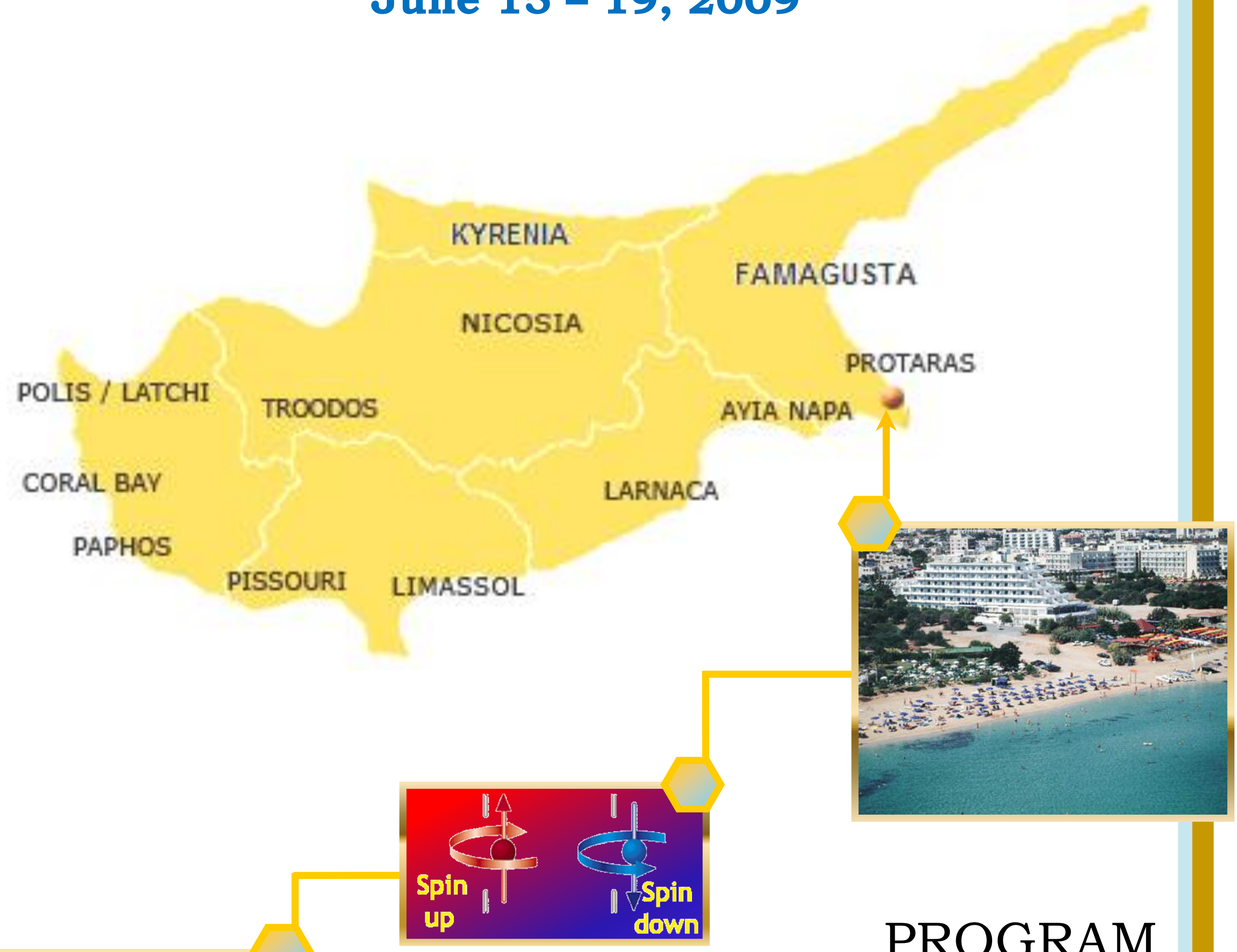
NAGC 2009

Third North America – Greece – Cyprus Workshop on Paramagnetic Materials

Protaras, Paralimni, Cyprus

June 15 – 19, 2009



PROGRAM

and

ABSTRACT BOOK

ΚΥΠΡΙΑΚΗ ΔΗΜΟΚΡΑΤΙΑ ΕΥΡΩΠΑΪΚΗ ΕΝΩΣΗ ΔΙΑΡΘΡΩΤΙΚΑ ΤΑΜΕΙΑ UNIVERSITY of FLORIDA

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SCOPE

The NAGC Workshops are held every two years, alternating between Cyprus and Greece. They were established to provide a regular forum for the faculty and students of universities in Greece and Cyprus to meet and interact with their North American counterparts, as well as a select few people from other European countries and elsewhere. The Republic of Cyprus has been very actively trying to build up its higher education institutions, particularly since it joined the European Union on May 1, 2004. Its first and still main university was founded just 16 years ago.

Following the outstanding success of the previous NAGC Workshops in 2005 and 2007, NAGC 2009 will again bring together a wide range of researchers working in diverse fields and applications. We anticipate that this NAGC workshop will be the biggest yet. The program will span various areas of chemistry, physics, and materials science, and encompasses any kind of study on any kind of system involving unpaired electrons: molecular or nonmolecular; organic, inorganic, biochemical or biological; ground state or excited state; solid, liquid or gas.

Note that this is not a magnetism workshop (although some talks may be on magnetic materials) – instead, it is the objective of the workshop to bring together people from very different areas who would not normally attend the same meeting, to listen and learn from each other. As a result, and for maximum benefit to everyone, it is expected that senior speakers will present talks that have a strongly tutorial component to them - perhaps 50% or so of the allocated time, with the rest on research results. Junior speakers (postdocs and students) will just present research results.

GENERAL INFORMATION

NAGC 2009 is held on the beautiful island of Cyprus in the eastern Mediterranean, in the Protaras region of the east coast. The accommodations and lecture facilities are situated in two adjacent beach hotels, the Vrissiana Hotel and the Constantinos the Great Hotel. Information about the hotels and the Protaras area may be found at the following websites:

http://www.vrissiana.com/
http://www.tsokkos.com/pages_eng/constantinos.php

Cyprus is an island of great beauty and archaeological interest, full of UNESCO World Heritage sites (of which ten are Byzantine churches). Other areas not to be missed are the capital Nicosia, Paphos on the west coast, and the central Mount Troodos (approximately 2000 metres or 6400 feet high) with its many picturesque villages. We have organize a half-day excursion as part of the workshop, to Kourion, one of the most famous tourist attractions in Cyprus, but there is much, much more worth seeing. For general information about the Republic of Cyprus, see:

http://www.visitcyprus.com/wps/portal

NAGC 2009 PROGRAM JUNE 15-19

ALL TALKS ARE IN THE CONSTANTINOS THE GREAT CONFERENCE ROOM

Monday June 15	Tuesday June 16	Wednesday June 17	Thursday, June 18	Friday June 19
Chair: R. Raptis	**Chair: A. Blackman**	**Chair: C. Kubiak**	**Chair: N. Frank**	**Chair: S. Hayes**
8.55-9.00 Welcome – G. Christou 9.00-9.30 C. Silva 9.30–10.00 G. Itskos 10.00–10.30 D. Kovala-Demertzi 10.30–11.00 D. Coucouvanis	9.00–9.30 M. Fardis 9.30–10.00 N. Frank 10.00–10.30 V. Tangoulis 10.30–11.00 C. Sanudo	9.00–9.30 K. Wieghardt 9.30–10.00 I. Margiolaki 10.00–10.30 K. Gordon 10.30–11.00 S. Hayes	9.00–9.30 A. Escuer 9.30–10.00 C. Raptopoulou 10.00–10.30 J. Zaleski 10.30–11.00 G. Papavasiliou 11.00–11.30 S. Hill	9.00–9.30 S. Pantelides 9.30–10.00 T. Stamatatos 10.00–10.30 A. Othonos 10.30–11.00 A. Blackman
11.00–11.30 Coffee Break	*11.00–11.30 Coffee Break*	*11.00–11.30 Coffee Break*		*11.00–11.30 Coffee Break*
			11.30–12.30 Quick Lunch	
Chair: S. Pantelides	**Chair: P. Koutentis**	**Chair: D. Coucouvanis**		**Chair: A. Veige**
11.30–12.00 D. Britt 12.00–12.30 V. Psycharis 12.30–12.45 A. Odysseos 12.45-1.00 S. Ioannou	11.30–12.00 A. Efstathiou 12.00–12.30 K. Preuss 12.30–12.45 A. M. Christou 12:45-13:00 C. Konstantinidis	11.30–12.00 S. Perlepes 12.00–12.30 L. Gahan 12.30–13.00 C. Kapnissi	**EXCURSION: DEPART 12.30**	11.30–12.00 N. Chronakis 12.00–12.30 R. Raptis 12:30–13:00 Y. Sanakis 13.00–13.15 C. Drouza 13.15-13.30 D. Dermitzaki 13.30 Closing Remarks
13.00–15.30 Lunch	*13.00–15.30 Lunch*	*13.00–15.30 Lunch*		
				Workshop Ends
Chair: S. Hill	**Chair: K. Gordon**	**Chair: S. Perlepes**		
15.30-16.00 P. Koutentis 16.00-16.30 A. Veige 16.30-16.45 K. Konidaris 16.45- 17.00 E. Moushi	15.30–16.00 N. Richards 16.00–16.30 A. Boudalis 16.30-16.45 M. Stylianou 16.45-17.00 C. Lampropoulos	15.30-16.00 D. Nocera 16.00-16.30 D. Veige 16.30-16.45 C. Krasos 16.45-17.00 K. Alexopoulou		
17.00–17.30 Coffee Break	*17.00–17.30 Coffee Break*	*17.00–17.30 Coffee Break*		
Chair: Y. Sanakis	**Chair: K. Preuss**	**Chair: A. Boudalis**		
17.30–18.00 G. Christou 18.00–18.30 S. Choulis 18.30–19.00 D. Koumoulis 19.00-19.15 E. Manos	17.30–18.00 V. Nastopoulos 18.00–18.30 C. Kubiak 18.30–19.00 T. Kyratsi	17.30–18.00 E. Leontidis 18.00–18.30 N. Aliaga-Alcalde 18.30–19.00 A. Dendrinou-Samara 19.00-19.15 N. Papatriantafyllopoulou		
	WORKSHOP DINNER		**EXCURSION DINNER**	
	Return to Hotels		Return to Hotels	

SOCIAL ACTIVITIES PROGRAM

1. **Sunday, June 14th**:

   Welcome Reception, 18:30.

   Vrissiana Beach Hotel (swimming pool bar area)

2. **Tuesday, June 16th:**

   Conference Dinner, 21:00.

   Departure from the hotels at 20:45

3. **Thursday, June 18th:**

   Conference Excursion and Dinner.

   Departure from Constantinos the Great hotel at 12:30

ACKNOWLEDGMENTS

The organizers wish to officially thank the following organizations and institutions that have contributed to the 3rd North America – Greece – Cyprus Workshop on Paramagnetic materials:

University of Cyprus

University of Florida

University of Patras

Inst. Mat. Science, NCSR ``Demokritos´´

Cyprus Research Promotion Foundation

Paralimni Municipality

Cyprus Tourism Organization

Cyprus Department of Antiquities

C. Georgiou Lab Supplies

Abstracts

Initial Employment of Pyridine-2,6-dimethanol as a Route to Polynuclear Divalent 3d- Metal Complexes

Nadia Alexopoulou,[a] Gina C. Vlachopoulou,[a] Matina Tsapardoni,[a] Catherine P. Raptopoulou,[b] Aris Terzis,[b]
V. Tangoulis,[c] Albert Escuer,[d] Th. C. Stamatatos*,[a], Spyros P. Perlepes*,[a]

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[d] *Departament de Quimica Inorganica, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain*
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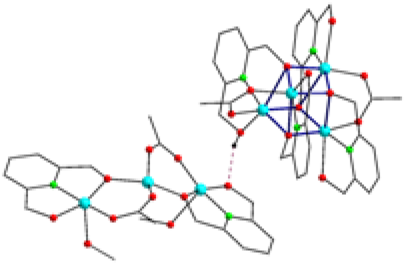
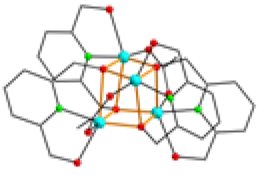
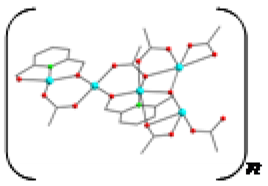
The last two decades have witnessed an explosive growth in interest in the polynuclear complexes (clusters) of 3d metals at moderate oxidation states with primarily oxygen- and/or nitrogen-based ligation. Among the diverse reasons for this are (i) the aesthetically pleasing structures that many such molecular clusters possess, (ii) the search for various nuclearity oxide-bridged metal clusters to model M_x sites in biomolecules, and (iii) the discovery of compounds with interesting magnetic properties, such as high-spin molecules and single-molecule magnets.

The future health of the field of 3d metal clusters will undoubtedly benefit from the continuing development of new synthetic procedures to high nuclearity species. There are now several empirically established approaches to a variety of clusters. In Mn and Fe chemistry, for example, alcoholysis has proven to be a very useful method for obtaining both oxo- and hydroxo-containing complexes. Another fertile approach is the investigation of new reaction systems using appropriate chelating organic ligands, such as those containing alkoxide or oximate functionalities since these are good bridging groups that can foster formation of polynuclear products. Indeed, alkoxide-based ligands such as deprotonated pyridyl alcohols, diols and triols, have yielded a number of 3d-metal clusters with various structural motifs and interesting magnetic properties. Across this line, we have recently started a program aiming at the systematic exploration of a pyridyl alcoholate ligand, namely pyridine-2,6-dimethanol ($pdmH_2$), in *divalent* 3d-metal cluster. Despite its rather extensive use in *trivalent* 3d-metal cluster chemistry, there has been only very limited use of $pdmH_2$ in Co^{II}, Ni^{II} and Cu^{II} chemistry. In the present talk, we shall describe our initial results on the reactions of $pdmH_2$ with Co^{II}, Ni^{II} and Cu^{II}. Emphasis will be given on the synthetic, structural and magnetic chemistry of the products.







