

Spin-crossover and π - π stacking in heteroleptic Fe(II) complexes functionalised with alkyl chains

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A series of neutral Fe(II) complexes based on the ligand 2,2'-dipyridyl-N-C_n-amide (L-C_n) (where C_n = 4-18) of formula trans-[Fe(L-C_n)₂(NCX)₂].solvate, where X = S (1C_n) and Se (2C_n), have been synthesised and characterised structurally and magnetically. Single crystal X-ray diffraction measurements reveal a low-spin Fe(II) atom at the centre of the complexes in 1C₄, 1C₁₀ and 2C₁₀ at 100 K consistent with typical Fe-N bond lengths around 2.00 Å. All other complexes were high-spin at 100 K with Fe-N bond lengths of around 2.20 Å. In the solid state π ··· π interactions between adjacent pyridyl groups of neighbouring complexes result in the formation of 1D chains, with the π ··· π contact distances increasing slightly as alkyl chain length increases. Magnetic susceptibility measurements reveal a semi-abrupt, quasi-two-stepped spin transition between 75-175 K in 1C₄. Variable temperature crystallographic studies show that the orthorhombic *Pna*2₁ space group remains throughout the spin-crossover event and is accompanied by an increase in the Fe-N bond lengths and unit cell volume as temperature increases.

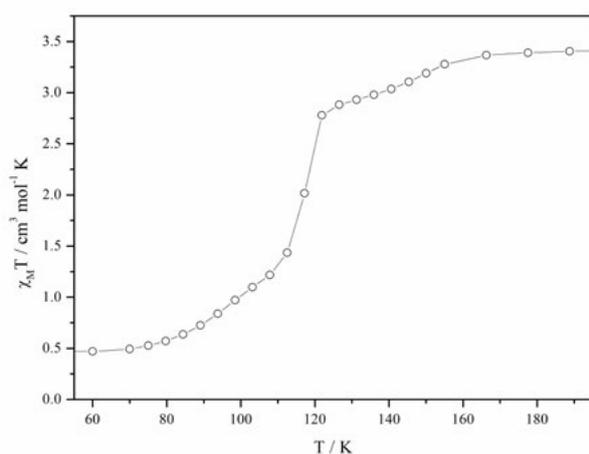


Fig. 1 Variable temperature magnetic susceptibility data for 1C₄ in an applied DC field of 0.5 T. Data were collected in Settle mode at a rate of 10 K min⁻¹.

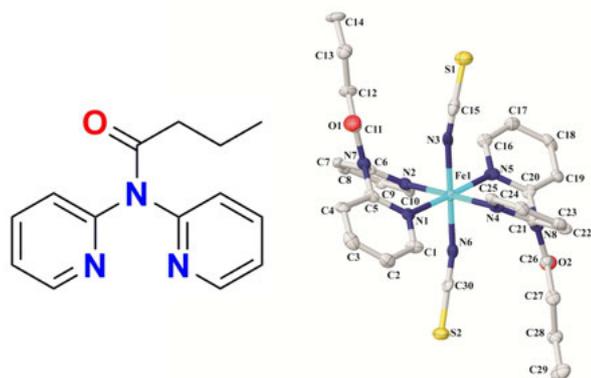


Fig. 2 Schematic drawing of the ligand L-C₄ (left) and asymmetric unit of 1C₄ with numbering scheme (right). Ellipsoids are at 50% probability. Legend: iron; turquoise, nitrogen; blue, oxygen; red, sulphur; yellow, carbon; grey. Hydrogen atoms omitted for clarity.

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A mixed-ligand coordination cage expands a family of luminescent chemical reactors

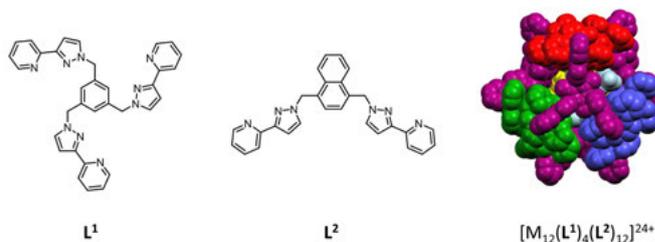
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The Ward group recently reported one of the best-characterised examples of catalysis in a synthetic cavity, whereby a hollow metal/ligand coordination cage facilitates very fast reaction of a guest molecule (bound in the central cavity) with anions that accumulate around the cage surface.¹

The role of the cage in bringing together the two reaction partners into close proximity is crucial; the propensity of particular guests for binding in our cubic cage $[M_8L_{12}]^{16+}$ ($M = \text{Co(II)}$ and Cd(II) , volume ca. 400 \AA^3) can be accurately predicted using GOLD protein-ligand docking software.² Guests and substrates encapsulated so far show shape and chemical complementarity with the cage interior. They have also been constrained by Rebek's 55% rule – an empirical observation that optimum guest binding occurs where the host cavity is approximately half-filled.³

In order to broaden the scope of guests and substrates applicable for investigation inside our coordination cages we have been trying to expand the family of ligands and topologies used in cage construction. This poster presents an exciting new member of the cage family in which two ligands L^1 and L^2 combine with Co(II) or Cd(II) to preferentially form a dodecanuclear cuboctahedral mixed-ligand cage. The new cage $[M_{12}(L^1)_4(L^2)_{12}]^{24+}$ encapsulates a volume of ca. 1000 \AA^3 and presents a very different interior surface to the smaller cubic cage. The luminescent properties of the naphthyl spacer in L^2 lend themselves to exploitation of cage-guest energy and electron transfer processes as observed in previous cage systems.⁴



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Metal-Organic Framework Glasses: A New, 4th Category of Melt Quenched Glass

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Metal-organic frameworks (MOFs) are a family of chemically diverse materials, consisting of inorganic nodes or ions linked by organic ligands. They have applications in a wide range of fields, covering engineering, physics, chemistry, biology and medicine. Until recently, research has focused almost entirely on crystalline structures, with over 60,000 structures now known. However, now a clear trend is emerging, shifting the emphasis onto disordered states, including 'defective by design' crystals, as well as amorphous phases such as glasses.

We have recently shown a subset of metal-organic frameworks (MOFs), called zeolitic imidazolate frameworks (ZIFs), to melt, and quenching of the resultant liquids forms a new category of glass.¹ Several structures (e.g. ZIF-4 [Zn(C₃H₃N₂)₂]) melt between 400 and 600 °C, and the glasses obtained upon cooling retain the short-range order (i.e. local bonding under 6 Å) present in their crystalline counterparts.²

Here, we introduce the concept of a **liquid metal-organic framework**,³ and explore the mechanism of melting of ZIF-4, via *in-situ* pair distribution function measurements and associated Reverse Monte-Carlo modelling, coupled with density functional theory based molecular dynamics calculations. We show that melting proceeds with significant structural retention, due to breakage of only part of the metal coordination sphere. The structure of the liquid phase is characterized, as is the mechanism of vitrification upon cooling. The atomic configuration obtained bears striking similarities to that for *a*SiO₂.

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De Novo Design And Characterization Of A Protein Binding An Abiotic Tetranuclear Zinc Cluster

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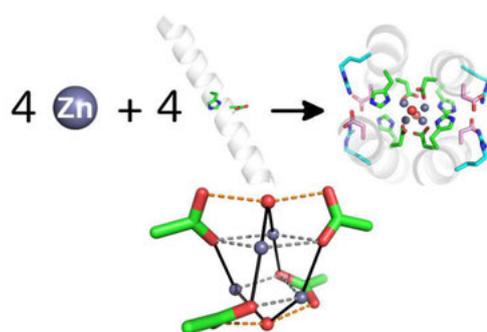
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The protein matrix finely tunes metal cofactor geometry and reactivity, despite the limited number of ligands.^[1] *De novo* protein design is particularly appealing in gaining new insights on the concurring interactions providing specific functions.^[2] While there has been considerable progress in designing proteins that bind mononuclear as well as multinuclear metal cofactors,^[3-5] the design of tetranuclear clusters with oxygen-rich environments has not been accomplished. Here, we describe our recent work on the design, structural and spectroscopic characterization of tetra-Zn²⁺ carboxylate-bridged clusters. The distorted cube-like structure is deeply inserted into the hydrophobic core of a four-helix bundle scaffold, and largely stabilized by a fully connected hydrogen-bonded network, unprecedented in protein design, consisting of 16 polar side chains. By varying the metal-bridging and the interfacial residues in the bundle, we show that subtle changes (in the order of few angstroms) have a great impact on the coordination geometry, as well as oligomeric state and stability. The crystal structures of the first four analogues confirm the validity of the design process in two cases, and define general rules for subsequent designs.^[6] Three of these newly designed proteins have been fully characterized by CD and NMR spectroscopies. Solution studies strongly suggest that the desired structure is achieved also in the *apo* state, providing evidence that the peptide is able to actively impart the designed geometry to the metal cluster.^[7]

In perspective, such abiotic tetra-Zn²⁺ cluster will be adopted as catalyst for both complex transesterification, and hydrolysis reactions.^[8] It may also constitute the basis for the construction of the first *de novo* designed oxygen evolving complex, by replacing zinc with designated redox-active metals.



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Exploring reactivity and anticancer properties of cyclopentadienone iron(0) N-heterocyclic carbene-amino complexes.

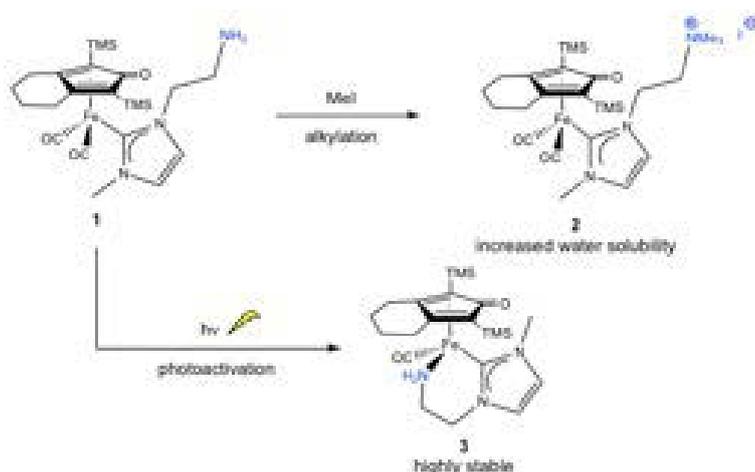
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Recently, we have communicated the synthesis of new carbonyl iron(0) complexes combining different non-innocent ligands, such as cyclopentadienones (CpO) and N-heterocyclic carbenes (NHC). [1] Within the application of those complexes in bio-inorganic chemistry, we herein report on the insertion of a terminal amino group on the lateral chain of the NHC (**1** in Scheme 1). This functional group, by varying the solubility of such iron compounds in water, made them candidates as antitumoral agents. Indeed, they display high activity against AsPC1 cells, at a level equal to carboplatin. [2] Furthermore the photochemical properties of **1** and **2** complexes were investigated, showing in the case of **1** the photoactivated release of one CO ligand actually favoured by the chelating coordination of the terminal amine to the iron centre. Addition of a quaternary amine instead of a neutral amino group enhances the solubility in aqueous solution, although to the detriment of antitumoral performance.



Scheme 1.

The present research has been developed with the contribution of PRIN 2015 20154X9ATP_003.

