innersphere binding to O4 of uracil

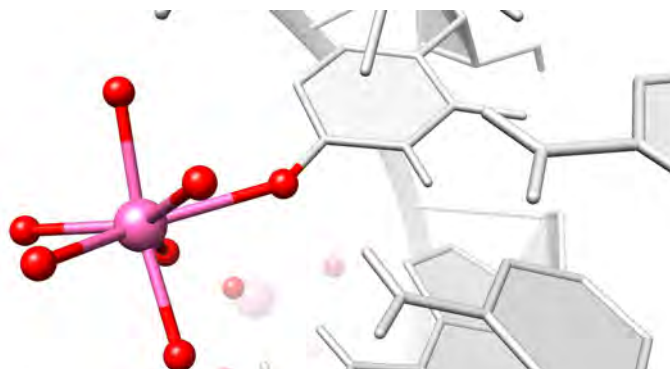
Michelle F. Schaffer¹, Joachim Schnabl¹, Bernhard Spingler¹, Guanya Peng², Vincent Olieric², Roland K.O. Sigel¹ *

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The principle of charge neutralization and electrostatic condensation require cations to overwhelm the repulsive forces of the negatively charged backbone of RNA to adopt its three-dimensional structure [1, 2]. A precise structural knowledge of RNA-metal ion interaction is crucial to understand the role of metal ions in the catalytic or regulatory activity of RNA [1, 3]. In our study we use an octameric RNA duplex as a model system to investigate the coordination of various metal ions to specific binding sites and to understand the interactions between metal ions and RNA.

We solved the crystal structure of six octameric RNA duplexes in the presence of different di- and trivalent metal ions and could carefully assign the positions of the metal ions by considering different parameters.

The results reveal the strong influence of cations to induce a more compact RNA structure. Beside several other specific metal ion binding sites, two prevalent positions were characterized in the investigated octameric RNA structures. One is located at the phosphate backbone; the second cation is in the centre of the RNA, interacting by a particular innersphere binding to O4 of uracil in presence of calcium (II), cobalt (II) and copper (II).



Financial support by the ERC, the Swiss National Science Foundation and the University of Zurich is gratefully acknowledged.

[1] R. K. O. Sigel, *Eur. J. Inorg. Chem.* **2005**, 2281-2292.

[2] E. Freisinger and R. K. O. Sigel, *Coord. Chem. Rev.* **2007**, 251, 1834-1851.

[3] A. M. Pyle, *J. Biol. Inorg. Chem.* **2002**, 7, 679-690.