Development of Nanomolecular Aggregates with Multifunctional Properties

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A major aim of nanochemistry is the rational synthesis of metallo-aggregates and self-assembled systems with new functions based on novel magnetic properties, light responsiveness, biomedical applications, catalytic activity, or redox properties, among others.[1-3] These useful and interesting properties may lead to the application of such assemblies in, for example, sensors, compact information storage devices for next-generation computers, catalysts in industrial processes, and medical applications such as implants, contrast agents for CAT scans, and others.[4-6] Therefore, a most challenging project is the development of organic-inorganic hybrid materials with emphasis on their multifunctional properties.

Our aim is the design, synthesis and characterization of molecular assemblies with a strong emphasis on their materials properties in order to develop homo and heterobimetallic aggregates incorporating d and f-orbital carriers. The synthetic approach in this project involves the specific combination of polydentate ligands that can accommodate a number of transition metals and lanthanides, providing interesting optic and/or electronic features, in conjunction with bridging ligands which allow and facilitate the magnetic communication among such metallic centers. In order to achieve this goal the present work engages the design of novel polyhydroxylated ligands.

[1] P. D. Beer, P. A. Gale, *Angewandte Chemie-International Edition* **2001**, *40*, 486.
[2] J. M. Lehn, *Reports On Progress In Physics* **2004**, *67*, 249.
[3] R. Neumann, M. Dahan, *Nature* **1997**, *388*, 353.
[4] A. Cornia, A. F. Costantino, L. Zobbi, A. Caneschi, D. Gatteschi, M. Mannini, R. Sessoli, in *Single-Molecule Magnets And Related Phenomena, Vol. 122*, **2006**, pp. 133.
[5] S. M. Saini, N. Singh, T. Nautiyal, S. Auluck, *Indian Journal Of Pure & Applied Physics* **2007**, *45*, 66.
[6] Y. Gandon, J. F. Heautot, F. Brunet, D. Guyader, Y. Deugnier, M. Carsin, *European Journal Of Radiology* **1991**, *12*, 195.

Molecular Inactivation: The Synthesis and Characterisation of Acid-stable Carbonate Complexes

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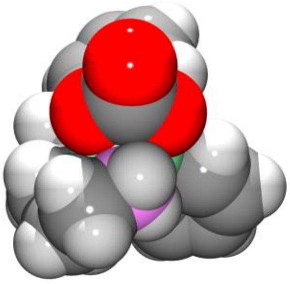
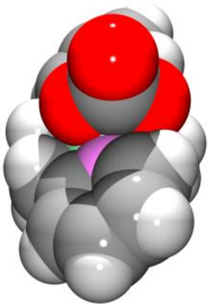
The reaction which dominates the chemistry of both free and metal-coordinated carbonate is its rapid reaction with acid to form CO_2(g). Carbonate can therefore be easily replaced as a ligand in a transition metal complex simply by treatment with acid, a reaction which has proven to be synthetically useful in the preparation of numerous coordination compounds.

We have prepared a series of complexes of general formula $[Co(N_4)O_2CO]^+$ (N_4 = a tripodal tetraamine ligand) which contain a chelated carbonate ligand. These complexes show extraordinary stability in aqueous acidic solution, having half-lives for hydrolysis in 6 M HCl ranging from minutes to days, and the stability appears to derive from the steric characteristics of the ancillary ligand. Such stability allows both protonation and metallation at the non-coordinated carbonate O atom to form rare chelated bicarbonate species and carbonate-bridged complexes, respectively. The carbonate complexes display an unusual range of colours due to the differing ligand-field strengths of the N_4 ligands, and this is also manifested in the range of ^{59}Co NMR chemical shifts.





The syntheses, structures and physical properties of these complexes will be reported. Results of DFT calculations aimed at understanding the nature of the bonding of the chelated carbonate ligand to the metal ion will be outlined. And finally, a justification for the discussion of Co(III) complexes at a Paramagnetic Materials Workshop will be given.

An old system revisited: Mössbauer and magnetic studies of two extended series of basic iron(III) carboxylates

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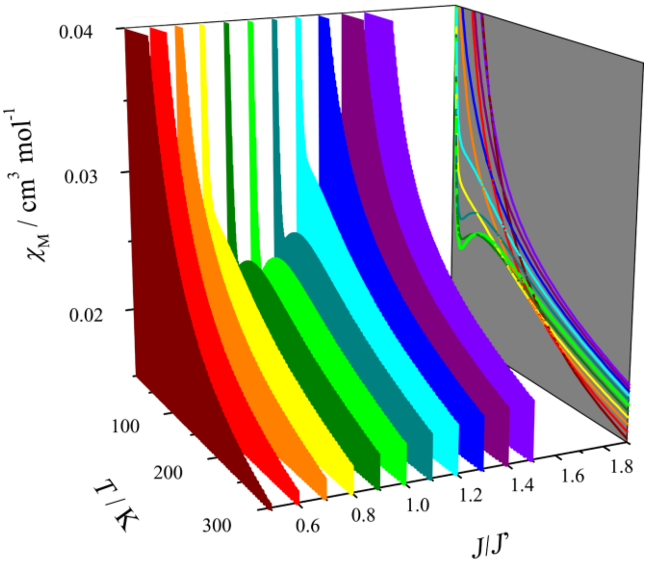
Basic iron(III) carboxylates are complexes of the type $[Fe_3O(O_2CR)_6(L)_6]^+A^-$, (L = terminal monodentate neutral ligand) and constitute a very well studied class of complexes. The field of research having mostly benefited from this family of complexes is the study of magnetic exchange between metal ions. Following Welo's magnetic studies and conclusions on their nuclearity [1], Kambe correctly interpreted the nature of the magnetic interactions within their cores [2], thus setting the foundation for the subsequent development of Molecular Magnetism.

Although great advances have been made in the understanding of these complexes, many issues still remain, concerning the precise nature of the magnetic interactions within their core and the influence of R and A^- on their properties. Here, we describe our spectroscopic and magnetic studies on two series of basic iron(III) carboxylate complexes $[Fe_3O(O_2CR)(H_2O)_3]A$ ($A^- = ClO_4^-$, NO_3^-), comprising twelve members each. Our approach is to study a large number of R/A^- variants with various techniques (magnetic susceptometry, and Mössbauer and EPR spectroscopies), instead of only studying a single complex. We thus hope to provide an extended body of experimental data, from which trends may emerge.



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[1] L. A. Welo, *Phil. Mag. 7th ser.*, **1928**, *6*, 481.
[2] K. Kambe, *J. Phys. Soc. Jpn.*, **1950**, *5*, 48.

Pulsed EPR Studies of Photosynthetic Pigment Synthesis Enzymes and the Oxygen Evolving Complex

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Photosynthesis efficiently converts solar energy to chemical energy, serving as a paradigm for designing practical solar bioenergy systems. One important aspect is light harvesting. We are using advanced EPR spectroscopy to study redox steps in the synthesis of light harvesting pigments. For example, linear tetrapyrrole pigments are used by cyanobacteria to gather light at wavelengths were the chlorophylls are poor absorbers. The parent molecule is biliverdin, but this is modified by specific enzymes to form an array of pigment molecules. We are targeting a ferredoxin dependent biliverdin reductase enzyme that uses two sequential PCET steps to reduce the two vinyl groups of biliverdin.

Advanced EPR is also being used to probe the substrate and amino acid coordination sphere of the Mn cluster of the Oxygen Evolving Complex of Photosystem II. A comparison of the spectroscopic results with the current state of X-ray diffraction models will be presented.

Advanced EPR includes the use of multiple frequencies, particularly high frequencies that require large magnetic fields, as well as pulse coherence methods such as ESEEM and HYSCORE and double resonance methods such as ENDOR.

Molecular Electronic Materials and Devices

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Molecular semiconductors are of increasing interest as new materials for electronic devices, owing to their easy processing on flexible substrates and potential for low-cost fabrication. Molecular light-emitting diodes, [1] field-effect transistors (FETs),[2] photodiodes, and solar cells [3] are the electronic applications under the most intense study. The presentation will discuss the material properties and device structures-design requirements for molecular electronic devices. The presentation will focus on the device physics parameters that control charge transport [4], charge injection/extraction [5], charge separation/recombination [6] and issues connected with their lifetime performance [7]. Several strategies for optimizing the above key parameters for high performance devices will be presented. Since this type of materials can be processed by solutions at low temperatures may ultimately allow for the printing of organic electronic devices. The application of printing technology as a fabrication tool indicates the potential of these novel materials for future electronic applications [8, 9].

[1] R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Bredas, M. L. Logdlund,W. R. Salaneck, *Nature 397*, 121, (1999)
[2] G. Horowitz, *Adv. Mater. 10*, 365, (1998)
[3] Kim, Y., Cook, S., Tuladhar, S.M., Choulis, S.A., Nelson, J., Durrant, J.R., Bradley, D.D.C., Giles, M., McCulloch, I., Ha, C.-S., Ree, M., *Nature Materials*, 5 (3), pp. 197-203, *(2006)*.
[4] Choulis, S.A. et al, *Applied Physics Letters*, 87 (11), (2005).
[5] Choulis S. A., et al., Advance Functional Materials, 16, 1975, (2006)
[6] Nelson, J., Choulis, S.A., Durrant, J.R., *Thin Solid Films*, 451-452, pp. 508-514. *(2004).*
[7] Hauch H et al, *Solar Energy Materials and Solar Cells*, .92, 727, (2008).
[8] Hoth, C.N, Choulis S.A., Schilinsky P and Brabec C. J., *Advanced Materials*, 19 (22), pp. 3973 (2007).
[9] Hoth, C.N, Choulis S.A., Schilinsky P and Brabec C. J., *Journal of Materials Chemistry*, accepted (2009).

Water Contamination by Pharmaceuticals: A New Environmental Public Health Concern

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Worldwide use of over-the-counter (OTC) and prescription medications continues to increase. In the United States alone, sales in the pharmaceutical industry generate over $200 billion each year [1]. This increasing usage of medications for a variety of human and animal purposes has led to concern about the fate and effects of these chemicals in the environment. Discharge of raw and treated sewage, excretion in feces and urine, bathing and improper disposal of unwanted medications has led to detectable concentrations of pharmaceuticals in surface water, ground water and treated drinking water all over the world [2]. The Associated Press has reported the presence of pharmaceuticals in the drinking water supplies of at least 46 million Americans [3]. Studies have also shown that existing surface and ground water contamination has the potential to disrupt aquatic life.

This talk will discuss the scope of worldwide pharmaceutical water contamination and the long-term implications to both humans and the environment.

[1] IMS Health. IMS Retail Drug Monitor January 2009. http://www.imshealth.com/imshealth/Global/Content/StaticFile/Retail_Drug_Monitor_January_2009.pdf. Accessed May 2009.
[2] Glassmeyer, Susan T., Hinchey, Elizabeth K., Boehme, Susan E., et al. Disposal practices for unwanted residential medications in the United States. *Environment International.* Volume 35. 2009.
[3] Associated Press. AN AP INVESTIGATION: Pharmaceuticals Found in Drinking Water. http://hosted.ap.org/specials/interactives/pharmawater_site/. Accessed May 2009.

Inorganic "Natural Product Synthesis": The Search for the Water Oxidizing Complex (WOC) of Photosynthesis

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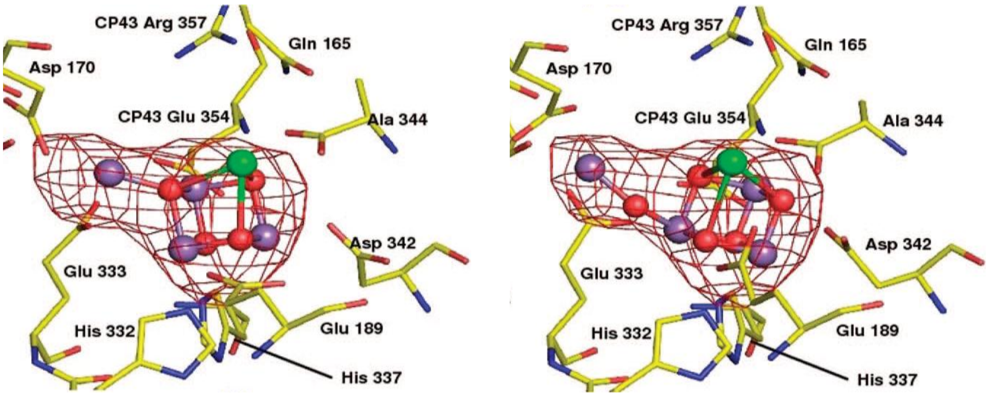
The water oxidizing complex (WOC), also known as the oxygen-evolving center/complex (OEC), is part of the photosynthesis apparatus of green plants, cyanobacteria and algae. It has long been known to contain four oxide-bridged Mn atoms, with organic ligation primarily by aspartate/glutamate side-chain carboxylates and some histidine imidazoles. Synthetic inorganic chemists have been seeking the synthesis of the WOC for over 30 years, but the absence of a crystal structure of the natural site has immensely hindered these attempts. Beginning in 2004, X-ray crystallographic data have become available at a sufficient resolution to provide structural information on the WOC, which is now realized to be a heterometallic Mn_4Ca cluster containing a Mn_3CaO_4 distorted-cubane with another Mn attached on the outside, most likely in one of the two ways shown [1, 2]. A more defined structural target is now available to synthetic chemists, and the field is re-energized.