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Synthesis and characterisation of a copper(II) complex with 2-phenyl-imidazole-4,5-dicarboxylic acid - a surprising violation of apicophilicity.

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A copper (II) complex was formed with 2-phenyl-imidazole-4,5-dicarboxylic acid (2-Ph-HImDC). The ligand was synthesised as per literature [1] which involved the nitration of D-tartaric acid followed by reaction with excess ammonia and benzaldehyde. Equimolar amounts of the ligand and copper (II) sulfate were dissolved in N,N-dimethyl formamide (DMF) and water, respectively. The solutions were then combined and the resultant precipitate was recrystallized from DMF. The crystal structures of both the ligand and the complex were obtained, revealing an unexpected arrangement of the atoms of the complex, in that the electronegative oxygen atoms were found to be in an equatorial position around the central copper atom rather than in the axial positions. The compounds were further analysed by NMR, UV and IR spectroscopy.

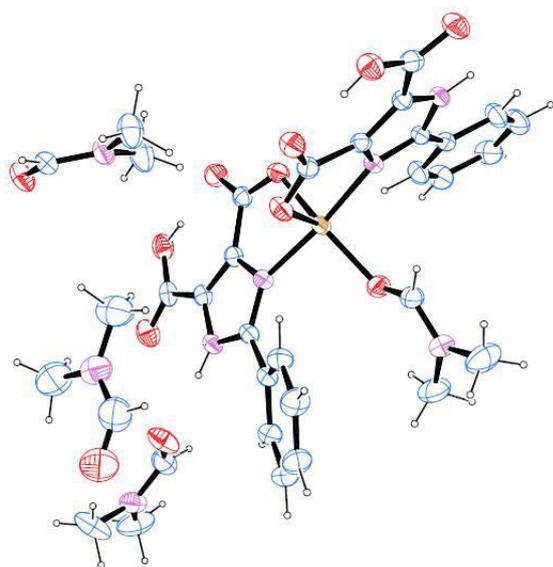


Figure 1: ORTEP plot of the Cu(II) 2-Ph-HImDC complex.

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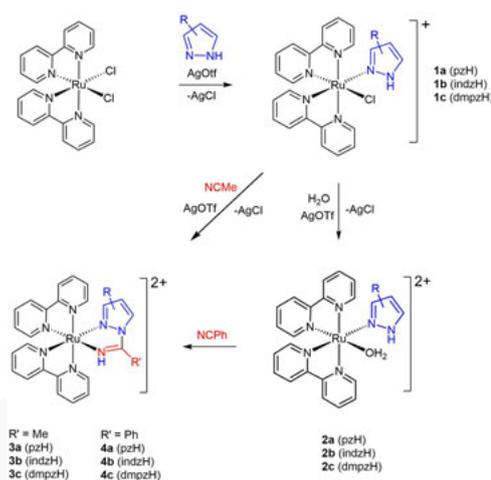
Luminescent bis(bipyridyl)ruthenium(II) complexes with pyrazolamidino ligands: photophysical and electrochemical studies

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The luminescence of d^6 $[\text{Ru}(\text{bipy})_2(\text{diimine})]^{2+}$ complexes is related to their long-lived triplet metal-to-ligand charge transfer ($^3\text{MLCT}$) excited state, and has allowed to develop many and diverse applications for them. The presence of an acidic hydrogen in the diimine ligand may give rise to particularly interesting PCET processes, or might also afford fascinating supramolecular assemblies. One of the diimine ligands meeting these requirements are pyrazolamidino ligands, and this report describes the first bis(bipyridyl)ruthenium(II) complexes $[\text{Ru}(\text{bipy})_2(\text{NH}=\text{C}(\text{R})\text{pz}^*-\kappa^2\text{N},\text{N})](\text{OTf})_2$ ($\text{R} = \text{Me}, \text{Ph}$; $\text{pz}^* = \text{pz}, \text{indz}, \text{dmpz}$), which are synthesized via chloride abstraction from $[\text{Ru}(\text{bipy})_2\text{Cl}(\text{pz}^*\text{H})](\text{OTf})$, after a subsequent base-catalyzed coupling of the appropriate nitrile with the pyrazole previously coordinated (Scheme 1). All the compounds have been characterized by ^1H , ^{13}C and ^{15}N NMR, IR and by monocrystal X-Ray diffraction. Photophysical and electrochemical studies have been carried out on both the pyrazolamidinocomplexes and their precursors. The photophysical data support the phosphorescence of the pyrazolamidino complexes. The electrochemical study reveals reversible $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ oxidations for all pyrazolamidino complexes between 1.13 and 1.25 (vs. SCE).



Scheme 1. Syntheses of the new pyrazolamidino complexes.

Surprising Discoveries on the Way to an Old Compound: Four Transient Iodido Antimonates

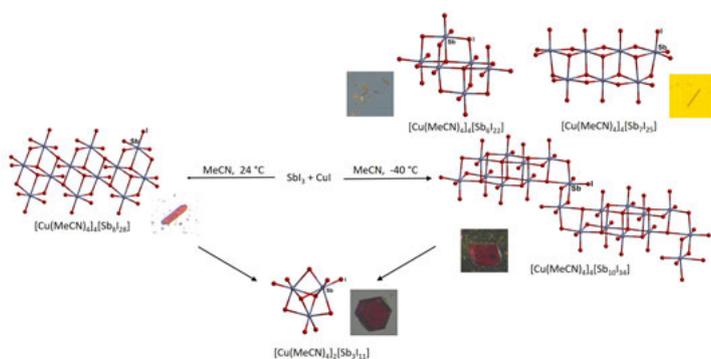
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Our group focuses on the synthesis of new iodidoantimonates and –bismuthates. These compounds show a great structural variety, with four, five or sixfold coordination at the central metal atom. Especially the antimonates tend to form complex anionic motifs with a high degree of condensation.^[1]

Attempting to reproduce a literature known synthesis, we could recently find four transient iodidoantimonates, crystallizing prior to $[\text{Cu}(\text{MeCN})_4]_2[\text{Sb}_3\text{I}_{11}]$, a compound reported nearly 30 years ago.^[2] All four compounds possess anionic motifs that are unknown for the compound class of halogenidoantimonates.

The compounds form within hours or days and dissolve entirely in the mother liquor subsequently.^[3] This phenomena has not been described for iodidopentelates yet. It emphasizes the structural variety of the material class and the chance to clarify fundamental formation processes via *in situ* methods.



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Binary and Ternary Organotin Sulfide Clusters with Extreme Optical Nonlinearity

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Tetrelchalcogenide clusters featuring organic ligands have attracted increasing attention during recent years due to their intriguing chemical and physical properties.^[1] The organic ligands influence their optical properties as well as their reactivity towards molecules and surfaces.^[2] Recent investigations on organotin chalcogenide clusters $[(R\text{Sn})_4\text{S}_6]$ featuring an adamantane-like topology have demonstrated extreme optical nonlinearity, allowing for either strong second harmonic generation or white light emission when driven by an IR laser diode.^[3]

Reactions of binary organotin chalcogenide clusters with coinage metal complexes yield ternary clusters that allow for fine-tuning of the optoelectronic properties by extension of the inorganic core.^[4] The reaction of $[(\text{PhSn})_4\text{S}_6]$ with AuCl and excess PMe_3 , for instance, leads to the formation of an adamantane-type cluster with one phenyl moiety being replaced by an $[\text{Au}(\text{PMe}_3)_3]$ fragment, thus under formation of a tin-gold bond.

In a similar fashion, by reaction of $[(\text{PhSn})_4\text{S}_6]$ with the molybdenum complex $[\text{Mo}(\text{CO})_3\text{CpCl}]$ the adamantane core can be expanded by a $[(\text{CpMo})_3\text{S}_3\text{Cl}]$ cage that reminds of a very small section of the MoS_2 layer structure.

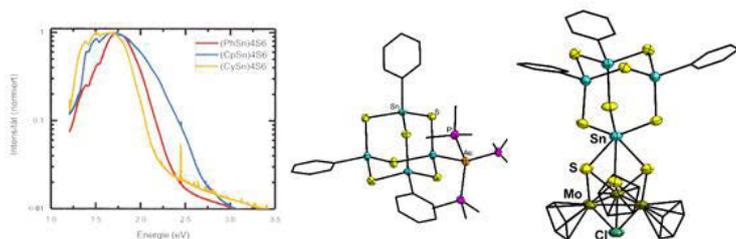


Figure 1: Left: Emission spectra of $[(R\text{Sn})_4\text{S}_6]$ ($R=\text{Ph}, \text{Cy}, \text{Cp}$) for an excitation wavelength of 980 nm. Center: Molecular structure of $[(\text{PhSn})_3(\{\text{Me}_3\text{P}\}_3\text{AuSn})\text{S}_6]$. Right: Molecular structure of $[(\text{PhSn})_3\text{S}_6\text{Sn}(\{\text{CpMo}\}_3\text{S}_3\text{Cl})]$.

Future studies aim at further variation of organic substituents, tetrel and chalcogen elements to get a better understanding of the mechanism causing the optical nonlinearity as well as investigating potential applications, for example in data storage.

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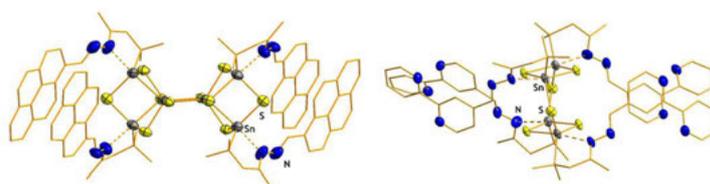
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Modification of the organic functionalization of tin sulfide clusters and their interaction with transition metals

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A large variety of organotin sulfide clusters were synthesized and investigated with regard to their characteristics during the last years.^[1] Directed derivatization of the organic ligands that are attached to the cluster allows the introduction of further functionalities that affect the physical properties of the cluster and their reactivity towards complementarily functionalized molecules. By reaction of functional binary clusters with organic molecules of complementary reactivity, hetero- and polyaromatic ligands that lead to interesting optical properties can be attached.^[2] Recent work led to the attachment of smaller polyaromatic and heteropolyaromatic ligands by utilizing their hydrazine derivatives.^[3] Current investigations aim at the attachment of extended polyaromatic groups and of chelating ligands to the binary clusters. The π -aromatic systems of organic ligands have shown to significantly influence the optoelectronic properties of the compounds.^[4] Moreover, the attachment of polyaromatic ligands will allow for interaction of the compounds with solid surfaces.^[5] The attached chelating ligands may serve to trap transition metal atoms or complex fragments from solution, as has been shown by our most recent results that will be presented herein.



Molecular structures of pyrene-functionalized (left) or 4-(hydrazonomethyl)-2,2'-bipyridine-terminated (right) tin sulfide clusters with [Sn₆S₆] or [Sn₄S₄] core, respectively.