Color code: Mn violet, Ca green, O red

My group has long been interested in synthesizing structural analogues of the WOC, and this talk with survey the various ups and downs we have encountered over the years in our bioinorganic project. Included will be complexes that we synthesized as potential WOC analogues but which also took us into molecular nanomagnetism directions.

[1] Ferreira, K.N., Iverson, T.M., Maghlaoui, K., Barber, J. and Iwata, S. Architecture of the photosynthetic oxygen-evolving center, *Science* **2004**, *303*, 1831–1838.
[2] Barber, J. Crystal structure of the oxygen-evolving complex of photosystem II, *Inorg. Chem*. **2008**, *47*, 1700-1710.

C_3-Symmetrical [60]Fullerene Trisadducts with Inherently Chiral Addition Pattern. Synthetic Methodology Utilizing Enantiomerically Pure *cyclo*-tris-Malonate Tethers

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The synthesis and characterization of [60] fullerene trisadducts with an inherently chiral addition pattern is a challenging topic in the area of fullerene chemistry[1]. Enantiomerically pure C_{60} trisadducts represent attractive building blocks for the construction of chiral macromolecular architectures such as dendrimers and spherical amphiphiles[2]. The tether-directed remote functionalization method utilizing optically active D_3-symmetrical *cyclo*-tris-malonate tethers was proved highly regioselective for the *all-e* addition pattern and afforded the ^{f}C- and ^{f}A-enantiomers in good yields. Separation and purification was achieved by flash column chromatography on SiO_2. Their enantiomeric relationship due to the inherent chirality of the *e,e,e* addition pattern is clearly reflected in their circular dichroism (CD) spectra, which show almost perfect mirror-image behaviour and pronounced Cotton effects[3]. Following the same concept, we have targeted the pure enantiomers of the *trans*-3,*trans*-3,*trans*-3 addition pattern in order to provide a complete methodology for the synthesis of all the pure enantiomers of C_3- and D_3-symmetrical trisadducts of C_{60} with an inherently chiral addition pattern. The synthetic methodology targeting the enantiomerically pure trisadducts of C_{60} with *e,e,e* and *trans*-3,*trans*-3,*trans*-3 addition pattern and the methods for their complete characterization will be presented.

[1] Djojo F., Hirsch A., Grimme S., *Eur. J. Org. Chem.*, **1999**, 3027.

[2] Nierengarten J. -F., Habicher T., Kessinger R., Cardullo F., Diederich F., Gramlich V., Gisselbrecht J. -P, Boudon C., Gross M., *Helv. Chim. Acta*, **1997**, *80,* 2238.

[3] Chronakis N., Hirsch A., *Chem. Commun.*, **2005**, 3709.

Synthesis structures and magnetic properties of 4,5-dithiocatechol. A new hybrid, “non-innocent” , ligand and its metal complexes.

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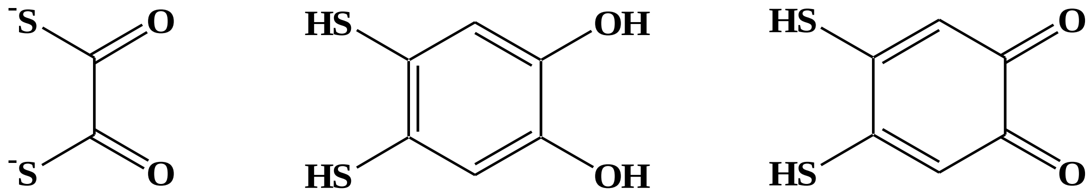
The origin of “non-innocense” for certain ligands often is attributed to a similarity in energy of metal orbitals to ligand based redox orbitals. In such situations the ambiguity concerning the site of oxidation or reduction within a coordination complex (metal vs. ligand) allows for an expression (and appreciation) of the ligand’s “non-innocense). A class of, structurally similar , non-innocent ligands are the dithiolenes, dioxolenes and o-phenylene diamines. The electronic structures and redox properties of their compounds are unique and have been studied and discussed in detail for many years, most recently by K. Wieghardt and coworkers.

The dithiooxolene-dithiolene “hybrid” molecules /ligands $H_2(Dtcat)$, (Fig. 1B), $(Dtcat)^{2-}$ $(Dtcat)^{4-}$, H_2Dtoq (Fig. 1C) and $(Dtoq)^{2-}$are unique non-innocent ligands and are either redox related or conjugate to each other.



A **B** **C**

Fig. 1

Until now the “parent” dithiocatechol (Fig. 1B) was not known. The 4,5 dithio-o-quinone, H_2Dtoq, (Fig. 1C) may be obtained by oxidation/deprotonation of the 4,5-dithio catechol , H_2Dtcat, (Fig. 1B). The deprotonated form of H_2Dtoq is expected to be more stable but functionally similar to the Dto ligand, (Fig.1A). The synthesis and structure of (1B), obtained as a Ph_4PBr double salt, $[Ph_4PBr^-]_2\,[(SH)_2C_6H_2(OH)_2]\cdot H_2O$ will be described. The syntheses molecular structures, electronic structures and magnetic properties of the $[(Dtcat^{2-})_2M][Ph_4P]_3Br_2$ complexes, (M = Ni ; M=Cu) also obtained as Ph_4PBr double salts, and of the dimeric $[(Dtcat)_2Fe]_2[Ph_4P]_2\cdot 4DMF$ complex as well as the $[(Dtoq)_2Ni][Ph_4P]_2$ and $[(Dtoq)_2Cu][Ph_4P]$, orthoquinone derivatives will be presented.

Tailoring the shape of magnetic nanoparticles

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Magnetic nanoparticles have attracted great interest because of their crucial applications in the fields of high-density magnetic storage devices, magnetic fluids, magnetic refrigeration systems, contrast enhancement in magnetic resonance imaging, magnetic carriers for drug targeting and catalysis. The large contribution of surface energy in nanoscale materials can stabilize and favor the origin of phases which are not known or thermodynamically unstable in the bulk. Synthetic control over the nanocrystal phase is therefore an additional degree of freedom in the search for new nanoscale materials property.

Continuing our studies[1] on controllable synthesis of magnetic nanoparticles, herein we report a facile one-pot chemical synthetic protocol for the controlled synthesis of i) fcc and hcp Ni nanoparticles, aiming to a better understanding of the role of amines as a factor governing the crystal structure and morphology of the obtained nanomaterials and ii) Co_xPt_{1-x} alloy nanostructures with morphologies that range from nanowires, 30 nm flower-like structures as well as ~ 3 nm spherical particles, via the thermal decomposition of cobalt precursors and platinum acetylacetonate in organic solvents. Parameters such as the concentrations of the starting reagents and the reaction temperature are the key factors for the structural properties of the nanomaterials. The magnetic features of fcc-Ni nanoparticles were quite similar to the corresponding 'bulk' ones. On the other hand, the hcp-Ni particles showed weak magnetic features, reflected by low magnetization values, the absence of saturation magnetization and by blocking temperatures far below room temperature. For the Co_xPt_{1-x} alloys, annealing at 700^{o}C in inert gas was proved to provoke the transformation to fct-CoPt, more 'ordered' phases, with 'harder' magnetic response, as shown by a remarkable increase in coercivity values, even at room temperature.

[1] K. Simeonidis, S. Mourdikoudis, I. Tsiaoussis, M. Angelakeris, C. Dendrinou-Samara, O. Kalogirou *J. Magnetism & Magnet. Mat.*, **2008,** *320*, 1631, b) S. Mourdikoudis, K. Simeonidis, I. Tsiaoussis, M. Angelakeris, C. Dendrinou-Samara, O. Kalogirou *J. Nanopart. Res.*, **2009,** 000

Synthetic Routes to 3d/4f-Metal Clusters Featuring the Methyl 2-Pyridyl Ketone Oximate Ligand

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Intense attention has been directed in the recent years toward the synthesis and magnetic study of polynuclear 3d-metal clusters, because some of them behave as single-molecule magnets, SMMs [1], providing a new "bottom-up" approach to nanoscale magnetic materials. On the contrary, 3d/4f-metal SMMs have been less investigated [2]. The advantages of using lanthanide(III) ions (Ln^{III}) in the synthesis of new SMMs are that these ions can provide both large spin (e.g., 7/2 for Gd^{III}) and considerable single-ion anisotropy. These properties could help to generate SMMs with properties different from those of homometallic, 3d-metal SMMs. We have thus joined ongoing efforts in this area and have focused to date primarily on Ni^{II}-containing species.

Two general synthetic approaches have been employed. The first is the "metal complexes as ligands" strategy. We use mononuclear Ni^{II} complexes with uncoordinated O-donor groups; such complexes can be considered as "ligands" (as a matter of fact "metalloligands") and further react with the oxophilic Ln^{III} ions. The second approach is based on "one-pot" procedures and requires a mixture of appropriate 3d- and 4f-metal starting materials, and a carefully chosen ligand featuring distinct coordination compartments for preferential binding of the transition metal ion and the lanthanide. We have been using the mononuclear complexes $[Ni(L)_2(LH)]$ (**1**), $[Ni(NO_3)_2(LH)_2]$ (**2**) and $[Ni(NO_2)_2(LH)_2]$ (**3**), among others, as metalloligands, where LH is methyl 2-pyridyl ketone oxime. We have up-to-now isolated three new families (**4**, **5**, **6**) of Ni^{II}/Ln^{III} clusters. Typical preparations are illustrated by the chemical equations (1)-(4):

$$\underset{\mathbf{1}}{[Ni(L)_2(LH)]} + Tb(NO_3)_3 \cdot 6H_2O \longrightarrow \underset{\mathbf{4}}{[NiTb(NO_3)_3(L)_2(LH)]} + 6H_2O \qquad (1)$$

$$2\,\underset{\mathbf{1}}{[Ni(L)_2(LH)]} + 2\,Dy(NO_3)_3 \cdot 6H_2O + 2\,Et_3N \longrightarrow \underset{\mathbf{5a}}{[Ni_2Dy_2(NO_3)_4(L)_6]} + 2\,Et_3NH(NO_3) + 2\,Et_3NH(NO_3) + 12\,H_2O \qquad (2)$$

$$2\,\underset{\mathbf{2}}{[Ni(NO_3)_2(LH)_2]} + 2\,Tb(NO_3)_3 \cdot 6H_2O + 2\,LH + 6Et_3N \longrightarrow \underset{\mathbf{5b}}{[Ni_2Tb_2(NO_3)_4(L)_6]} + 6\,Et_3NH(NO_3) + 12\,H_2O \qquad (3)$$

$$2\,\underset{\mathbf{1}}{[Ni(L)_2(LH)]} + Tb(NO_3)_3 \cdot 6H_2O + 2Et_3N \longrightarrow \underset{\mathbf{6}}{[Ni_2Tb(L)_6](NO_3)} + 2Et_3NH(NO_3) + 6H_2O \qquad (4)$$

Complex **6** can also be prepared by the reaction of **1** with **4** in the presence of a base. All the complexes have also been prepared by the "one-pot" approach. We shall briefly report the structures and preliminary magnetic properties for one representative member of each family of Ni^{II}/Ln^{III} complexes. Our initial synthetic work on the $Co^{II}/Ln^{III}/LH$ chemistry has led to $Co^{II}/Co^{III}/Ln^{III}$ clusters, e.g. $[Co^{III}_4Co^{II}Tb_2(OH)_4(OMe)_4(L)_8(MeOH)(H_2O)](ClO_4)_4$ (**7**).

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Vanadium (IV/V) Hydro/Semi-Quinonate Complexes

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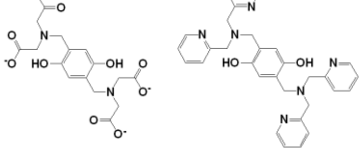
The investigation of the association between the electron and proton transfer in the metal ion - hydroquinone/semiquinone/quinone interacting systems is particularly important in order to understand the factors which regulate the redox potentials and the pathways in electron transfer reactions between transition metal centers and *p*-semiquinone radicals. The interaction of *p*-hydroquinones with vanadium in high-oxidation states presents additional interest due to the participation of vanadium in redox reactions in biological systems such as the reduction of vanadium(V), to vanadium(III) in the blood cells of tunicates.

Our focus in this work is on the synthesis and characterization in solid state and solution of stable complexes of vanadium with *p*-semiquinonate radicals as well as the investigation of the H^+ induced electron transfer between the V^{IV}/V^V metal centers and the coordinated semiquinonate/hydroquinonate ligands. Substituted hydroquinones with chelate groups (Scheme 1) were used to stabilize vanadium complexes. The V^{IV}/V^V–semiquinonate / hydroquinonate tetranuclear and dinuclear species produced from this electron transfer were isolated from aqueous solutions and the oxidation states of the ligand were indisputably determined by X-ray crystallography. UV-Vis and NMR spectroscopies and electrochemistry were employed for the investigation of the speciation and redox properties of these complexes in aqueous solution[1].



Scheme 1. Hydroquinone ligands.

Acknowledgements: The authors would like to thank PRF of Cyprus (ΑΝΑΒΑΘΜΙΣΗ/ΠΑΓΙΟ/0308/32) for their financial support.

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Towards Clean and Green Low-Temperature (T<200^{o}C) Industrial NO_x Control Catalytic Technologies for Stationary Sources: H_2-SCR?

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The current industrial practice for the catalytic removal of NO_x from the flue gas of *stationary polluting sources* (e.g., power plants, industrial furnaces, boilers and incinerator units) makes use of *ammonia* and *urea* as reducing agents mainly over V_2O_5/TiO_2 catalysts promoted with WO_3 or MoO_3, and also over some noble metal-supported catalysts operated in the 200-400^{o}C range (ammonia selective catalytic reduction, NH_3-*SCR* technology). However, this technology is under re-examination due to various technical (e.g. ammonia slip, corrosion of equipment, deposition of sulfate salts on heat exchangers) and operational problems, such as high investment and running costs.