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Tetraphosphonate Cavitands as Ligands for Metal Coordination

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Supramolecular cages and capsules based on supramolecular building blocks have been widely studied and found application in many fields, including mimic biological systems,¹ catalysis,² gas adsorption and storage.³ Coordination driven self-assembly offers the possibility of reticulating these systems in 3D structures, yielding porous MOF-like functional materials.⁴ Most of structures reported so far lack internal binding sites for specific complexation. Tetra-phosphonate cavitands provide a pre-organized cavity delimited by 4 P=O bridges pointing inward the cavity. P=O bridges act as interaction sites as they hydrogen bond to guests.⁵ Along this line of research, we functionalized tetra-phosphonate cavitands with chelating moieties and studied their coordination ability to different metals. The moieties chosen were pyridines and hydroxyls. Pyridine are good coordinating groups to Zinc and Copper, while hydroxyls can complex Lanthanum and Barium. Synthesis was achieved in 4 steps in both cases, starting from readily available resorcinarene. Complexes were characterized in solution by NMR studies and in the solid state by single crystal XRD (Figure 1). Moreover, guest binding was investigated in solution, by NMR titration.

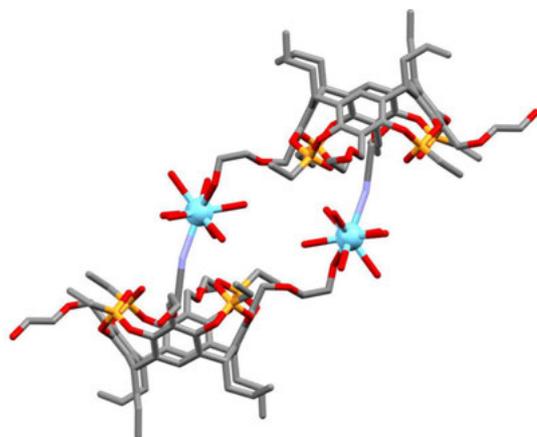


Figure 1. Structure of the dimer obtained when OH-functionalized Tiii and La (cyan) are reacted in ACN.

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f-Element Complexes of hybrid Schiff-base/Calix[4]arene Ligands: Synthesis, Structures and Properties

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The host-guest chemistry of calix[4]arenes has been well-investigated over the past several decades.[1] The ease of functionalization and versatile complexation properties along with unique three-dimensional structures has also aroused considerable attention in the field of coordination chemistry.[2] To modify the coordination behavior of the parent calix[4]arenes, derivatives with up to four dangling ligand arms at the lower rim have been synthesized.[3] Recently, we have investigated the coordination behavior of calix[4]arene-based ligands exhibiting dangling phosphonate ester and picolinamide groups positions towards a series of lanthanide ions.[4,5] We have now focused our attention on calix[4]arene ligands carrying Schiff bases as dangling units at the lower rim.[6] A series of monofunctionalized compounds of the general type 1 has been synthesized. Herein, we report on the synthesis of these ligands and demonstrate their ability to act as effective supporting ligands for dinuclear lanthanide complexes.

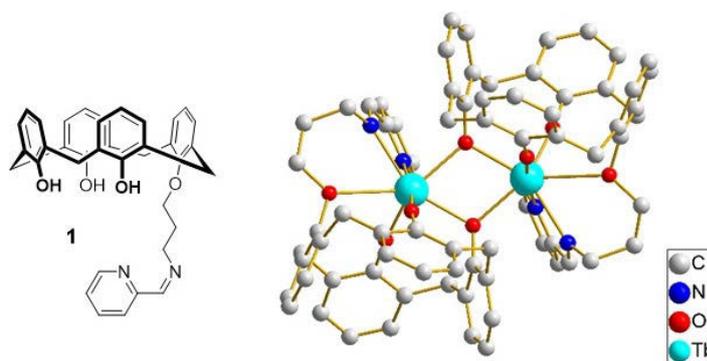


fig. 1: Structure of ligand **1** and its corresponding terbium(III) complex.

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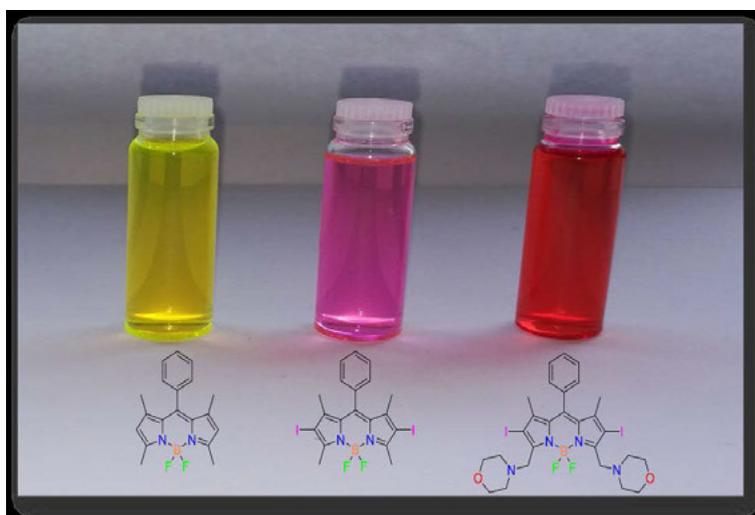
Morpholino-Substituted BODIPY Species: Synthesis, Structure and Electrochemical Studies.

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Functionalization of boron-dipyrrin (BODIPY) chromophores at (2,6-positions) by halogen substituents affords molecules with strong absorbance in the visible spectrum and remarkable electronic properties.¹ We have investigated the halogenation and subsequent reactions of BODIPY species which are methylated in the 3,5-positions. The use of an excess of the halogenating reagent leads to selective halogenation of the α -methyl groups, which can be post-functionalized *via* nucleophilic substitution with morpholine, allowing the investigation of the effect of the combination of halogen atoms and non-conjugated tertiary amine substitution. The effect of such substitution on the solid-state arrangements, absorption, fluorescence, and electronic properties of these dye molecules is reported. The spectroscopic and spectroelectrochemical measurements display intense absorptions, bathochromic shift, a positive shift in redox potentials, due to improved electron donation to the BODIPY core from the methylene and morpholino groups and fluorescence quenching due to the presence of the amine functionality.



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Investigations into the Syntheses and Analysis of Ruthenium-Based Photoactive Porous Materials

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Multifunctional materials that respond to the stimulus of visible light is an ever-growing area of materials chemistry. Compounds of interest include metal organic frameworks (MOFs) which have become increasingly popular in recent years. These frameworks have shown many uses, but interest to us is their potential to incorporate light harvesting properties and catalysis into a single material. This allows for the conversion of solar light energy into chemical energy in a single platform, through an artificial photosynthetic route. Inspired by current research on MOFs, we have created a series of metal organometallic frameworks (MOMFs), where the organic ligand is replaced by a photoactive organometallic complex.

To achieve this, we have successfully synthesised and characterised a library of ruthenium-terpyridine complexes for their incorporation into MOMFs. These complexes have been successfully characterised using UV-Vis, cyclic voltammetry, IR, ^1H - and ^{13}C -NMR. These complexes are of varying length to alter the pore sizes and contain a series of different terminal groups to alter the chemical and topological properties of the materials. These complexes have been combined with zinc acetate to identify an ideal synthetic procedure for MOMFs. Initial studies of synthetic procedures using thiolated functional groups have been studied using IR, showing the presence of the metalloligand in the structure. However, porosimetry measurements have concluded that the material is not porous. Further studies will be presented with other functional groups and metals with a combination of IR, UV-vis, porosimetry and x-ray diffraction data.

Towards preventing interparticle ligand exchange on gold nanoclusters

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Nanoparticles have attracted significant attention over the last several decades for their potential uses in directed biological, catalytic, and material applications. The ability to fine-tune these compounds by incorporating dopants into the metal core and functionalizing the surface ligand layer has especially shown promise for their development.^{1,2} In recent work, however, nanoparticles have shown a propensity to continuously undergo alterations by interchanging both surface ligands as well as metal atoms with other nanoparticles.^{3,4} This phenomenon raises new, unsolved challenges for developing nanoparticles with predictable long-term properties. We seek to address this problem in this work by probing the impact of ligand characteristics such as multidenticity, structural rigidity, and binding motif on interparticle ligand exchange processes in gold nanoclusters. By investigating these aspects of the surface ligand monolayer, we aim to facilitate the production of nanoparticle-based materials that exhibit long-term stability.

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Structure and crystal field considerations of Eu(III) nitrates in solution using luminescence spectroscopy and total x-ray scattering

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Understanding the coordination chemistry and structure of lanthanide ions in solution is an essential step for developing improved methods for selective rare-earth extraction as well as nuclear fuel recycling.¹⁻² It is well established that the photophysical properties of the **f-f** transitions unique to these ions is strongly dependent on coordination sphere and complex symmetry.³⁻⁴ Furthermore, it has been proved that total x-ray scattering can be used to probe the solution structure of heavy elements.⁵⁻⁶ Therefore we chose to examine the properties and structure of Eu(III) in methanol as solvate and as complexes with nitrate. The structure of $[\text{Ln}(\text{NO}_3)_x]^{3-x}$ complexes is highly relevant to rare earth separation and nuclear fuel recycling⁷. By using steady-state and time-resolved luminescence spectroscopy we are able to identify changes in symmetry, determine the number of solvent molecules (**q**)⁸ associated to the Eu(III) ion, and to probe the crystal field. The optical data are supported by structural changes observed by total x-ray scattering. Total scattering reveals that Eu-N distances replace Eu-C and hint that the coordination geometry shifts between a tricapped trigonal prism and a capped square antiprism.

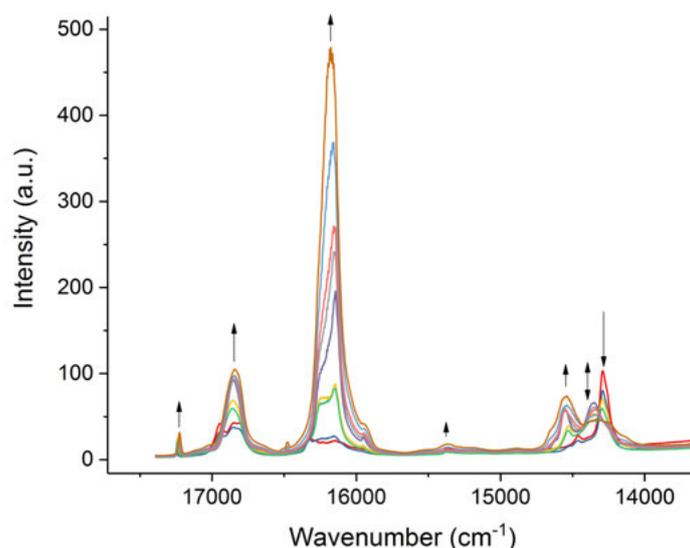


Figure 1. Emission spectra of Eu(III) in methanol with increasing concentrations of LiNO_3

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Novel series of $3d-3d'-4f$ -complexes on a basis of organometallic ligands

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Heterometallic complexes containing one of the metal atoms as a part of organometallic ligand represent relatively poorly studied type of compounds. In recent years we have obtained and studied several series of $3d-4f$ -heterometallic complexes containing cymantrene¹ (Cym = $(\eta^5-C_5H_4)Mn(CO)_3$) or ferrocene^{1,2} (Fc = $(\eta^5-C_5H_4)(\eta^5-C_5H_5)Fe$) and benchrotrene³ (Bcr = $(\eta^6-C_6H_5)Cr(CO)_3$) fragments.