The development of new industrial NO_x control catalytic technologies operated in the 120-180^{o}C range and based on other than ammonia reducing agents remains a very important target since it could reduce significantly the operational and investment costs compared to the present NH_3-SCR.

Hydrogen (H_2) appears to be a benign *clean* and *green reducing agent* for a potential H_2-*SCR* of NO_x catalytic technology (see reaction network below). Thus, if a catalyst with excellent activity and selectivity towards N_2 formation (X_{NO} and S_{N2}>90%) in the 120-180^{o}C range could be found, the development of H_2-SCR would pose as an alternative to NH_3-SCR *clean* and *green* NO_x control technology for many industrial applications (stationary sources).

$$2\,NO + 4\,H_2 + O_2 \rightarrow N_2 + 4\,H_2O \qquad (\Delta H^o = -\,573.7\ \text{kJ/mol NO}) \qquad (1)$$

$$2\,NO + 3\,H_2 + O_2 \rightarrow N_2O + 3\,H_2O \qquad (\Delta H^o = -\,411.9\ \text{kJ/mol NO}) \qquad (2)$$

$$H_2 + 1/2\,O_2 \rightarrow H_2O \qquad (\Delta H^o = -\,241.7\ \text{kJ/mol}\ H_2) \qquad (3)$$

The Heterogeneous Catalysis Laboratory of the University of Cyprus has developed a novel catalytic system that consists of nano-particles of Pt (d ~ 1.2 nm) deposited on a pre-sulfated mixed metal oxide of $MgO-CeO_2$ that enables the use of hydrogen in the 120-180^{o}C range to selectively reduce NO to N_2 gas under strongly oxidizing conditions (H_2-*SCR*)[1]. This novel catalytic system is under commercial exploitation by Linde Engineering AG (Geramny) through a License Agreement.

This novel catalytic system presents N_2 selectivities larger than 80% and NO conversions larger than 90% in the 140-180^{o}C range and in the presence of H_2O, CO_2, SO_2 and CO in the feed stream (NO=100-1000 ppm, O_2=0-5 vol%, H_2=0.4-0.8 vol%). This catalytic system was successfully deposited as a thin film (washcoat) on a ceramic monolith (cordierite) and the thus formed monolithic reactor was tested successfully under industrial flue gas conditions (power station).

This talk will review the current state of research in H_2-SCR both from catalyst development and performance and the fundamental catalytic chemistry point of view. For the latter, results from the use of isotopes and other transient techniques towards the elucidation of important mechanistic aspects of the H_2-SCR will be presented. For example, the effect of support, Pt metal particle size and reaction temperature on catalyst performance, the nature, location (metal vs. support) and surface concentration of active and inactive NO_x adsorbed reaction intermediate species, and the role of gaseous oxygen on the reaction rate and selectivity will be reviewed.

[1] A.M. Efstathiou, C.N. Costa, Jose-Luis G. Fierro, "Novel Catalyst for the Reduction of NO to N_2 with Hydrogen under NO_x Oxidation Conditions", US Patent No. 7,105,137 B2 (2006); EP No. 1 475 149 B1 (2008).

Serendipitous design of polynuclear systems with magnetic interest

A. Escuer

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The research interest of the Molecular Magnetism group in Barcelona is focused in the synthesis of high nuclearity/dimensionality magnetic systems. For years, our main target was the high dimensional M^{II}/pseudohalide chemistry with special attention to the azido derivatives but more recently, the synthesis of high nuclearity/spin clusters with magnetic interest is our principal goal.

In this talk, an overview of magnetic properties and synthetic strategies applied to our current work will be presented, which will include the study of the reactivity of politopic polinucleating ligands poorly explored until now, as pyridildioximato or diaminoalcoxo ligands, together with fully unexplored oximato ligands containing cyano or pyrazine groups. This search of new ligands is combined with the inclusion of azido ligand which joins its good donor character with the ability to generate ferromagnetic clusters with interesting magnetic properties, Fig 1.

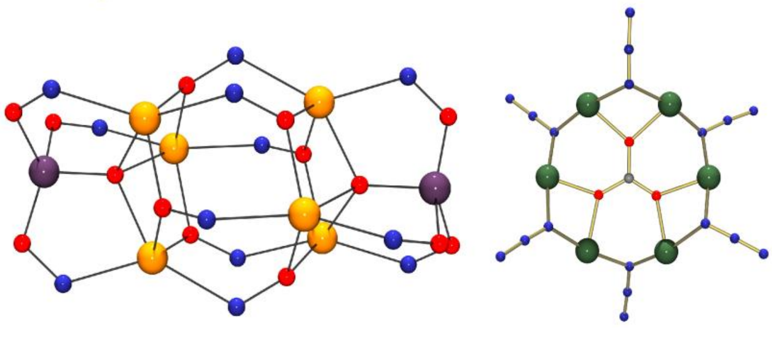

Figure 1. Left, octanuclear $Mn_6^{II}Mn_2^{III}$ cluster derived from 2,6-pyridildioximato (dapdoH$_2$). Righ, example of hexanuclear Ni^{II}/azido system template around of one 6.222 carbonate anion.

Superparamagnetism in Magnetic Nanoparticles as observed by Nuclear Magnetic Resonance relaxation

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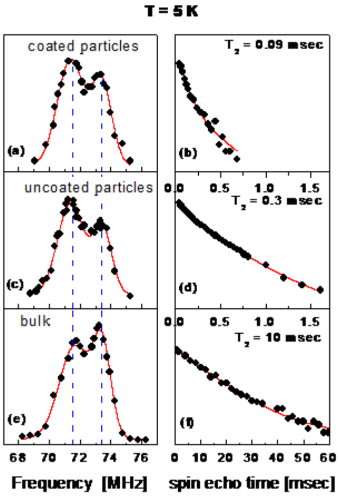
Superparamagnetism is a unique feature of magnetic nanoparticles. Since the pioneering works of Luis Néel on magnetic grains [1], superparamagnetism and the properties of magnetic nanoparticles have been widely studied both in basic and applied research. [2]

In the present work we report on the observation of Nuclear Magnetic Resonance (NMR) on a series of γ-Fe_2O_3, Co and $La_{1-x}Ca_xMnO_3$ nanoparticles. NMR is a local probe and has been frequently employed for the study of the static and the dynamic properties of magnetic materials. We demonstrate that the superparamagnetic features of the magnetic nanoparticles may be investigated using NMR relaxation. In particular, the T_2 spin-spin relaxation – which probes hyperfine filed fluctuations – can be used to elucidate the dynamic properties of single-domain nanoparticles as a function of temperature and size.



Zero magnetic field ^{57}Fe NMR spectra (left column) and T_2 relaxation decays (right column) of coated (a, b), uncoated (c, d) γ-Fe_2O_3 nanoparticles and bulk γ-Fe_2O_3 (e, f) respectively. The dashed lines in the NMR spectra correspond to hyperfine fields of 52 and 53.4 T. In the T_2 decays, note the difference in scale for the bulk material. The measuring temperature is 5 K.

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[2] S. Bedanta and W. Kleeman, J. Phys. D: Appl. Phys. **2009**, *42,* 013001.

Photoresponsive Magnetic Materials

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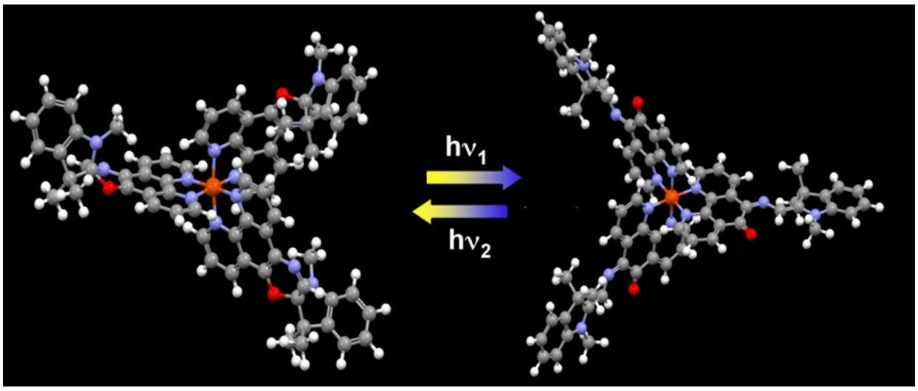
As we rapidly approach the physical limits of conventional silicon–based devices, the need for entirely new types of materials in the design of molecular electronics becomes necessary. Design and synthesis have led to the development of magnetic materials, nonlinear optical (NLO) materials, conductors, and superconductors in which careful design and synthesis leads to control of the bulk properties of the material. The possibility exists however, or creating hybrid materials, in which the magnetic, optical, or conducting functionalities can be combined into one material. The presence of two properties that exhibit cooperativity in the same crystal lattice may result in new physical phenomena and novel applications.



A particularly attractive goal is the design of molecular materials incorporating optical properties that are difficult or impossible to combine in a conventional inorganic solid with a continuous lattice. Toward this end, we have synthesized new classes of magnetic materials incorporating photochromic spirooxazine ligands. Three distinct magnetic motifs will be discussed: Tris(spirooxazine) metal complexes $M(SO)_3(BPh_4)_2$ (M = Fe^{II}, Fe^{III}, Cu^{II}, Mn^{II}, Ni^{II}, Co^{II}, SO= spirooxazine ligand), cobalt semiquinone complexes, and two-dimensional networks of Ni^{II} and Fe^{III} cations bridged by cyanide ligands. Changes in the strength of the ligand field associated with photoisomerization of the spirooxazines are evidenced, leading to switching of the relative populations of the redox and spin states of the central metal ion.

Structural and Catalytic Models for Phosphoesterases

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The prolonged and widespread agricultural application of organophosphate pesticides (OPs) has contributed to increased agricultural production but also to environmental problems[1]. OP-degrading compounds are therefore of interest for environmental detoxification and also as agents for protection against bioterrorism; the nerve gas agents VX and sarin are both OPs. As well, several of these OP-degrading enzymes, for example the Purple Acid Phosphatases (PAPs), are targets for drug design against a wide variety of human disorders [1,2].

Our principal interest is in systems which model the active sites of metallohydrolases, including PAP[1], the glycerophosphodiester degrading enzyme from *Enterobacter aerogenes* (GpdQ) and the structurally related triesterase from *Agrobacterium radiobacter* (OpdA) [2]. PAP is predominantly a phosphomonoesterase, while OpdA is primarily a phosphotriesterase. PAPs are the only binuclear metallohydrolases where the necessity for a heterovalent active site (Fe(III)-M(II), M = Fe, Zn or Mn) for catalysis has been established [1]. The enzyme isolated from mammalian organisms is a ~35 kDa monomeric protein with an asymmetric binuclear active site with a hard NO_5 Fe(III) site and a softer N_2O_4 divalent metal site (Figure 1). The promiscuous enzyme GpdQ shares six of seven donor ligands with PAP (Figure 2), the difference being the lack of a tyrosine ligand. The native metal ion composition of GpdQ is unknown, but enzymatic activity can be reconstituted in the presence of Zn^{2+}, Co^{2+} and Mn^{2+}. GpdQ is unusual in that it is a universal phosphoesterase [2].

We will discuss the aspects of the chemistry of the metalloenzymes themselves and report on attempts to synthesize structural and functional models.

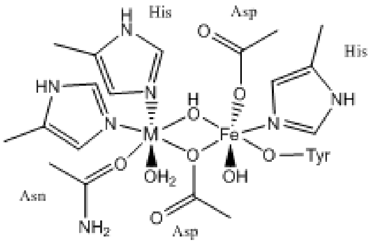

Figure 1

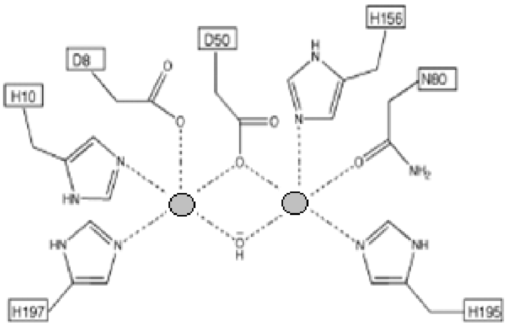

Figure 2

Acknowledgements: This work was funded by grants from the Australian Research Council (DP0558652 and DP0664039).

[1] F. Ely, J-L. Foo, C. J. Jackson, L. R. Gahan, D. Ollis, G. Schenk, *Current Topics in Biochemical Research.* **2007**, *9*, 63.

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Understanding molecular excited and polaron states using computational chemistry and spectroscopy.

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Molecular materials have the potential to dramatically change the face of the electronics industry. However molecular materials by their nature or much more varied in their properties than traditional semiconductor materials; the key intermediates that need to be understood in these systems are polarons and excited states. are interested in trying to aid the design of new molecular electronic materials by understanding the type and extent of interaction that occurs to the electronic structure when units are covalently linked. We have used density functional theory to model these interactions; validating the calculations using vibrational spectroscopy. Using this strategy we have provided design inputs to: dramatically improve absorption cross sections in porphyrin systems; understand reactivity in conducting polymer growth; understand coupling properties in organic light emitting diode materials; develop new materials with potential in solar cells. This talk will present some of our work in these areas, illustrating the synergies between synthesis, spectroscopy and theory.

UV Resonance Raman Spectroscopy as a Tool for Structure Determination: Application to TTR(105-115).

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Understanding the various interactions between amino acid residues or backbone groups that determine protein structure, involves probing the local environment they experience upon folding. Resonance Raman (RR) spectroscopy has been used extensively for investigation of structure and structural changes in a variety of protein systems, where it can observe overall secondary structure, as well as probe local structural changes involving amide groups, aromatic side-chains, and protein cofactors. As the structure of a protein in solution might differ from that in the solid state, where it is usually studied by x-ray diffraction, it is critical to possess a tool that provides insights on the structure in the native environment.