It seemed interesting to prepare compounds including three different metals in the molecule. Using $FcCO_2H$ and triethanolamine (H_3tea), we obtained new isostructural trimetallic complexes $[Ln_2Cr_2(OH)_2(FcCO_2)_4(NO_3)_2(H_2tea)_2] \cdot 2MePh \cdot 2THF$ (Ln = Tb (**1**), Dy (**2**), Ho (**3**), Er (**4**), and Y (**5**)) having defect-dicubane structure of the metal core.⁴ In all of the complexes, doubly deprotonated triethanolamine chelates the chromium ion (Fig. 1, left), however, for Tb an isomeric complex **1a**, in which Tb^{3+} is chelated by triethanolamine as a tetradentate ligand, was also isolated. For Dy, a similar complex on a basis of $CymCO_2H$ and Fe^{3+} ions, $[Dy_2Fe_2(OH)_2(CymCO_2)_4(NO_3)_2(Htea)_2] \cdot 2MeOH \cdot 2MeCN$ (**6**), was obtained. DC magnetic studies revealed ferromagnetic interactions in the metal cores of complexes **2** and **3** at $T \approx 25$ K, and in Y complex below 20 K. Complexes **1**, **2**, **3**, **4**, and **6** display the properties of single-molecule magnets (SMMs) with magnetization reversal barriers Δ_{eff}/k_B of 56, 80, 48, 14, and 20 K, respectively. Thermolysis of **1** - **5** under air brings about mixed oxides $LnFe_{1-x}Cr_xO_3$.

Using $CymCO_2H$ and $Fe(\eta^5-C_5H_4P(O)Ph)_2$ ligand ($DppfO_2$), a series of new heteroleptic mononuclear $3d-3d'-4f$ -heterometallic complexes $[Ln(CymCO_2)_2(DppfO_2)_2]NO_3 \cdot Solv$ (Ln = Tb (**7**), Dy (**8**), Ho (**9**), Er (**10**); *Solv* are the lattice solvent molecules, CH_3CN and/or $CHCl_3$) was obtained. The Ln^{3+} ions in the unique bulky $[Ln(CymCO_2)_2(DppfO_2)_2]^+$ cations are eight-coordinate; both kinds of organometallic ligands are bidentate (Fig.1, right). According to AC magnetic studies, complexes **9** and **10** are the SMMs with Δ_{eff}/k_B values of 3.8 and 10.1 K, respectively.

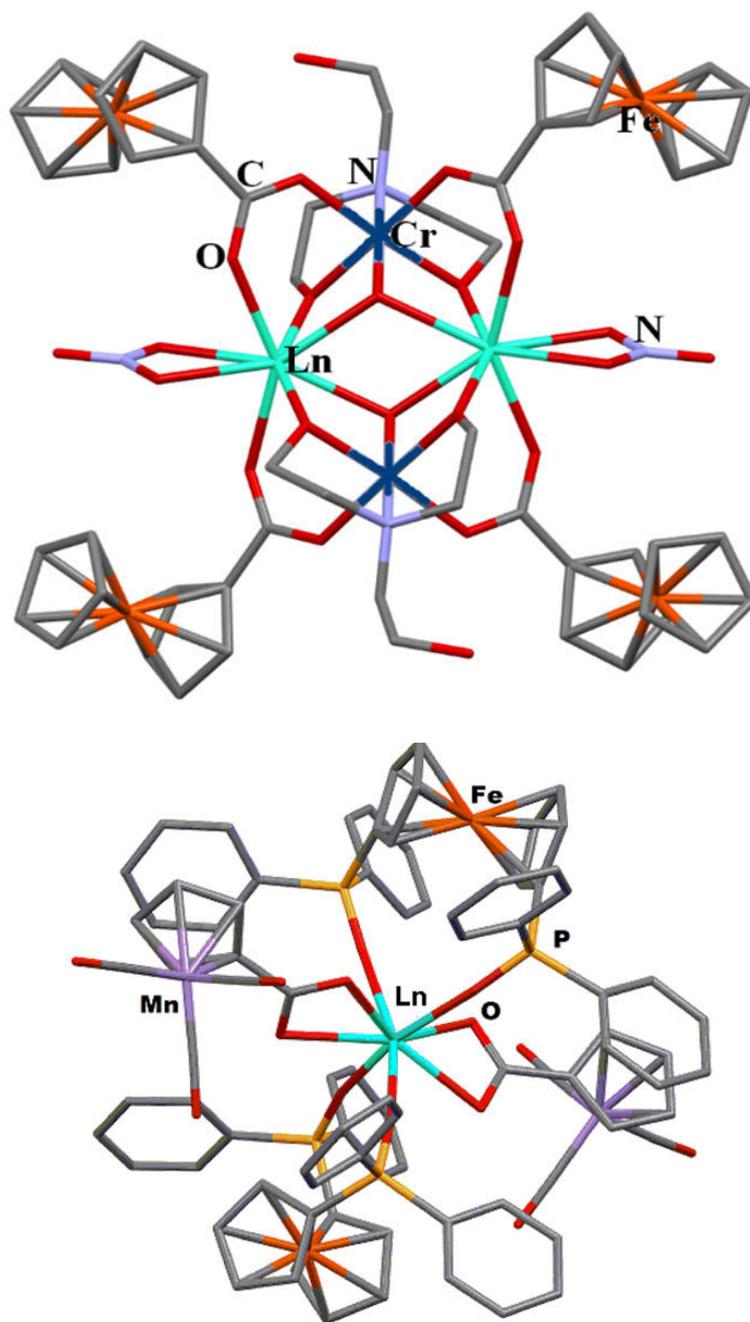


Fig. 1. Structures of complexes **1-5** (left) and of bulky cations in compounds **7-10** (right).

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In situ high-pressure synthesis of compounds and silicon allotropes in Na-Si system.

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Silicon is the second abundant element, after oxygen, in the earth crust. It is essential for today's electronics because of its ability to show various electronic behaviors that allow covering the numerous fields of cutting-edge applications. Moreover, silicon is not a pollutant and, therefore, an ideal candidate to replace the actual materials in photovoltaics, like compounds based on the arsenic and heavy metals. It has not replaced them so far because Si is an indirect gap semiconductor and cannot absorb directly the solar photons without thermal agitations of crystal lattice (phonons). This puts it apart from the next-generation applications (light diode, high-performance transistor). That justifies the attempts to create silicon with direct gap that can absorb and emit light. Our recent high-pressure studies of the chemical interaction and phase transformations in the Na-Si system [1], revealed a number of interesting routes to new and known silicon compounds and allotropes [2,3]. The pressure-temperature range of their formation is suitable for large-volume synthesis and future industrial scaling. The variety of properties observed (e.g. quasi-direct bandgap of open-framework allotrope Si₂₄ [2] and narrow gap Si-III with BC8 structure [4]) allows us to suggest future industrial applications.

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Sky-Blue-Emitting Dendritic Alkynylgold(III) Complexes for Solution Processable Organic Light-Emitting Devices

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A new class of tridentate ligand-containing cyclometalated gold(III) complexes featuring dendritic alkynyl ligands with carbazole moieties as dendrons and peripheral groups has been synthesized up to the third generation. High-performance solution processable organic light-emitting devices (OLEDs) with maximum current efficiency of up to 23.7 cd A⁻¹ and external quantum efficiency of up to 6.9 % have been realized by a simple spin-coating technique. With the incorporation of bulky carbazole moieties to form higher generation dendrimers, the undesirable excimeric emission could be effectively reduced, allowing the fine-tuning of the emission color toward the blue region. This represents the first successful demonstration of sky-blue-emitting alkynylgold(III) complexes and its application in solution-processable OLEDs.

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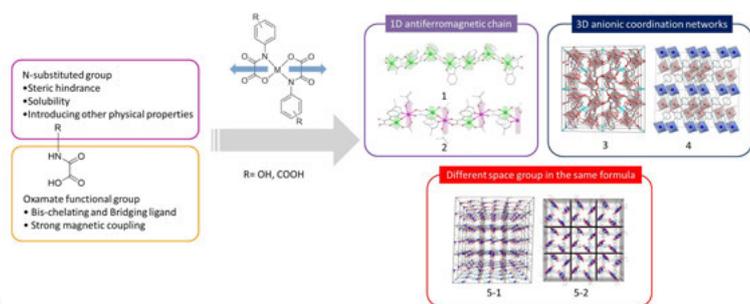
New Oxamate-based architectures and their magnetic properties

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The design and synthesis of multifunctional magnetic coordination polymers (MMCPs) lies in the interdisciplinary crossing point between chemistry, physics and material science and attracts a large number of research teams due to their potential applications in nanoscience^[1,2]. The family of N-substituted aromatic oxamate ligands are considered as ideal candidates for obtaining structure with predictable dimensionality and magnetic properties^[3]. They present several advantages: the bis-bidentate ligand through its N,O-oxamato donor group and free oxygen atoms favours the 'complex as ligand' (metalloligand) synthetic strategy ; the oxamato bridge is able to mediate a strong magnetic coupling between the neighbouring metal ions; changes on the N-substituted groups, that allow a tuning of steric hinderance effects or solubility properties, have proven to be effective towards the preparation of magnetic coordination polymers, including porous metal-organic frameworks^[4]. In this communication, a series of new oxamate-based ligands with additional carboxylato and hydroxo coordinating groups were prepared and used to synthesize novel multidimensional coordination architectures : the 1D chains (HNEt₃)[Cu(ohpma)] (1) and [Cu(ohpma)Co(oAC)(DMF)₂] (2) (H₃ohpma= (2-hydroxyphenyl)oxamic acid), the 3D oxamate-based coordination architectures [Mn(Hpaba)H₂O] (3), (TMA)₂[Cu(paba)₂Mn₂(ox)](DMF)₂ (4), and the polymorphic (TMA)[Cu(paba)] (5-1; 5-2) (H₃paba= 4-oxamatobenzoic acid), all synthesized using solvothermal technique, which had never been developed for oxamate chemistry so far.



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Non-aqueous Sol-Gel Routes to Magnetic Nanoparticles

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Nanosized oxides play a major role in the development of functional nanoscaled devices. As a part of this research flow, bimetallic, metal oxide and multi-metal oxide nanoparticles (NPs) have emerged for applications in the fields of heterogeneous catalysis, electrochemistry, magnetic storage, spintronics, biomaterials, and biomedical systems.

It is essential to understand the relationship between NPs synthesis and the resultant properties. Moreover, the tendency is to achieve the goal of a single domain within one NP, which will allow the tailoring of resulting magnetic properties. Therefore, making ultrasmall NPs (below the single magnetic domain size limit), with a narrow size distribution (monodisperse), is crucial to increase the maximum information density in magnetic recording, to optimize the magnetic coupling, and to increase the volume of soft magnetic phase in permanent magnet nanocomposites.

We extended the “benzyl alcohol route” to the synthesis of magnetic nanoparticles. We present here the synthesis, characterization and magnetic behavior of bimetallic CoPt_3 and multi metal oxide CoFe_2O_4 nanoparticles. This non-aqueous sol-gel method is suitable in this case as it allows the synthesis of high quality nanocrystals where no other solvent was involved on the reactions. In these systems, the magnetic properties seem to be strongly dependent on the metal oxide precursor and thus, on the synthetic conditions.