This tutorial will review the use of RR as such a tool, as well as present our efforts in characterizing the conformation of the 11-residue peptide TTR(105-115) (YTIAALLSPYS) in solution. TTR(105-115) is part of the sequence of the human amyloid-forming protein transthyretin, corresponding to a naturally-occurring β-strand in the crystal structure of the protein. This peptide fragment has been shown to form ordered amyloid fibrils *in vitro*, constituting it an ideal model for the study of fibril formation in general.

Our present studies have provided insights on the conformation of this peptide in different environments that serve as a first step in understanding the structural changes that lead to fibril formation, our long-term goal. Tyrosine has been reported repeatedly in the past, as part of UVRR studies, to be a good probe for investigating the local environment of a protein. Therefore, we focused our efforts on the characterization of the environment experienced by tyrosines in the peptide, via determination of the pKa of the tyrosine side-chains, as well as a function of temperature and solvent.

[1] Z. Chi X. G. Chen, J. S. W. Holtz, S. Asher, *Biochemistry* 1998, **37**, 2854.

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EPR Spectroscopy at the National High Magnetic Field Laboratory: Shameless Advertising

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Most electron paramagnetic resonance (EPR) research is performed at the X-Band frequency of 9.5 gigahertz (GHz). More specialized commercial instruments also exist operating at K-Band (25 GHz), Q-Band (35 GHz) and W-Band (95 GHz). The EPR facilities at the US National High Magnetic Field Laboratory (NHMFL) offer scientists from all over the world opportunities to use several home-built, high-field/high-frequency instruments providing continuous coverage from 9 GHz to 1 terahertz (THz), with additional discrete frequencies available up to 2.5 THz using a molecular gas laser. Magnets are also available providing fields up to 45 tesla. EPR performed at high frequencies and fields can offer tremendous advantages for certain problems spanning diverse research fields from condensed matter physics, to chemistry, to biology. These advantages include: increased ability to resolve small differences in Landé g values; the ability to study anisotropic magnetic ions with large energy splittings in zero-field (e.g. transition metals); enhanced sensitivity to small samples; and the possibility to study magnetic relaxation effects on very short time scales. The facilities at the NHMFL offer the highest frequencies and fields for both continuous-wave and pulsed EPR anywhere in the world. After an introduction to high-field EPR, this talk will provide an overview of the kinds of research conducted at the NHNFL, both by in-house scientists and by our external users. As such, this talk represents a shameless exercise in advertising, albeit with the goal of attracting new users from the participants of this workshop.

Spin Injection from Paramagnetic and Ferromagnetic Contacts into Semiconductor Structures

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The use of the spin degree of freedom is explored in the emerging field of spin electronics or spintronics. Spin-based electronics have the potential to be faster, smaller in size and more energy efficient compared to conventional electronics. A spin-based technology requires the realization of a spin-device that can perform simultaneously memory and logic operations: the spin transistor. A necessary requirement for the realization of such a device is the efficient injection, transport, control and detection of spins in a semiconductor structure.

Modified light emitting diodes known as spin-LEDs[1] employ a magnetic contact to electrically inject spin-polarized carriers into a semiconductor diode structure. The radiative selection rules directly relate the spin polarization of carriers injected from the magnetic contacts to the optical polarization of the emitted light. Spin-LEDs have been the only semiconductor spin-based structures where the combined efficiencies of spin-injection/transport/detection can be investigated reliably and in a model-independent way. The talk will review our work on various spin-LED structures where electrical spin injection is provided by paramagnetic semiconductor1 and ferromagnetic metal[2,3] contacts into semiconductor quantum well and quantum dot structures.

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TRAPPING OF NORADAMANTENE AS ITS NICKEL COMPLEX: A USEFUL COMPLEX FOR THE FORMATION OF ORGANIC POLYCYCLIC COMPOUNDS

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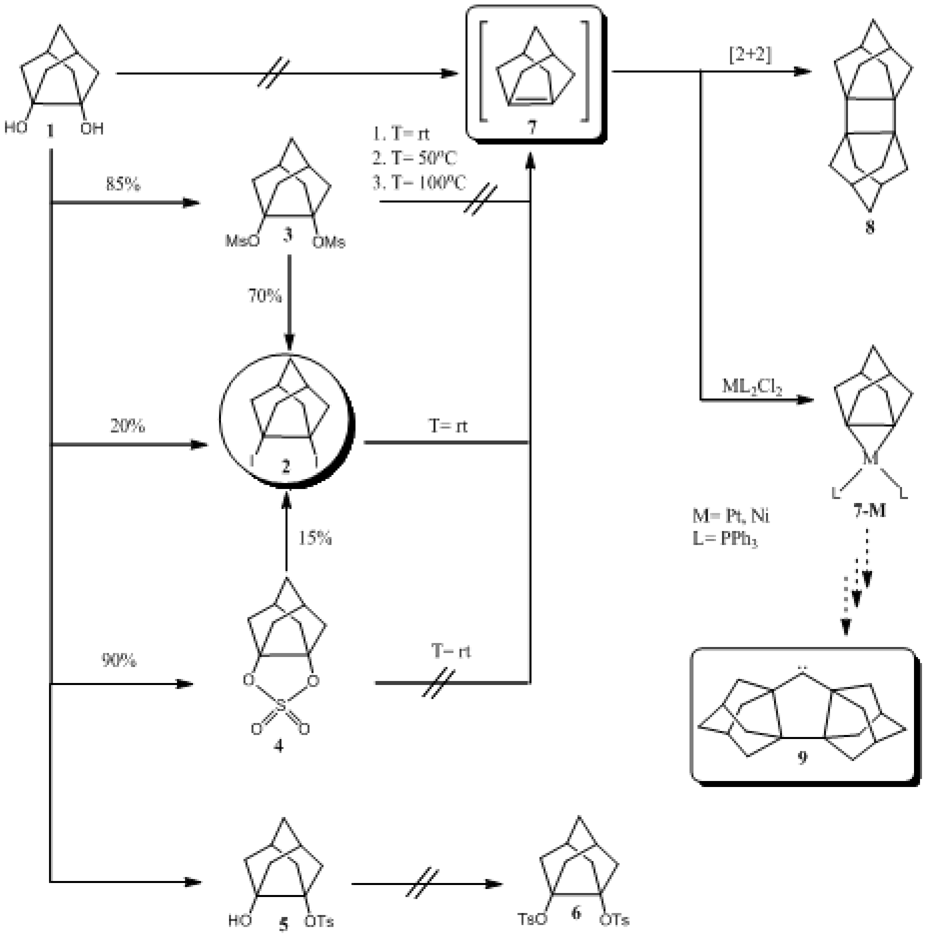
In pyramidalized olefins, unlike the common olefins which have planar geometries, the doubly bonded carbons have a pyramidal geometry.[1] The strain of the double bond increases as the pyramidalization of the carbon increases. The highly pyramidalized alkene **7** is very reactive and is not isolable at ambient conditions. If **7** is generated in solution in the absence of a trapping agent, the formal [2+2] cycloaddition product **8** is isolated. Olefin **7** has been trapped with dienophiles to give the corresponding Diels-Alder products.

The purpose of this research project is the isolation of the nickel complex **7-Ni**.[2] This complex is expected to be a very useful intermediate for the synthesis of larger polycyclic compounds with theoretical interest like carbene **9**.[3]



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Capillary Electrophoresis: Important Tool for Clinical, Toxicological and Pharmacological Applications

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The main objective of this research is the separation of nine cholinesterase inhibitors by use of capillary electrochromatography (CEC) and micellar electrokinetic chromatography (MEKC). Cholinesterase inhibitors [rivastigmine, edrophonium chloride, pyridostigmine bromide, neostigmine bromide, galanthamine, eserine or physostigmine, methylphysostigmine, eseroline fumarate, and 1,5-Bis(4-allyldimethylammoniumphenyl)pentan-3-one dibromide] are a class of drugs approved by the U.S. Food and Drug Administration to treat Alzheimer's disease (AD) and Myasthenia Gravis (MG). In both CEC and MEKC, different polymers and polymeric surfactants are used for optimizing the separation conditions. Additionally, in this study, the open-tubular (OT) mode of CEC is used, in which fused-silica capillaries coated with thin films of physically adsorbed charged polymers are developed by use of a polyelectrolyte multilayer (PEM) coating procedure. The PEM coating is constructed *in situ* by alternating rinses of positively and negatively charged polymers. In addition, MEKC is used for the chiral separation of huperzine A. Huperzine A is an important compound used to treat AD. However, only the (-) form of this compound is biologically active, while the (+) form can inhibit the activity of the (-) form. Therefore, the separation of the (-) form from the (+) form of huperzine A is of greatest importance, particularly in the pharmaceutical industry. Finally, optimum conditions are applied to blood samples in order to establish the ability of the methods to separate the drug compound rivastigmine from all the other components that might exist in the blood sample.

In situ monitoring of Cement Gel growth dynamics. The use of a miniaturized permanent Halbach magnet for precise ^{1}H NMR Studies

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The most critical parameter that affects important cement paste properties, such as strength, shrinkage, creep, and permeability, is its pore structure [1]. Pores in hydrated cement form an extremely complicated network, with a very broad size distribution, ranging from nanometers to millimeters [2], which changes with the chemical composition, relative humidity, temperature, and applied load. Here, without recourse to drying methods, we monitor the evolution of the pore structure during the progressive hydration and setting of three white cement pastes with different hydration kinetics. By combining ^{1}H NMR spin-lattice relaxation T_1 and diffusion measurements performed in a portable 0.29 Tesla Halbach magnet, it is possible to distinguish among gel and capillary pores, and study the growth dynamics of cement gel (T_1 measurements), and the associated shrinkage of the capillary pore system (diffusion measurements). In this way, aspects of the hydration kinetics are unveiled, which are difficult to observe with other techniques.

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Zn^{II}/Pyridyl Oxime Complexes: Synthesis, Structural Characterization and Biological Activity

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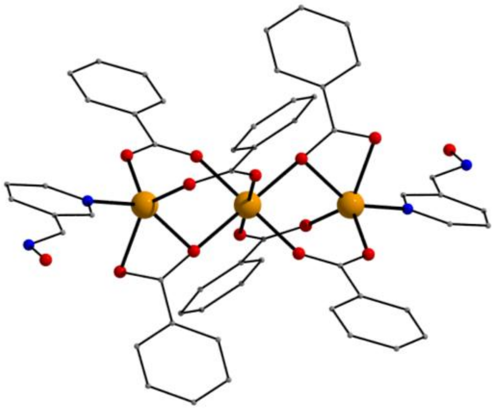
There is currently a renewed interest in the coordination chemistry of oximes. The research efforts are driven by a number of considerations, concluding the solution of pure chemical problems, the desire to provide useful bioinorganic models, the application of metal ion/oxime systems as simple and efficient catalysts, and the employment of oximate ligands in the synthesis of homo- and heterometallic clusters and coordination polymers with interesting magnetic properties [1]. Furthermore, the strong nucleophilicity of the oximate anion, $RCH{=}NO^-$, is associated with many biological processes, such as the transfer of an acyl, phosphoryl or a sulfuryl group by attacking an electrophilic center. Among these actions, the fact that a series of pyridyl oximes have the ability to reactivate the enzyme acetylcholinesterase (AChE), when it is fully inhibited by organophosphorous compounds, is of particular pharmacological interest. The coordination chemistry of pyridyl oximes with Zn(II) is poorly studied. Our interest in this chemistry is focused on (i) the synthesis of Zn(II)/pyridyl oxime complexes and the study of their physical properties, e.g. photoluminescence, and ii) testing the nucleophilic properties of selected new complexes in biological substrates.

Employing a series of pyridyl oximes as ligands, such as (2-py)C(R)NOH [R = -H, $-CH_3$, $-NH_2$], (3-py)C(H)NOH, (4-py)C(H)NOH) etc. and various synthetic procedures, a number of Zn(II)/pyridyl oxime complexes have been isolated and structurally characterized, e.g.: $[Zn(O_2CMe)_2\{(2\text{-}py)C(H)NOH\}_2]$ (**1**), $[Zn(O_2CPh)_2\{(2\text{-}py)C(Me)NOH\}_2]$ (**2**), $[Zn(O_2CMe)_2\{(2\text{-}py)C(NH_2)NOH\}_2]\cdot(NO_3)$ (**3**), $[Zn_3(O_2CPh)_6\{(3\text{-}py)C(H)NOH\}_2]$ (**4**) and $[Zn_2(O_2CPh)_4\{(4\text{-}py)\ C(H)NOH\}_2]$ (**5**).



The biological evaluation of selected compounds by a) DNA binding/cleavage experiments and b) the reactivation of inhibited-AChE by selected Zn(II)/pyridyl oxime complexes, is under investigation.

Acknowledgements

We thank the Research Committee of the University of Patras (C. Karatheodory Programme 2008, No C.584) for funding this work.

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The NMR and Neutron Scattering signature of charge and spin stripes in $La_{1-x}Ca_xMnO_3$ (x>0.5) manganites. Striking similarities and differences with underdoped $La_{2-x}Sr_xCuO_4$ cuprates.