The nanopowders have been investigated by various analytical techniques such as powder X-ray diffraction, methods (whole powder pattern modelling), dynamic light scattering (DLS) high-resolution scanning transmission electron microscopy (HR-STEM), X-ray photoelectron spectroscopy (XPS), Raman, superconducting quantum interference device (SQUID) and Mössbauer spectroscopy. After excluding the presence of secondary phases, the magnetic behavior was studied by susceptibility measurements.

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Lanthanum zirconate ($\text{La}_2\text{Zr}_2\text{O}_7$) powders: Synthesis and characterization

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The interesting chemistry of the rare-earth pyrochlore materials [1] originates from the variety of cations and anions present in the lattice structure with general formula of $\text{A}_2\text{B}_2\text{O}_7$ (where A is usually a trivalent rare-earth ion and B can be a 3d, 4d or 5d transition ion) and compositions, isolated under the different synthetic conditions. In particular, the rare-earth zirconates ($\text{Ln}_2\text{Zr}_2\text{O}_7$) [2], have interesting physicochemical and thermal properties that render them excellent materials for (among others) high oxygen mobility [3], oxygen ion sensing [4], catalysis [5] and photoluminescence [6]. Moreover, these materials have been proposed to have applications as novel thermal barrier coatings (TBCs) in aircraft gas-turbine engines [7] and in the fixation of actinides from the nuclear wastes [8]. Thus, their structural and physicochemical studies impose major challenges upon the variety of the synthetic methodologies. In our studies, we are focused on the lanthanum-based zirconate pyrochlore (La_2O_3 - ZrO_2 ; $\text{La}_2\text{Zr}_2\text{O}_7$; LZ) materials synthesized using bottom up approaches [9] and we are targeting homogeneous composition, high purity, high melting point powders and controllable fabrication cost [10]. Co-precipitation method takes place between the raw materials; namely, zirconium oxychloride (ZrOCl_2) and lanthanum nitrate ($\text{La}(\text{NO}_3)_3$), in aqueous media (pH=12). Alternatively, we are focused on preparation of the LZ powders by means of hydrothermal synthesis, spray drying and plasma spraying of the precursors at moderate and high temperatures. Detailed structural investigation which includes the phase composition, lattice constants, and space group, covered by both X-Ray and Neutron Diffraction as a function of temperature and/or time, are applied to the isolated LZ materials. In addition to the structural analysis, representative microscopic techniques (TEM and SEM), provide useful information on the morphology and size of the synthesized particles.

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Metal cages and extended networks assembled with novel hydroxamic acid building blocks.

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The inherent pharmacological, toxicological and pathological properties of hydroxamic acids gives rise to their rich bioactivity.¹⁻⁴ More specifically, these organic acids are able to act as efficient siderophores as well as effective selective enzyme inhibitors for histone deacetylase, ureases and prostaglandin H₂ synthases.¹ Such behaviour stems from their binding affinity towards transition metal ions and an ability to disrupt / occupy catalytic active sites.^{1,2} Our own recent work has probed the coordinating ability of a plethora of hydroxamic acids, which has produced a number of interesting magnetic cages⁵ and coordination polymers.⁶

Here a novel family of hydroxamic acid ligands in the form of *N*-hydroxy-2-((2-hydroxy-3-methoxybenzyl)amino)benzamide (L₁H), 4-amino-2-(acetoxyl)phenyl hydroxamic acid (L₂H; Figure 1b) and 2-(methylamino)phenyl hydroxamic acid (L₃H) has been synthesised towards investigations into their subsequent metal ligation. The pre-designed 'catcher's mitt' ligand *N*-hydroxy-2-((2-hydroxy-3-methoxybenzyl)amino)benzamide (L₁H) readily forms the pentametallic 12-MC-4 metallacrown [Cu(II)₅(L₁)₄(MeOH)₂](NO₃)₂ (**1**). Variable temperature magnetic susceptibility studies indicate dominant antiferromagnetic exchange between the Cu(II) centres in **1**. The ditopic ligand L₂H highlights its ability to produce extended network topologies as evidenced by the wave-like 2D [4,4] nets in {[Cu(L₂)(H₂O)(NO₃)]·H₂O}_n (**2**) (Fig. 1), while the 1D chains in [Zn(II)(L₃)₂]·MeOH (**3**) are propagated by η¹: η²: m-bridging L₃ moieties.

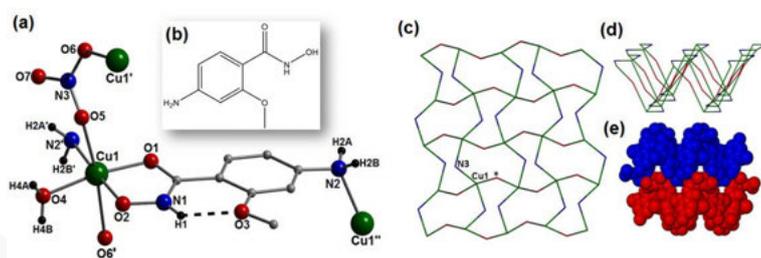


Figure 1: (a) The asymmetric unit in {[Cu(II)(L₂H)(H₂O)(NO₃)]·H₂O}_n (**2**) along with the connector atoms (N2', O5', Cu1' and Cu1'') that propagate the 2D extended network in **2**. The wave-like [4,4] net topology in **2** as viewed perpendicular (c) and parallel (d) to the plane of the 2D sheets. (e) A space-fill

representation of the packing motif between two wave-like sheets in **2** as viewed along the *c* unit cell direction.

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Five in one: Silver and Corroloato-Based Mixed-Valency in a novel Corrole Dimer

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Tetrapyrrolic macrocycles like porphyrins or corroles essential for many of life's functions^[1] and yield a great potential for future technological and catalytic applications^[2]. The field of porphyrinoid compounds as extended pi-systems poses many challenges for synthetic chemistry as well as spectroscopy which makes it especially intriguing^[3].

Mixed-valent compounds are fascinating entities that are useful as models for the investigation of electron-transfer reactions, and find use in a host of biologically relevant redox processes. Though the bio-relevant metal copper is well established in mixed-valent chemistry, the $\text{Ag}^{\text{II}}/\text{Ag}^{\text{III}}$ mixed-valent combination of its higher congener in a molecular complex has rarely been reported before.

This work^[4] reports the synthesis of a new β,β' -linked bis{corroloato-silver(III)} complex and its characterization in five different redox states. A combination of electrochemistry, spectroelectrochemistry, and DFT calculations point to the existence of a mixed-valent $\text{Ag}^{\text{II}}/\text{Ag}^{\text{III}}$ and an iso-valent $\text{Ag}^{\text{II}}/\text{Ag}^{\text{II}}$ form. Additionally, characterization of the $\text{Ag}^{\text{III}}/\text{Ag}^{\text{III}}$ form and ligand-based corroloato-centered mixed-valency is presented as well. These results thus open new avenues for bis-corroloato ligands and for mixed-valency in disilver compounds.

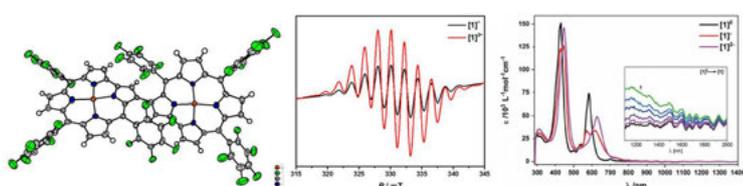


Figure 1. Structure of the title compound [1](left), EPR spectra of the *in-situ* reduced title compound ($[1]^{\bullet-}$, $[1]^{2\bullet-}$; middle) and UV-Vis-NIR spectra of the *in-situ* reduced title compound ($[1]^{\bullet-}$, $[1]^{2\bullet-}$; right).

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Computational studies on actinide endohedral metallofullerenes: Cage dependent metal-to-cage charge transfer and presence of actinide-actinide bond

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The spherical shape of fullerenes makes them able to encapsulate metals or clusters inside forming endohedral metallofullerenes (EMFs). These compounds are stabilised by a formal electron transfer from the metal or cluster to the fullerene cage.

EMFs containing lanthanides have been intensively studied in recent years. By contrast, actinide endohedral fullerenes remain largely unexplored. Here we present theoretical studies on uranium and thorium EMFs. With a combination of experimental and theoretical results we have found that $\text{Th}@C_{3v}(8)-C_{82}$ is the first monometallofullerene with four electrons transferred from the metal to the cage and the first actinide EMF fully characterized reported with single crystal structure.¹

Since the detection of $\text{La}@C_{82}$, in 1991, it has been observed that the oxidation state of a given encapsulated metal is always the same, regardless of the cage size. We have observed for the first time a dependence of the metal oxidation state on carbon cage isomerism for *mono*-EMFs. Results from DFT calculations at BP86/TZP(D3) level show that for $\text{U}@D_{3h}-C_{74}$ and $\text{U}@C_{2v}(5)-C_{82}$ there is a formal transfer of four electrons, $\text{U}^{4+}@D_{3h}-C_{74}^{4-}$ and $\text{U}^{4+}@C_{2v}(5)-C_{82}^{4-}$, whereas for the isomeric $\text{U}@C_{2v}(9)-C_{82}$ we find $\text{U}^{3+}@C_{2v}(9)-C_{82}^{3-}$.²

Finally, we present the dimetallic actinide EMF $\text{U}_2@I_h(7)-C_{80}$. The nature of actinide-actinide bond has attracted considerable attention for a long time, especially since the recent theoretical studies suggested that a triple and up to quintuple bonds should be possible. For this diuranofullerene there is a six-electron transfer from the U_2 unit to the carbon cage. Therefore the formal charge of the U atoms trapped inside the cage is +3 (f^3 electronic configuration). The crystallographic data revealed that the U-U distance is within the range of 3.46-3.79 Å, suggesting the presence of a U-U bond. Computational studies confirm the presence of a U-U bonding interaction and suggest that the weak U-U bond in $\text{U}_2@I_h(7)-C_{80}$ is strengthened upon reduction and weakened upon oxidation.³

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Why Is Nitric Acid Capable of Dissolving Silver and Incapable of Dissolving Gold?

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Silver and gold are members of the same family in the Periodic Table. They are also the two precious coinage metals in the history of mankind and commonly used in jewelry. Further, the dissolution of each (in its elemental form) in dilute nitric acid is an oxidation-reduction (redox) reaction that involves 3 moles of electrons transferred per mole of the reaction. Still, elemental silver is soluble in dilute nitric acid but elemental gold is not. Electrochemical data and calculations were used to analyze the dissolution process of each of the two metals in dilute nitric acid. For each of the two dissolution reactions, the equilibrium constant (K_{eq}) at 25 degrees Celsius was determined, and the behavior of each metal was compared to that of the other in light of the half-reactions and standard reduction potentials. The key distinguishing factor in the two different behaviors was determined to be that elemental gold is a much weaker reducing agent than elemental silver.