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Understanding the intriguing properties resulting from the interplay between magnetic, charge and orbital degrees of freedom in strongly correlated heavily doped manganites (x>0.5), still remains a highbrowed field for the study of unconventionally condensed matter physics phenomena. Such phenomena are presumably due to the cohesion/balance between localization forces such as repulsive Coulombic forces (electron-electron repulsion) and the delocalization effects (elastic or kinetic energy) which have tendency to produce an inhomogeneous spin/charge distribution in the overdoped region of manganites. Recently, X-ray diffraction and neutron scattering studies in heavily doped manganites revealed the formation of superstructures with special periodicities associated with the presence of superlattice magnetic and structural Bragg peaks. Correlations between these magnetic/structural superlattices and stripe ordered phases have been found in other complex oxides such as high-T_c cuprates, cobaltites and nickelates. Moreover, a link between stripe ordering and wipeout effect of the NMR/NQR signal was observed in lightly doped high-T_c superconductors. Here we will demonstrate that the results obtained by NMR and neutron scattering in overdoped manganites confirm the same phenomenology with underdoped cuprates. In the overdoped region of manganites the wipeout effect and the temperature dependence of the NMR linewidths is consistent with the presence of a peculiar spin/charge order at temperatures T<30K. This temperature is consistent with both the magnetization measurements (SQUID) and the spin-spin relaxation time (T2) results. The mechanism at microscale remains unclear, but may be due to static incommensurate magnetic order like the stripe type charge – ordered antiferromagnetism or static lattice inhomogeneities (Jahn – Teller effect).

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Synthesis and Chemistry of New Benzo[1,2,4]triazine Radicals

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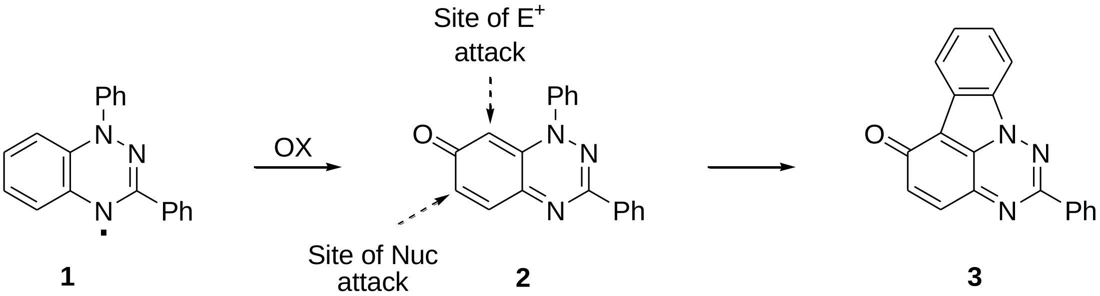
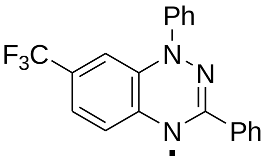
1,3-Diphenyl-1,4-dihydro-1,2,4-benzotriazinyl **1** has been prepared from the *N*-phenylbenzamino phenylamidrazone.[1] Studies have shown the radical, which displays antiferromagnetic interactions[2] at low temperatures, to be "stable indefinitely"[1] or even "superstable".[3] In our hands the radical was found to suffer from oxidation leading to the formation of 1,3-diphenylbenzo[*e*][1,2,4]triazin-7(1*H*)-one **2**. The synthesis and chemistry of this heterocyclic quinonimine is investigated and leads to the synthesis of the alkaloid like triazafluoranthenone **3**. Further studies identify 7-trifluoromethyl-1,3-diphenyl-1,4-dihydro-1,2,4-benzotriazinyl **4** that is resistant to analogous oxidation and surprisingly displays 1D-ferromagnetic interactions in the crystalline state. An improved parallel synthesis of a variety of benzotriazinyl analogues is presented which affords rapid access to this "born again" radical.





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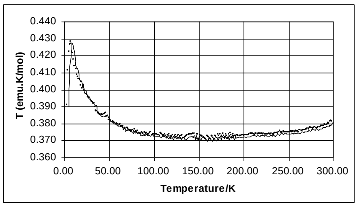
1D-Ferromagnetic Behaviour



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Recent advances on non-steroidal anti-inflammatory drugs, NSAIDs: transition metal complexes and organotin adducts of NSAIDs

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Synthesis and study of metal complexes with active drugs as ligands is a research area of increasing interest for inorganic, pharmaceutical and medicinal chemistry and has concentrated much attention as an approach to new drug development. The goal is to prepare new compounds with better or different pharmacological profile than that of the free ligand.

Non-steroidal anti-inflammatory drugs, NSAIDs, from the carboxylic acid family, derivatives of N-phenylanthranilic acid, such as tolfenamic acid, diclofenac acid and mefenamic acid, flufenamic, meclofenamic, and from the oxicam family, piroxicam, tenoxicam, meloxicam, lornoxicam and isoxicam, are widely used in inflammatory and painful diseases of rheumatic and non-rheumatic origin. The anti-inflammatory activity of NSAIDs and most of its other pharmacological effects are related to the inhibition of the conversion of arachidonic acid to prostaglandins, which are mediators of the inflammatory process.

An overview is given of the results of metal-NSAIDs and organotin-NSAIDs interactions. Several transition metal complexes and organotin adducts with NSAIDs, derivatives of the carboxylic acid family and oxicam family, have been synthesized and characterized by spectroscopy and x-ray crystallography at the University of Ioannina.[1,2]

Results concerning the biological activity of these metal complexes and organotin compounds will be referred.

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Theoretical investigations on the isomerization of aziridine

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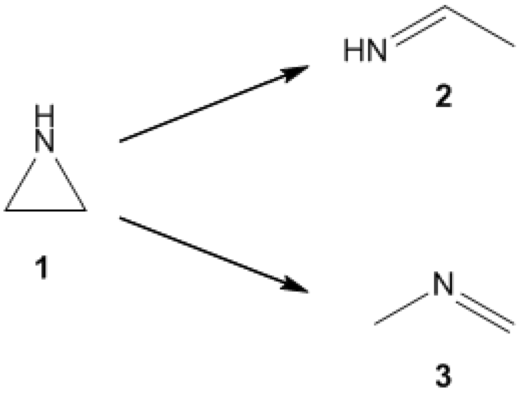
The thermal ring opening of cyclopropane has been studied extensively both experimentally and computationally. The ring-opening of aziridine (**1**) is less well known. Substituted aziridines are known to ring-open via cleavage of the C-N or the C-C bond leading to the formation of derivatives of ethanimine (**2**) or N-methylmethanimine (**3**) respectively, depending on the nature of the substituents.

Various possible pathways have been studied computationally involving either C-N or C-C bond cleavage of the aziridine system, in an effort to map its potential energy surface and identify important intermediates and transition states involved in this isomerisation process.



Electron Self-Exchange between Trinuclear Ruthenium Clusters: Proton Coupled Mixed Valency

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Electron self-exchange rate constants for trinuclear ruthenium clusters of the type $[Ru_3O(OAc)_6(CO)(L)_2]^{0/-}$ where L is 4-cyanopyridine, pyridine, or 4-(dimethylamino)pyridine were determined by ^1H NMR line broadening experiments in CD_3CN, CD_2Cl_2, and THF-d_8, and range from $6.5x10^6$ to $2.5x10^8$ s^{-1} M^{-1}. Faster self-exchange is observed with more electron withdrawing substituents on the ancillary pyridine ligands. This effect is attributed to increased orbital overlap between donor and acceptor as more electron density is drawn onto the pyridine ring. This view is supported by measured NMR contact shifts of the pyridyl protons which reflect increased electron spin density with increasing pyridine ligand electron withdrawing ability.

These rate constants are comparable in magnitude to those found by NMR line broadening methods for many other 0/+ and 0/- couples, though the range seen here of more than an order of magnitude of difference is remarkable for analogous self-exchange couples. The large difference in electron density on peripheral ligands leads to large differences in electronic coupling between neutral (diamagnetic) and reduced (paramagnetic) clusters, and the self-exchange must be in the adiabatic regime to achieve rate constants of 10^6 - 10^8 s^{-1} M^{-1} for clusters with reorganization energies on the order of 1 eV. Recent results in self-exchange reactions between hydrogen bonded nicotinic acid substituted ruthenium clusters will be described. Differences between binding constants nicotinic acid hydrogen bonded dimers in the isovalent and mixed valent states provides a direct thermodynamic measurement of the electronic coupling matrix element, H_{AB}, in these systems.

Optimizing Thermoelectric Materials

Application of Powder Techniques on Nanocomposite Chalcogenides

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In the last decades there has been a great interest on the field of thermoelectrics. Some of the more significant features of thermoelectric modules include the ability to heat and cool with the same module, the ability to generate electrical power from "waste" energy, precise temperature control, spot cooling, friendliness and sensitivity to the environment, small size and weight and having no moving parts. Candidate materials for thermoelectric applications should possess high electrical conductivity, (σ) high Seebeck coefficient (S) and low thermal conductivity (κ), in order for the thermoelectric figure of merit $ZT=\sigma S^2T/\kappa$ to be maximized.

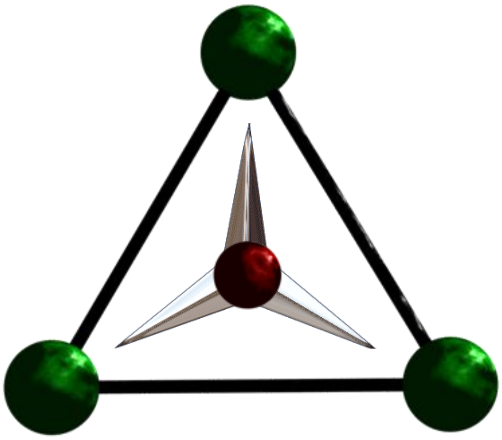
This presentation consists of two parts. The first part includes an introduction to the families and the properties of thermoelectric materials. Optimizing techniques such as the design of complex structured materials and the fabrication of nanocomposite materials will be also presented.

The second part focuses on our research results on chalcogenide compounds with promising thermoelectric properties. In alkali bismuth chalcogenide compounds, the alkali metals tend to create structural complexity in the crystal, which in turn can lead to complex electronic structure, high Seebeck coefficient and low thermal conductivity. Powder techniques, based on mechanical alloying and sintering process, are applied in order to prepare nanocrystalline materials of such complex chalcogenides as well as of PbTe-based systems. In both systems, such techniques are applied aiming to fabricate nanocomposite materials with improved properties.

Homo- and Heterometalic Manganese Triangles: New Single-Molecule Magnets, and Probes of Magnetic Interactions and Spin Frustration Effects

Christos Lampropoulos, Alina Vinslava, Khalil Abboud, and George Christou

Molecular magnetism refers to the study of the magnetic properties of individual molecules, some of which behave as single-molecule magnets (SMMs). A SMM derives its properties from a combination of a large ground-state spin (S) value and an Ising (easy-axis) type of magnetoanisotropy (negative zero-field parameter, D). Several complexes have been identified as SMMs, but only a handful containing a triangular core. Molecular triangles are of interest since they display in some cases spin-frustration effects, which lead to unusual ground state spins. Therefore, we have recently initiated efforts to target small molecules in order to further address the unusual SMM behavior of triangular SMMs, and deeply investigate spin-frustration effects. From this initiative three new triangular clusters will be discussed, one heterometallic $Mn^{IV}Gd^{III}_2$ complex, and two homometallic Mn^{III}_3 compounds. All three complexes have a triangular metal topology, bridged by a single oxide, giving an overall $[M_3O]^{n+}$ core. The comprehensive magnetic study of these complexes, a magnetostructural correlation, and theoretical investigation of spin-frustration effects will be discussed.



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Lampropoulos, C.; Vinslava, A.; Abboud, K. A.; Christou, G. *Inorg. Chem.* **2009**, *submitted*.

Silica-embedded cobalt and iron oxide nanoparticles: A novel synthetic procedure based on metal glycerolate complexes

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In previous work [1] we found that small ZnO nanoparticles, uniformly dispersed in amorphous silica, could be prepared using a three-step procedure involving zinc glycerolate. This procedure was further generalized and applied to cobalt and iron oxides [2]. The procedure involves three steps: (a) Preparation of the metal glycerolate particles under reflux conditions with a direct reaction between a metal salt and glycerol in the presence of organosilanes. (b) Copolymerization of the particles, the surfaces of which are suitably activated with the organosilanes, with tetraethyl- or tetramethyl-orthosilicate, to produce silica monoliths containing well dispersed metal centers. (c) Calcination of the thus formed composites at high temperatures and formation of metal oxide nanoparticles embedded within the silica framework.

The materials were characterized using HR-TEM, ED, and powder XRD. The surprising finding is that during step (b) the strong interaction of the surface of the glycerolate particles with the surrounding silicate medium leads to localized "dissolution" of the particles in the silica matrix. The magnetic properties of some cobalt oxide-containing composites were examined. M-H curves prove that cobalt oxide loses its antiferromagnetic properties in these materials, either because very small superparamagnetic particles are formed, or because of other surface spin confinement effects. These materials are still under study. A major issue is to improve step (a) of the synthesis by carrying out the reactions in confined spaces to guarantee that the size of the intitial glycerolate particles is in the range of nm. Such very small particles are much easier to disperse in the silica monoliths and lead to composite materials with more structural uniformity. The strength of the current procedure is its capability to combine more than one guest oxides in silica, thus potentially leading to interesting combinations of properties.

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Sequestration of Heavy and Radioactive Metal Ions from Water with Layered Metal Sulfides

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Clean water is of vital importance for humans; still, more than one billion people lack access to it. Heavy metal ions such as mercury, lead and cadmium and radioactive ions (e.g. $^{89}Sr^{2+}$) are released to the environment from industries (nuclear industry, industries producing electric lamps, gauges, batteries, chemicals, thermometers, paper etc) and other sources (e.g. mines) and constitute a serious health threat for humans and other species. Ion-exchange is a relatively low cost and very efficient method to eliminate toxic and radioactive ions from water. Inorganic ion-exchangers are generally of higher chemical, thermal and radiolytic stability as well as more affordable compared to the organic resins. The ion-exchange chemistry of metal sulfides is relatively unknown compared to that of oxidic ion exchangers. The affinity of their soft basic frameworks for soft (e.g. Hg^{2+}, Cd^{2+}, Pb^{2+}) or relatively soft (Cs^{+}, Sr^{2+}) Lewis acids is innate to these materials. Therefore, metal sulfide-based ion exchangers would be ideal candidates as highly selective sorbents for removal of heavy metal ions and some radioactive cations from water solutions.