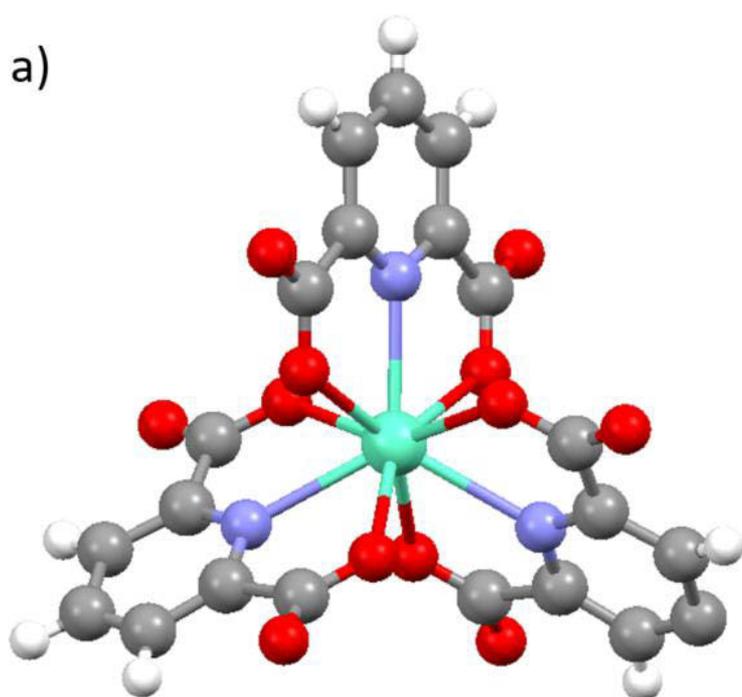
Direct determination of solution structure of europium(III) dipicolinate complexes

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The sharp transition peaks of lanthanides are characteristic for the f-block elements and are convenient in studying the structure-property relationships of Ln(III) complexes.¹ The *f-f* transitions are parity forbidden, but the selection rule restrictions can be adjusted by introducing various crystal-field perturbations. The effect of these crystal-field perturbations is related to the coordination sphere symmetry experienced by the lanthanide. This behavior can be accurately probed using optical spectroscopy. For this purpose, the non-degenerate emissive state of europium(III) makes it an ideal model system for Ln(III) photophysics, in conjunction with the well-studied 2,6-pyridinecarboxylate^{2,3} (DPA) tridentate ligand, as seen in Figure 1a.

Absorption spectroscopy grants information on speciation of the solution species, while steady-state and time-gated luminescence spectroscopy probes the photophysical properties of each constitutional conformer as well as the weighted average of the emitting species. For a structural corroboration of the luminescent studies, a combination of NMR, X-ray scattering and luminescence was used to confirm the solution symmetry of the species. Luminescence and scattering data are shown in Figure 1b and 1c.



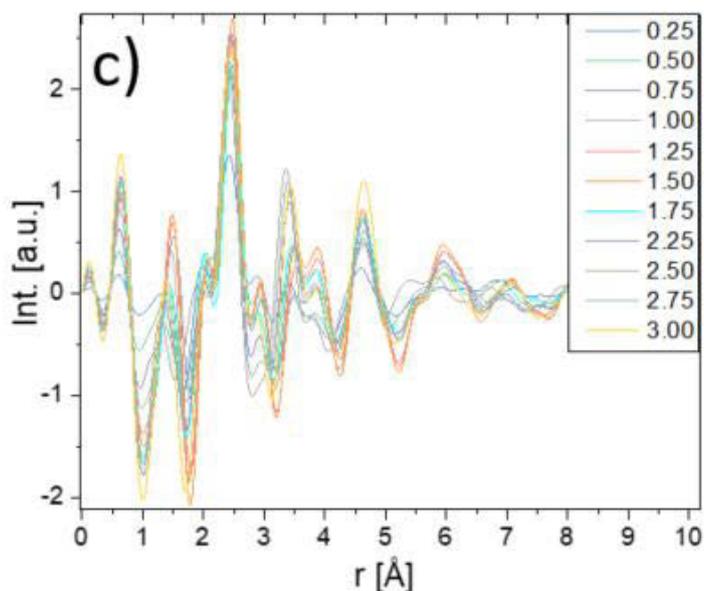
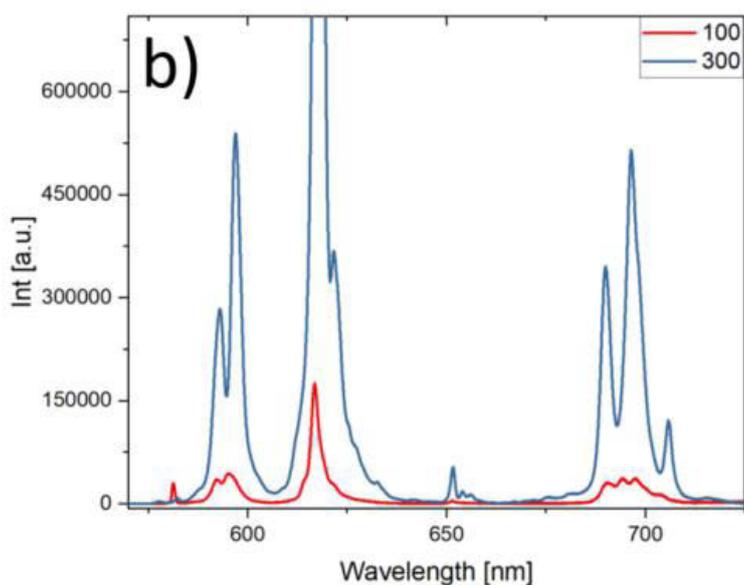


Figure 1: a) Modelled crystal structure of $\text{Eu}(\text{DPA})_3^{-3}$. b) Two emission spectra of EuDPA complex showing an example of the effect of perturbing the crystal-field of 1:1 (red) stoichiometry and 1:3 (blue). c) Fourier transformed X-ray scattering data presented in the form of the pair distribution function, showing interatomic distances in real space.

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Dinucleating Schiff base ligand in Zn/4f coordination chemistry: synthetic challenges and catalytic activity evaluation

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Four Zn/4f polynuclear coordination clusters (PCCs) were prepared with the employment of the dinucleating Schiff base ligand H2L derived from N,N'-bis(3-methoxysalicylidene)cyclohexane-1,2-diamine and ortho-vanillin and fully characterised for the first time, following two synthetic methodologies. These air-stable heterometallic PCCs, obtained in high yields from commercially available materials, were shown to remain stable in solution in their dinuclear $[\text{Zn}^{\text{II}}\text{Ln}^{\text{III}}\text{L}]$ form. Their catalytic activity was evaluated in various catalytic transformations including the Friedel–Crafts alkylation of 2-acyl imidazoles with indoles.¹

The results presented herein showcase the synthetic challenges revealed during the development of catalytic protocols that involve Zn/4f CCs and the present dinucleating ligand.² The present dinucleating Schiff Base ligand represents an ideal candidate for the synthesis of dinuclear 3d/4f catalysts, offering two different pockets for coordination (**Figure 1**), however unexpected species of different nuclearity can be obtained when different synthetic approaches are followed. The present results notify that in situ generated catalysts for catalytic screenings is not a good practice as it may overlook the possible formation of multiple 3d/4f species that may influence the observed catalytic behaviour. Our synthetic attempts yielded dinuclear and tetranuclear species that all exist as dinuclear species in solution (**Figure 2**). All four catalysts were found to promote, probably via a cooperative pathway, the addition of indoles on 2-acyl imidazoles as well as the Michael addition of β -diesters in good yields. The catalytic efficacy of the asymmetric version of these catalysts is currently being investigated.

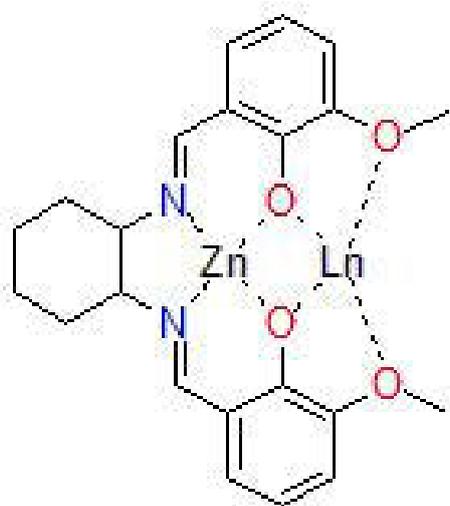


Figure 1

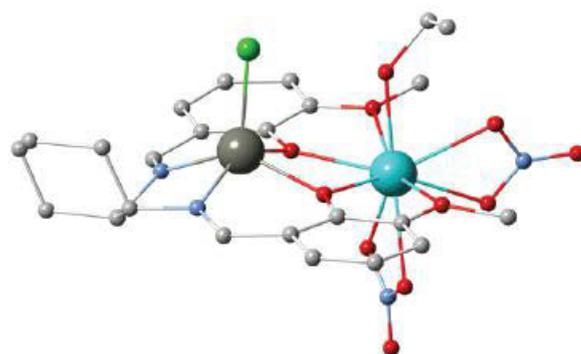
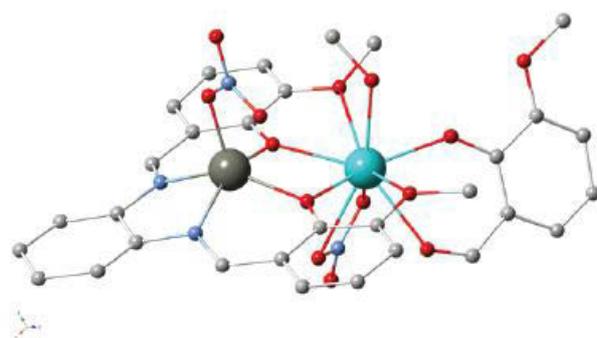
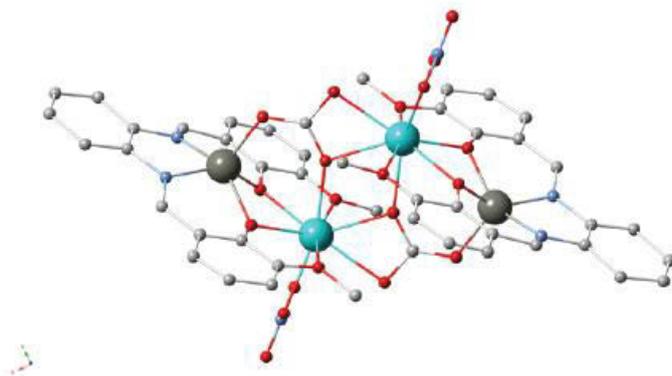


Figure 2

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Counterions for controlled dissolution, aggregation and cluster growth of metal-oxo clusters

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The behaviour of transition metal oxides in aqueous solution and interfaces is dictated by numerous complex and interrelated phenomena. While pH and concentration drive aqueous metal speciation as a first approximation, the important effect of counter-ions is usually overlooked and never considered in standard Pourbaix diagrams. Even for simple salt solutions, hydration of ions and formation of ion-pairs is not well understood.

Group V/VI polyoxometalates (POMs) offers an opportunity to investigate these multiple roles of the counter-ions. We showed recently [1] that a simple Nb-POM, $[\text{Nb}_{10}\text{O}_{28}]^{6-}$ ($\{\text{Nb}10\}$), converts to oligomers of $[\text{H}_x\text{Nb}_{24}\text{O}_{72}]^{(24-x)-}$ ($\{\text{Nb}24\}$) upon adding only alkali chloride salts, even in buffered neutral solutions. Raman and X-ray scattering revealed that the rate of $\{\text{Nb}10\}$ to $\{\text{Nb}24\}$ conversion increases with alkali cation radius and cation concentration. Computational studies and mass spectrometry indicate the alkalis open the compact $\{\text{Nb}10\}$ cluster in conjunction with protonation of a heptamer $\{\text{Nb}7\}$ intermediate, where alkali- $\{\text{Nb}10\}$ association at key locations on the cluster initiates the reaction. Computation also explains the alkali periodic trend for $\{\text{Nb}10\}$ to $\{\text{Nb}24\}$ conversion; larger alkalis more effectively destabilize $\{\text{Nb}10\}$.