In this presentation, the synthesis, characterization and investigations of the ion-exchange properties of layered metal sulfides are reported.[1] We demonstrate that these materials are a) exceptionally selective for Cs^{+} and Sr^{2+}, the radioactive versions of which represent major contaminants in the fission product of nuclear wastes and b) superior as heavy metal ion sorbents over known materials. These ion exchangers are inexpensive, easily prepared in large quantities and may play a role in addressing the global problem of water contamination with heavy and radioactive metal ions.

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Complementary methods for the study of biomaterials.

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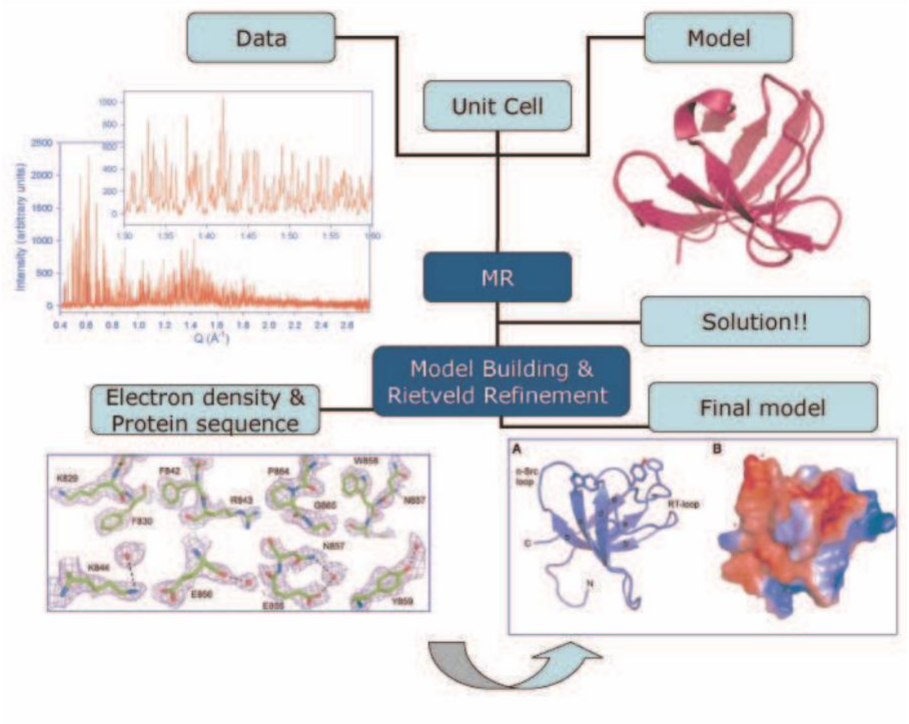

Figure 1: Powder diffraction data analysis procedure followed for structure solution via the molecular-replacement method, model building and structure refinement. The data and model shown correspond to the second SH3 domain of ponsin[2] and final omit maps are shown on the lower left.

Studying biological macromolecules in the absence of good quality single crystals is a challenging field attracting considerable scientific interest. Modern developments of X-ray powder diffraction have allowed the structural investigation of a range of proteins establishing the method as a useful complementary tool to traditional approaches.[1] Protein powder specimens consist of a large number of randomly oriented diffracting micro-crystals which are usually formed rapidly by batch crystallization under a variety of conditions. An overview of the most recent developments in this field will be presented including: (a) application of the molecular replacement technique and structure refinements of selected proteins (b) methods for successful cryocooling (c) experimental phasing and extraction of molecular envelopes (d) high throughput automated data collection allowing systematic investigations such as screening and phase diagram mapping and (e) application of the method on biologically interesting proteins.

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A Mn_{17} Octahedron with a Giant Ground-State Spin: Occurrence in Discrete Form and as Multidimensional Coordination Polymers

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The current intense interest in Manganese-carboxylate chemistry has resulted to a number of beautiful complexes, some of which contain a large number of metal ions (up to 84).[1] The main reason for this interest is the fact that such molecules can function as magnets below a critical temperature, providing a new 'bottom-up' approach to nanoscale magnetic materials.[2] Although there are now many species displaying SMM behavior, there is a continuing need for new structural types. One of the most successful synthetic approaches to new polynuclear clusters involves the use of chelates containing alcohol groups, since alkoxides are good bridging groups and thus favor the formation of polynuclear products.[3] Recently, we have been investigating the use of 1,3–propanediol (H_2pd) and 2-methyl-1,3-propanediol (H_2mpd) in Mn carboxylate chemistry.[4,5] A $[Mn^{III}_{11}Mn^{II}_6(\mu_4\text{-}O)_8(\mu_3\text{-}L)_4]^{25+}$ (L=N_3^- or OCN^-) octahedral unit is reported, occurring within 1D $(\mathbf{1})_\infty$- $(\mathbf{3})_\infty$ and 2D $(\mathbf{4})_\infty$ coordination polymers, as well as the corresponding 0D discrete cluster **5**. It possesses a giant ground-state spin value, determined in the case of **5** to be S=37, the second largest to be reported to date. In addition, compound **5** displays single-molecule magnet (SMM) behavior, and is thus the largest-spin SMM.

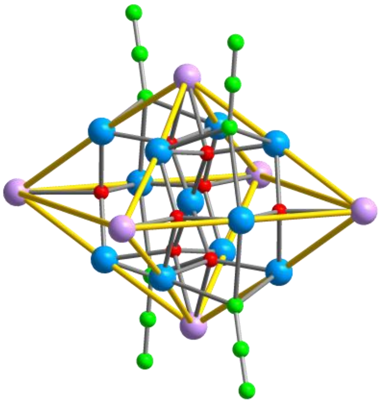

Figure: The structural core of the Mn_{17} repeating unit; The purple line connecting the manganese ions is to emphasize the octahedral topology.

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Crystal Polymorphism: Theoretical and Practical Aspects

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A polymorph is defined as a solid crystalline phase of a given compound resulting from the possibility of at least two different arrangements of the molecules of that compound in the solid state (McCrone)[1]. Commonly, polymorphism is divided into two types based on the geometry of molecular assembly in the crystal lattice: i) *Packing polymorphism*: packing the same molecules into different arrangements; it involves *rigid* molecules and the differences in the packing are directed by the intermolecular interactions. ii) *Conformational polymorphism*: packing conformational isomers into similar or different arrangements; it involves changes at the molecular level and occurs predominantly in *flexible* molecules. In addition, crystals formed by the same substance crystallized with different amounts or types of solvent molecules (resulting in large changes in crystal packing and density) are usually termed as *pseudopolymorphs*. The geometrical arrangements in polymorphic structures are governed by the competing thermodynamic and kinetic factors of the crystallization process[2].

Polymorphism is an interesting phenomenon because it induces important differences in the properties (e.g. physicochemical, electrical, optical) of the various forms. This has broad practical and economic implications for a number of industries, including pharmaceutical (drugs), textile (dyes and pigments), defense (high energy materials) etc.

Theoretical and practical aspects of polymorphism will be presented. These include thermodynamic and kinetic relations, control of polymorphic crystallization, concomitant and disappearing polymorphs, analytical techniques for studying and characterizing polymorphs, polymorphism and structure-property relations and polymorphism of substances of particular interest. Examples from the literature will be used to illustrate those concepts. Our initial results on polymorphic metal complexes will be reported.

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Self-Repairing Catalysts

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Multi-electron redox reactions of small molecules such as H_2O, O_2, N_2, and CO_2, entail that the metal centers of catalysts occupy multiple oxidation states that cycle among paired and unpaired spins. Because the most stable ground state of a metal in widely varying oxidation state and spin often possesses very different coordination environments, the same ligand field cannot stabilize the system across the entire multielectron transformation. If a ligand field is imposed about the metal, then excess overpotential will be introduced into the redox cycle. This talk will present a strategy to overcome this hurdle. By introducing a repair mechanism, the constraint of a structurally stable catalytic center may be relaxed while retaining functional stability at a low overpotential. Catalytic water-splitting will be the exemplar for the principle of self-healing.

Novel Superparamagnetic Hybrid Micelles Based on Iron Oxide Nanoparticles and Diblock Copolymers for In Vivo Molecular Imaging and Targeted Therapy

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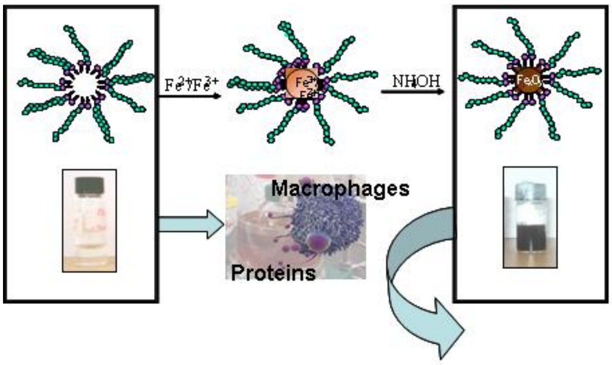
Molecular imaging (MI) is a growing research discipline aimed at developing and testing novel tools, reagents and methods to image specific molecular pathways in vivo[1]. MI is a multidisciplinary approach, involving (**a**) identification of a marker of disease, (**b**) attaching an appropriate beacon to the marker (e.g a metallic nanoparticle), affixed to the targeted marker via a chemical reaction or interaction, and (**c**) detection of the beacon and concentration indirectly by using magnetic techniques. While optical imaging techniques can detect molecular structures in pM concentrations and are three-six order of magnitude more sensitive than currently available MRI techniques, innovative MR contrast agents such as magnetic nanoparticles are expected to change MRI into a truly molecular imaging modality. While first generation nanoparticles were fairly non-specific, newer generations have been targeted to specific molecular targets via affinity ligands[1]. The ultimate goal is the creation of "theranostic" nanoagents, thus enabling the targeted diagnosis and treatment of disease.



Herein, we present a series of novel hybrid micelles based on iron oxide nanoparticles and well-defined diblock copolymers, as potential superparamagnetic contrast agents for MRI molecular imaging. The incorporation of β-ketoester ligands in well-defined, water-soluble and thermoresponsive diblock copolymers, consisting of poly (ethylene glycol) methyl ether methacrylate (PEGMA) and 2-(acetoacetoxy)ethyl methacrylate (AEMA) enabled the stabilization of iron oxide magnetic nanoparticles in water *via* encapsulation within the AEMA ligating core[2] of the block copolymer micelles generated by the aforementioned diblock copolymers in water. Morphologies as well as magnetic, optical and thermal properties of the resulting magnetic macromolecular aggregates were assessed. These materials exhibit superparamagnetic behavior which is tunable depending on the amount of iron oxide loaded inside the micellar core. Importantly, further to their magnetic properties, our results show that the novel superparamagnetic hybrids exhibit excellent biocompatibility as determined by the MTT cell viability assay, while upcoming animal studies will be essential to confirm their safety for clinical applications. Additionally, comparison with the clinically approved agent Resovist®, reveals that the novel superparamagnetic hybrids are largely excluded from macrophages and therefore from reticuloendothelial compartments, a property relating to their well-characterized PEGMA_x-*b*-AEMA_y outer shell and assuring prolonged circulation half-lives and improved in vivo efficacy. Hence these novel superparamagnetic hybrid self-assemblies are expected to have distinct and valuable biodistribution characteristics, rendering them potential candidates for applications in MRI molecular imaging and targeted drug delivery.

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Femtosecond Spectroscopy: *Probing Ultrafast Dynamics in Nanostructures*

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Advancements in ultrafast laser technology have provided the means for studying the dynamics of processes that may occur on a very short timescale that are of interest and significant in physics, chemistry, biology and most areas of science and technology. In our laboratory we utilize femtosecond laser spectroscopy to investigate the dynamics in semiconductors[1], nanostructures and organic materials thus gaining further insight into the fundamental nature of such material systems that are of interest for potential light emitting devices, photovoltaic devices, and for optoelectronic devices in general.

A typical ultrafast spectroscopy system consists of a Kerr-lens mode-locked Ti:sapphire oscillator producing femtosecond pulses typically 2nJ/pulse and centered around 800 nm. These pulses are used to seed a 1kHz Ti:sapphire amplifier system which generates ultra-short pulses with energy of about 2mJ per pulse thus amplifying 10^6 time the initial pulse. Under such excitation conditions one is able to observe and utilize nonlinear processes that are not possible under normal CW excitation conditions. The amplified laser pulses in conjunction with non-linear crystals in *Optical Parametric Amplifiers* and *White Light Super-Continuum Generation* provide tunable ultrafast pulses ranging from the UV to the IR part of the spectrum. Specially designed optical setups to minimize dispersion effects of the above propagating ultrafast pulses along with pump-probe techniques are employed in resolving the various interactions and process within the materials under investigation. We will discuss these pump-probe techniques utilized at the *Research Center of Ultrafast Science* alone with resent work on probing carrier dynamics in nanostructures.