On the other hand, group V and group VI clusters lead to opposite solubility trends: in group VI the solubility trend is $\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs}$ (normal solubility) whereas in group V does $\text{Cs} > \text{Rb} > \text{K} > \text{Na} > \text{Li}$ (anomalous solubility). We approach this phenomenon by both developing a predictive model based on molecular descriptors, and molecular dynamics simulations.

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Monodimensional compounds based on group 6 tetraoxometalates and transition metal complexes of the cyclam ligand

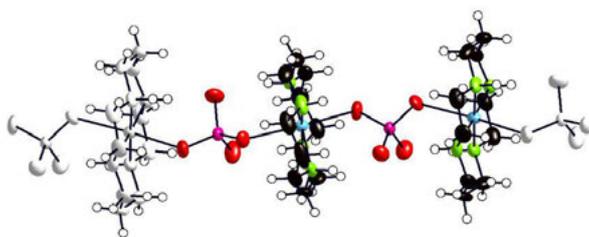
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In the course of our research on high-nuclearity transition metal oxoanions (polyoxometalates) in combination with transition metal complexes of macrocyclic tetradentate N-donor ligands, extended hybrid structures have been obtained, which have shown the ability to undergo thermally triggered structural transformations [1]. The reaction between group 6 tetraoxometalates and first row transition metal complexes of the cyclam ligand (1,4,8,11-tetraazacyclotetradecane) in basic aqueous media (pH = 10) affords six different monodimensional compounds, namely $[\text{Cu}(\text{cyclam})][\text{CrO}_4] \cdot 3\text{H}_2\text{O}$ (**1**), $[\text{Cu}(\text{cyclam})][\text{MoO}_4] \cdot 4\text{H}_2\text{O}$ (**2**), $[\text{Cu}(\text{cyclam})][\text{WO}_4] \cdot 5.5\text{H}_2\text{O}$ (**3**), $[\text{Ni}(\text{cyclam})][\text{CrO}_4] \cdot 2\text{H}_2\text{O}$ (**4**), $[\text{Ni}(\text{cyclam})][\text{MoO}_4] \cdot 3\text{H}_2\text{O}$ (**5**) and $[\text{Zn}(\text{cyclam})][\text{CrO}_4] \cdot 3\text{H}_2\text{O}$ (**6**). The prepared compounds have been chemical (FT-IR, TGA, CHN) and structurally (sc-XRD) characterized. In all the crystal structures, discrete $[\text{MO}_4]^{2-}$ oxoanions (M = Cr, Mo or W) exhibit tetrahedral geometry and are linked to each other through metal-organic complexes resulting in monodimensional compounds formed by parallel chains of $\{[\text{TM}(\text{cyclam})][\text{MO}_4]\}_\infty$ units (TM = Ni^{II}, Cu^{II}, Zn^{II}). The coordination spheres of the TM centres present distorted octahedral (TM)N₄O₂ chromophores with the four N atoms of the *cyclam* ligand forming the equatorial plane and the axial position occupied by terminal O atoms from the oxoanions. Additionally, the Cu^{II} derivatives **1-3** have been analysed by Electron Spin Resonance (ESR) spectroscopy, which show the rhombic signal of the axially elongated octahedral Cu^{II} centres. The differences observed in the spectra have been related to structural parameters.



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We are going to need a bigger bowl: Giving molecular cavity wall extensions to pseudo metallocalix[6]arenes.

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The complexation of Co(II), Ni(II) and Zn(II) ions with the ligand 2-methoxy-6-((methylimino)methyl)phenol (L_1H ; Fig. 1a) gives rise to the self-assembly of a family of pseudo metallocalix[6]arenes: $[M(II)_7(OH)_6(L_1)_6](NO_3)_2$ ($M = Co$ (**1**), Ni (**2**) and Zn (**3**). The bridging Schiff base ligand (L_1H) allows these complexes to exhibit double bowl architectures and molecular cavities, which have previously been investigated for their solid-state host guest chemistry (Fig. 1).³

In this work we present the upper rim modification (at R_1 position in Fig. 1) of the Schiff base ligand L_1H leads to a new family of ligands that include 4-phenyl-2-iminomethyl-6-methoxyphenol (L_2H ; $R_2 = H$ in Fig. 1e) and 5-(4-methylphenyl)-3-methoxy-N-methylsalicylaldimine (L_3H ; $R_2 = CH_3$ in Fig. 1e). These ligands were specifically designed to allow the formation of new $[M(II)_7]$ ($M = Co(II)$, Ni(II) and Zn(II)) pseudo metallocalix[6]arenes that deliberately form larger molecular cavity walls upon their assembly. To this end we report in this work the complexes (not exhaustive): $[M(II)_7(OMe)_6(L_2)_6](NO_3)_2$ ($M = Co$ (**4**), Ni (**5**) and $[Zn(II)_7(OMe)_6(L_3)_6](NO_3)_2$ (**6**).² The resultant architectures in **4-6** are discussed with respect to their structural and topological relationships with their ancestors **1-3**.

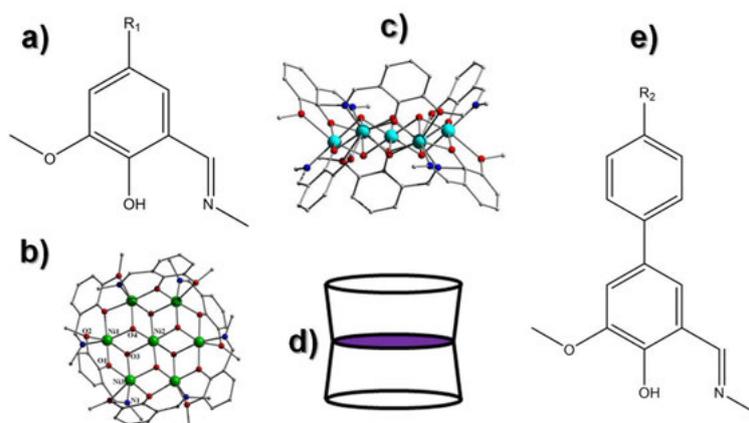


Figure 1 (a) The Schiff ligand 2-methoxy-6-((methylimino)methyl)phenol ($R_1 = H$ (L_1H)) used in the

construction of our heptanuclear double bowl metallocalix[6]arenes. Perpendicular (b) and side-on (c) views of a [Ni(II)₇] and [Zn(II)₇] metallocalix[6]arene, respectively. (d) Schematic highlighting the double bowl topology. (e) The new ligands 4-phenyl-2-iminomethyl-6-methoxyphenol ($R_2 = H, L_2H$) and 5-(4-methylphenyl)-3-methoxy-N-methylsalicylaldehyde ($R_2 = CH_3, L_3H$) used in this work to form larger molecular cavities upon metallocalix[6]arene assembly.

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Defect sites on a surface of activated silica: probing their structure and reactivity

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Amorphous silica belongs to the most studied oxide supports in a heterogeneous catalysis and has wide use in other disciplines as well (glass industry, construction engineering, pharmaceutical industry, tire manufacturing, etc.). Preparation of amorphous silica can be achieved by flame pyrolysis (i.e. fumed silica) or by sol-gel processes.[1] The structure consists of differently bound silanol groups (geminal, vicinal, interacting, isolated) and siloxane rings (12-membered to 4-membered, where the ring size creates/alleviates strain in the structure).[2] Introduction of defects into the surface of a supporting material plays important role as it creates reactive sites, which can influence mechanical properties, can be catalytically active or used as a target for metal deposition.

Here we will discuss how high temperature thermal treatment of a triethoxysilane modified silica (prepared by sol-gel deposition method) introduces extensive changes to the surface. In particular, a high density of paramagnetic and diamagnetic defects is generated, that corresponds to silicon-centered radicals and silylene groups, respectively. This treatment also leads to the disappearance of most silane and silanol groups, while maintaining a relatively large surface area (> 150 m²/g). These “defects” shows high reactivity towards a range of small molecules like H₂, O₂ and CH₄ as well as organometallic compounds.

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Synthesis and Complexation Studies of Novel Disubstituted Calix[4]arenes for *f*-element Complexation

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Calixarenes are an important part of the host-guest chemistry. They offer the possibility to build-up binding pockets for guest molecules step-by-step. Calixarenes, foremost calix[4]arenes, have been widely used as scaffold for the synthesis of versatile ligand systems, due to their conformational properties and their feature to exhibit reactive positions for attaching functional groups with various chemical and physical characteristics.[1-3] We are interested in calix[4]arene based ligands regarding to their extraction behavior towards rare earth metals. Previous investigations focused on tetrasubstituted calix[4]arenes with phosphonate ester and picolinamide.[4] Based on the work of Ullmann et al. on hybrid Schiff-base calix[4]arene [5-6] we use other Schiff-bases to design bifunctionalized calix[4]arenes. Herein, we report on the synthesis of two ligands and indicate their ability to act as effective ligands for lanthanide complexes. We show complexation studies and interaction experiments.

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Binding and Destruction of Nerve Agent Simulants within Self-assembled Supramolecular Cages

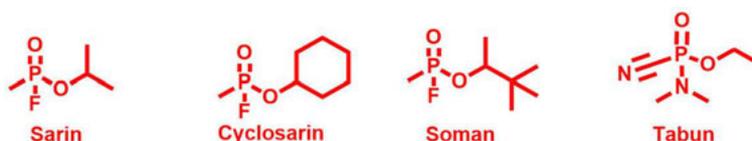
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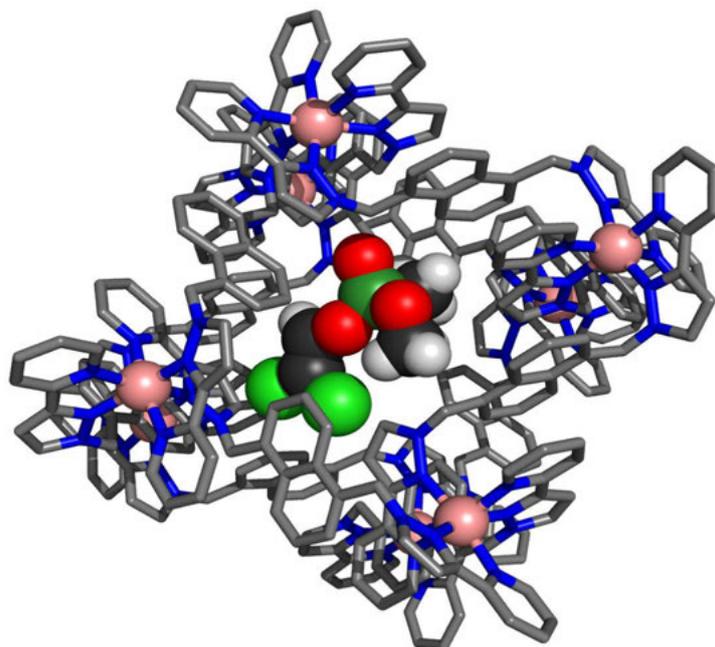
An increasing number of examples of self-assembled metal coordination cages have the ability to bind guests within an internal cavity. This host-guest chemistry mimics the encapsulation used in nature by enzymes and allows many similar applications such as drug delivery or even control of a reaction.

One potential application is to trap and catalyse destruction of G-series nerve agents such as Sarin. These topical deadly agents are colourless, odourless and very difficult to detect.

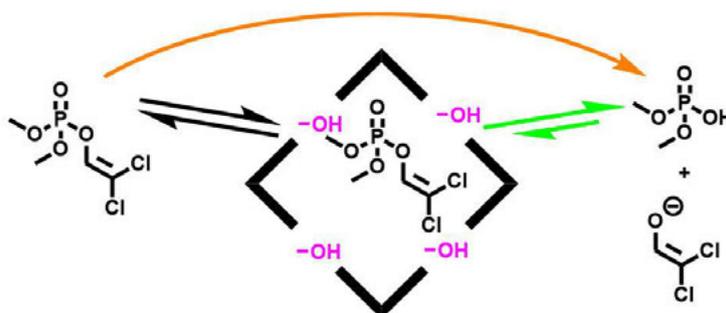


Using a combination of NMR and UV-Vis titrations along with X-ray crystal structures, it is possible to quantify the interaction between our host, a self-assembling cubic coordination cage, and the guests of interest. Binding of the guest, driven by the hydrophobic effect, is predictable and can be related to the guest's hydrophobic surface area and flexibility.

Indeed, it is possible to use protein docking software, such as GOLD, to reliably predict the binding of guests and allow screening of many potentially interesting small molecules.



Unique properties of this water soluble coordination cage allows for the catalytic hydrolysis of bound guests. It is possible to see a significant acceleration of hydrolysis for Sarin like simulants. While the solution remains at a neutral pH the guest is encapsulated in the cage complex where is it exposed to a substantially higher local pH.



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Synthesis and reactivity of Pt(II) rollover complexes

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Cyclometalation reaction constitutes one of the most versatile and widely used synthetic methods in organometallic chemistry. A variation on this theme is the so-called “rollover cyclometalation” where a bidentate ligand, such as 2,2′-bipyridine, leads to a cyclometalated species with an uncoordinated donor atom.¹ In the course of the reaction the ligand displaces one of the donor atoms from the metal, with subsequent rotation of the aromatic ring and activation of a remote C-H bond to give the rollover complex.

Even though the majority of studies have been dedicated to 2,2′-bipyridines, the reaction is not restricted to this family of ligands but may be extended to numerous chelated heteroaromatic ligands.

This class of organometallic compounds is currently attracting a growing interest: their reactivity and properties are different from those of classical cyclometalated complexes, mainly due to the presence in the complex of an uncoordinated donor atom, usually a nitrogen, available for coordination, protonation, or other chemical reactions. The reactivity of the second nitrogen has been thoroughly investigated only in the case of platinum(II) complexes.

Following our long-standing interest in this field we have undertaken an investigation on the influence of stereoelectronic factors both in the rollover cyclometalation process and in the properties of the resulting cyclometalated complexes.² In the case of platinum(II), a series of mono- and di-nuclear complexes of Pt(II) and Pt(IV) can be obtained, including species with a protonated nitrogen, where the zwitterionic cyclometalated ligand may be regarded as an *abnormal-remote* heterocyclic carbene.

Here we present our recent results regarding the reactivity of electron-rich platinum(II) precursors, such as [Pt(R)₂(DMSO)₂] (R=Me, Ph), with a series of substituted-2,2′-bipyridines, where the substituents furnish different electronic and steric properties both to the ligands and the resulting complexes.

The reactivity and properties of the new rollover complexes, which contain two potential nucleophilic centers (the uncoordinated nitrogen atom and the platinum center), have been investigated and will be reported.

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Formation and decomposition kinetics of simple *N*-chloro-amino acids

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The reactions of amines, amino acids, peptides and proteins with hypochlorous acid yields *N*-chlorinated compounds under a variety of conditions. In living organisms, these processes are involved in the defense mechanisms against invading pathogens. The very same species are also significant in water treatment technologies where they form spontaneously from dissolved organic species upon dosing chlorine or hypochlorous acid to water. They exhibit disinfecting activity and sufficiently kill microorganisms, though their efficiency is generally less than that of chlorine. In both situations, the biological activities of *N*-chloramines are attributed to their ability of penetrating into the cell where they induce oxidative stress. Ultimately these processes lead to the death of the cells. These processes are non-discriminative, thus the presence of *N*-chloramines in aqueous systems also present a health risk.

In recent years, physiological processes and environmental relevance have generated immense interest in the redox reactions of *N*-chloro-amino acids. Earlier literature results established that the formation of these species from hypochlorous acid and the corresponding amino acids is fast. In contrast, their decomposition is relatively slow and the reaction rate is strongly affected by the chemical environment of the amino group. Some of the earlier results strongly suggest that the decomposition rate does not depend on the pH while other papers reported definite pH dependencies.

Quite frequently, it was assumed that the decomposition proceeds via the Grob fragmentation mechanism and the final products are formed in a single concerted reaction step. Recently, we have shown that the decomposition of *N*-chloroglycine is a far more complex multi-step process.¹

In this presentation, we report our kinetic results on the formation and decomposition of a great variety of *N*-chloro-amino acids. The pH profiles of the reactions between hypochlorous acid and amino acids have been explored in detail using stopped-flow technique. The corresponding parameters of activation have been obtained from temperature dependent studies. The results indicates that to some extent the entropy of activation is affected by the substituents and the structure of amino acids.

N-chloro-amino acids exhibit characteristic spectral bands at around $\lambda_{\max} = 255$ nm in the UV spectral range, and the decomposition was monitored in this spectral region. Time resolved spectral changes revealed that the decomposition is kinetically coupled with further reaction steps. Kinetic profiles of individual species were also determined and compared by making use of ¹H-NMR spectroscopy. The experimental data have been used to establish mechanistic aspects of the decomposition processes. Most

importantly, it could be demonstrated how various substituents and the structural features of the amino acids affect the reactivities of these species and the formation of alternative products.

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A new synergy between organotin(IV) and dithiocarbamate compounds in combating the menace of microorganism in the environment

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The existence of microorganisms in our body and environment continues to pose significant problems. About 4800 species of bacteria have been named and many more are still being discovered by the day. These organisms are capable of exploiting a surprising range of ecological and metabolic opportunities. A large number of illnesses in humans are linked to these minute organisms. Although, much work has been conducted to combat this menace by the design and preparation of many antimicrobial agents, much work still needs to be done in order to combat the menace of microorganism in our environment. This is because most microorganisms are now developing resistance to the existing antibiotics. Various innovative platforms and new therapeutic strategies have been proposed to tackle this danger posed by microorganisms. Metal complexation with compounds known to have antimicrobial potentials is a very important strategy for the design of novel therapeutic compounds in recent years. They have proven to be capable of enhancing biological activities in organic fragments without the toxicity associated with such metal. The synergy exhibited by metal fragments and the ligand moieties in metal complexes has been reported to provide a new pathway for the discovery of useful therapeutic agents with enhanced activities. This has led to our interest in the study of organotin dithiocarbamate complexes. The unique stereo-electronic properties of organotin(IV) compounds containing sulfur donor ligands underline their relevance in medicine among many other useful properties. Organotin(IV)dithiocarbamate owe their functionality and usefulness to the individual attributes of the organotin and the dithiocarbamate moiety respectively. The synergy exhibited by these moieties has resulted in the enhanced biological activity in this hybrid molecule. In this report, a series of organotin complexes of different dithiocarbamate ligands [S₂CNRR'] (R= methyl, ethyl, butyl, allyl and R' = phenyl, allyl) have been synthesized and characterized. Single crystals X-ray analysis obtained for some of the complexes showed the geometry around the tin atom to be either a distorted bipyramidal or a distorted octahedral. The antimicrobial properties of the

complexes were studied using some gram positive bacteria (*Bacillus cereus* and *Staphylococcus aureus*), gram negative bacteria (*Escherichia coli*, *Klebsiella Pneumonia* and *Pseudomonas Aeruginosa*) and some fungi (*Candida albicans* and *Aspergillus flavus*). The complexes showed great potential as antimicrobial agents better than the individual compounds, and compared favorably with other standard drugs used as control.

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Interaction Of $\text{Eu}(\text{fod})_3$ With Coordinated Cyanide In An Analogue Of The sub-site Of [FeFe]-Hydrogenase

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Second coordination sphere interactions of metal centres involving hydrogen bonding, ion-pairing or dipolar bonding can play an important role in determining the physical and chemical properties of molecular and biomolecular systems. The second coordination sphere interactions of coordinated cyanide in a model for the diiron subsite of [FeFe]-hydrogenase has been examined¹⁻³. The natural subsite in its protein environment catalyses hydrogen evolution (or uptake) at very fast rates $ca\ 10^4\ \text{s}^{-1}$ near the reversible potential of the $\text{H}^+ / 1/2\ \text{H}_2$ couple but such rates have yet to be attained in model systems. Controlling the electronic and geometric properties of synthetic diiron subsites by hydrogen bonding or other interactions might provide a means of attaining the turnover rates of the natural system. This work takes some first steps towards introducing second coordination sphere interactions to modify subsite properties. A metal Lewis acid $\text{Eu}(\text{fod})_3$ is shown to bridge to CN ligands in the model subsite to change its spectroscopic and electrochemical behavior.

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Ni(II) and Cu(II) complexes of Heterocyclic Schiff base ligand: Spectroscopic, Characterization and Biological potentials

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In biological processes, inorganic compounds have played a critical role. It has been established that many organic compounds used in medicine are activated or bio-transformed by metal ions metabolism. Infectious diseases which are directly related to bacteria exhibiting multiple resistance to antibiotics have increased the world's mortality rate, resulting in about 17 million deaths globally per year in children and the elderly. Therefore, the need to develop novel antibacterial drugs with excellent mechanisms of action and the structural-activity relationship has become an urgent biomedical necessity.

In effort geared towards the development of chemotherapeutic agents with antimicrobial activities and play an important role in protecting the human system against damage by reactive oxygen species (ROS), we report the synthesis, characterization of heterocyclic tridentate Schiff base Cu(II) and Ni(II) metal complexes, their biological activities. All compounds were isolated as a coloured powder, characterized by elemental analyses, molar conductance, XRD, UV-Vis, FTIR, and NMR.

FT-IR spectral data suggest that the ligand behaves as a dibasic tridentate ligand with oxygen-dinitrogen donor atoms system towards central metal ions. The electronic spectra suggest square planar geometry for nickel and copper complexes. The XRD analysis showed that the complexes possess crystallite sizes. Conductance measurements indicated that the complexes are non-electrolytes. The compounds were screened against *S. aureus*, *E. faecalis*, *K. pneumoniae*, and *P. aeruginosa*. The antibacterial activity of the isolated compounds was found to possess MIC values in the range 1.564 – 12.5 mg/ml against the strains. Antioxidant activities of the complexes were investigated against DPPH radical. The obtained IC₅₀ value for the copper and nickel complexes were higher than the ligand, and hence their potential for developing the chemotherapeutic drugs for the elimination of pathological radicals related diseases from the living system.

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