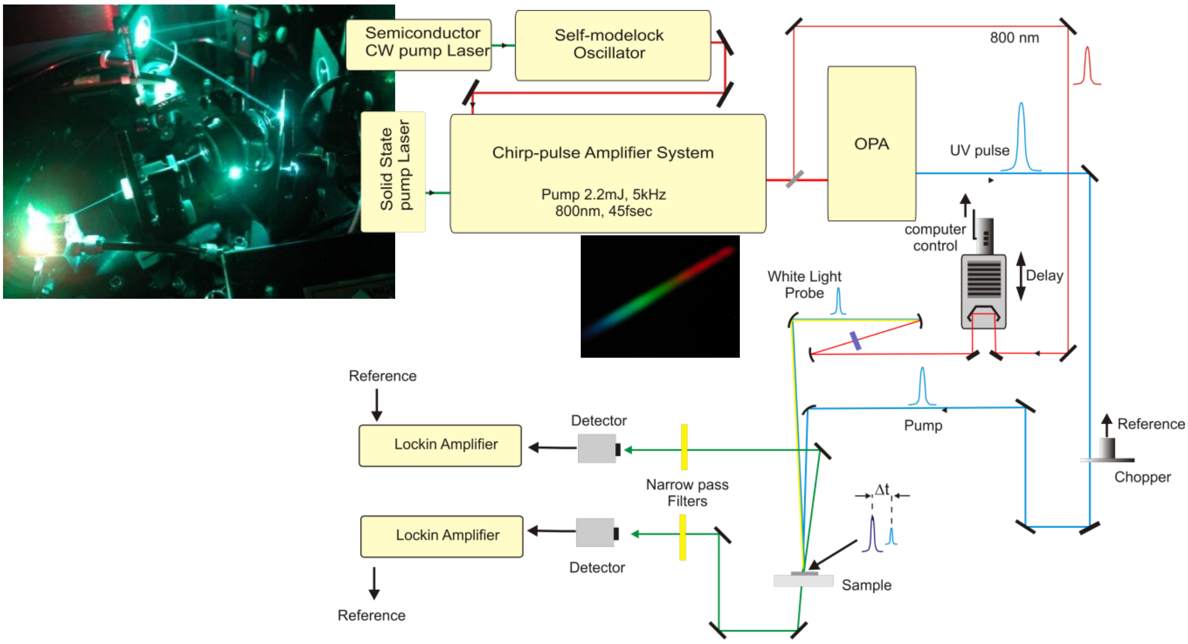

***Figure**: A pump-probe setup utilized to measure the induced absorption following femtosecond pulse excitation. The upper picture shows the TiSapphire oscillator pumped by a semiconductor cw laser at 532 nm.*

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Materials physics using a combination of density-functional theory and atomic-resolution electron microscopy

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This talk will mirror the broad range of systems and topics covered by the conference. It will use examples from a 15-year collaboration, involving numerous associates in both theory and microscopy, to illustrate the synergistic relationship between the “theoretical microscope” provided by first-principles density-functional calculations and the “experimental microscope”, a scanning transmission electron microscope capable of atomic-resolution Z-contrast imaging and electron-energy loss spectra (EELS). Both techniques are directly applicable to a wide range of materials, including semiconductors, metals, insulators, superconductors, etc. In some cases, such as segregation of As in Si grain boundaries, theory made predictions and Z-contrast imaging confirmed. In others, such as Ca segregation in MgO grain boundaries, microscopy found the unexpected, and theory provided an elegant explanation. Yet in other cases, such as the role of La in stabilizing catalytic γ-alumina, theory and microscopy independently arrived at precisely the same results and accounted for observations. In other cases, such as the role of Ca impurities in enhancing the critical current in polycrystalline high-temperature superconductors and the mechanism of room-temperature ferromagnetism in Co-doped TiO_2, all three ingredients (theory, imaging and EELS) were absolutely necessary to resolve long-standing puzzles. Finally, theory played a predominant role in accounting for the extraordinary catalytic properties of gold nanoparticles.

2-Pyridyl Alcohols/Carboxylate/Azide Combination for the Construction of Manganese Clusters: Structural and Magnetic Characterization

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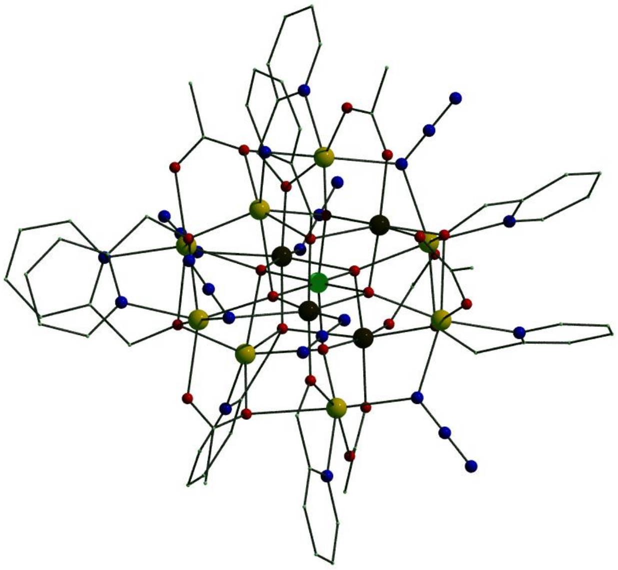
Synthetic procedures to new high-spin molecules are of continuing importance in order not only to discover new SMMs but also for a fundamental understanding of high-spin species. Large *S* values can result from ferromagnetic (or ferrimagnetic) spin alignments and/or from competing antiferromagnetic interactions (spin frustration) in certain M*x* topologies that prevent (frustrate) perfectly antiparallel spin alignments.

One of our approaches to new high-spin complexes is to employ bridging ligands that typically give ferromagnetic interactions and which can thus increase the chances of a large ground-state *S* value. The azide (N_3^-) group bridging in the 1,1-fashion (*end-on*) mode gives a ferromagnetic interaction for a wide range of M-N-M angles.[1] The initial simultaneous employment of *end-on* N_3^-s and carboxylates in Mn chemistry of 2-pyridyl alcohols led to rare nuclearity's Mn clusters with novel structural types and interesting magnetic properties. The structural variation derived by the incorporation of the N_3^-s and the resulting changes in the nature of the magnetic coupling between the metal centers will be discussed.



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Adventures in the Metal Cluster Chemistry of Di-2-Pyridyl Ketone and Related Ligands

Theocharis C. Stamatatos,[a] Constantinos G. Efthymiou,[b] Constantinos C. Stoumpos,[a] Spyros P. Perlepes[a,*]

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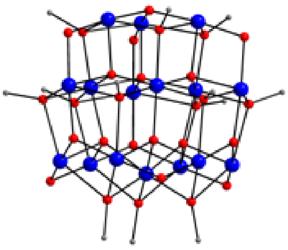
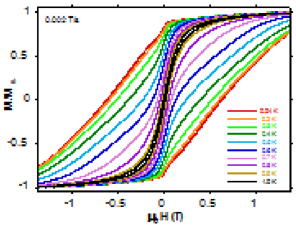
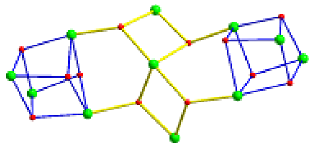
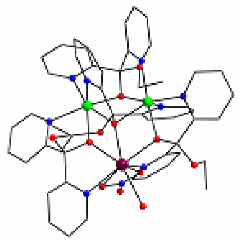
We shall give in our talk an overview of the metal cluster chemistry of ligands with the general formulae X-CO-X, X-CO-Y, X-CO-CO-X and X-CO-X-CO-X, where X and Y are donor groups.[1] Emphasis will be given on the coordination chemistry of di-2-pyridyl ketone.[2,3] Much of the chemistry, both published and unpublished, that will be reported comes from our group; however, reference to all appropriate work from the groups of Christou, Boudalis and Mak will be provided. The activation of the carbonyl group(s) of some of the ligands towards further reactions seems to be an emergent area of synthetic inorganic chemistry. The structural diversity of the complexes stems from the ability of the deprotonated diol- or hemiketal-type ligands to adopt a variety of bridging coordination modes depending on the number of carbonyl groups, the nature of the extra donor groups in the molecules and on the reaction conditions. Employment of a second organic or inorganic ligand in this chemistry gives an extraordinary structural flexibility in the resulting mixed-ligand systems.









The examples that will be given in our talk will hopefully serve to emphasize the breadth of the coordination chemistry of, and current interest in, di-2-pyridyl ketone and related ligands. This area of research has something for everyone: from organic and inorganic synthetic chemistry to metal complexes with impressive structures, and from high-spin molecules to single-molecule magnets.

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Metal Coordination Complexes and Salts of New Paramagnetic Thiazyl Quinones: Conductivity and Magnetic Properties

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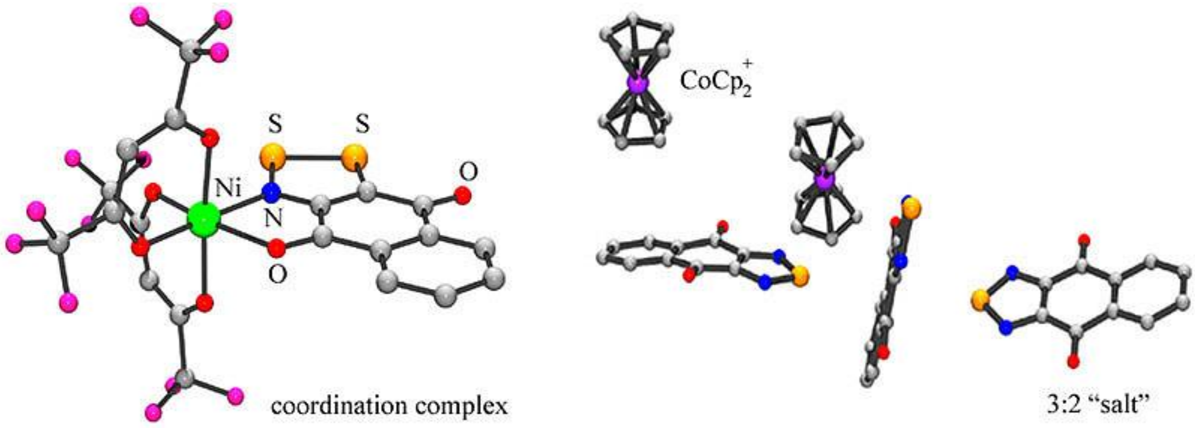
Thiazyl-based radicals, and their selenium analogs, continue to enjoy extensive investigation as potential neutral radical conductors[1], charge transfer salt donors (i.e. radical cations)[2], organic molecular magnets[3], and bistable systems.[4] Broadly stated, the goal of our research is to develop paramagnetic ligands from thiazyl radicals (and their Se analogs) in order to create new molecular species with enhanced magnetic and/or conductive properties.

Of the projects we are currently undertaking, the most interesting new results involve the combination of a paramagnetic thiazyl moiety and a quinone moiety. Novel coordination species of neutral radical ligands and semiconductive charge transfer salts of radical anion species have been prepared (examples shown in the figure below). Incorporation of Se is also under investigation. Current unpublished results will be discussed.



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Molecular Magnets and organic conductors with Modulated structures

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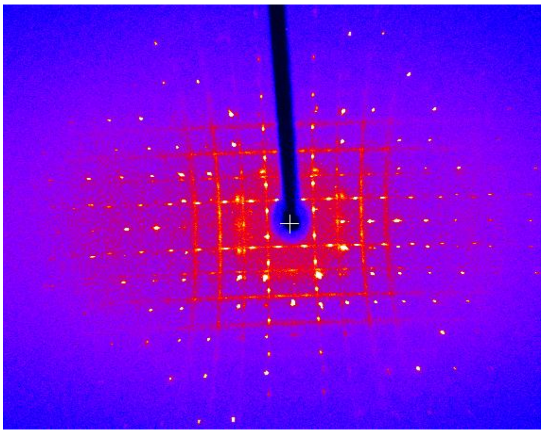
The installation in our Institute, of the Rigaku R-axis diffractometer with an Image Plate as detector has given us the opportunity to analyze in addition to compounds that crystallize as simple single crystals, compounds that form crystals with more complicated structures. An interesting case to study is the case of crystal that have a modulated structure. The modulated structures usually are a result of a phase transition at low temperatures and give characteristic diffraction patterns. The basic ideas for the interpretation of the diffraction patterns will be discussed and first results from the analysis of two such systems, one belonging to the organic conductors and the other to molecular magnets will also be presented.



Trinuclear and Hexanuclear Mixed-Valent Cu-Complexes

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A rigid [Cu-(μ-pz*)]$_3$ metallacycle (pz* = pyrazolato ligand) supports the pH-controlled equilibrium between pyramidal μ_3-OH and planar μ_3-O. The latter species is redox active forming a stable mixed-valent $[Cu_3(\mu_3\text{-}O)]^{5+}$ analogue, which has been classified as Robin-Day type-III species (delocalized) by analysis if their NIR intervalence charge transfer (IVCT) band.[1, 2] This $Cu^{II/III}$ complex is a structural analogue of the proposed catalytic intermediate of particulate Methane Monooxygenase (pMMO). Coupling of two [Cu-(μ-pz*)]$_3$ units into an hexanuclear trigonal prismatic [Cu-(μ-pz*)]$_6$ complex (Figure 1) leads to redox activity involving all-six Cu-centers.[3] The electronic structure of the trinuclear and hexanuclear complexes has been probed by spectroelectrochemistry, magnetic susceptibility measurements and theoretical calculations.

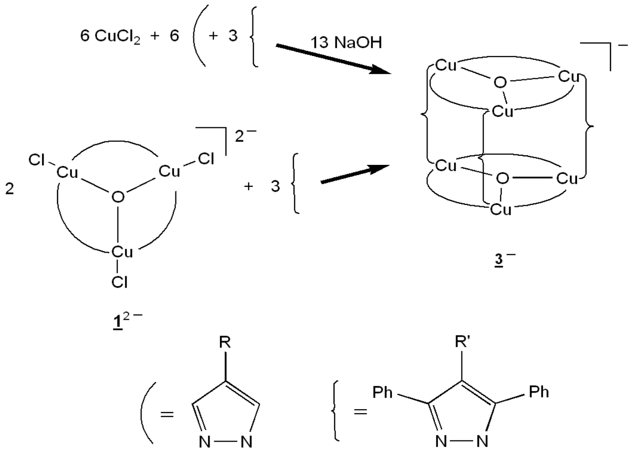

Figure 1.

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Maleamate(-1)/Copper(II)/*N*,*N*'-, *N*,*N*',*N*''-chelates Complexes: Synthetic, Reactivity, Structural and Physical Studies

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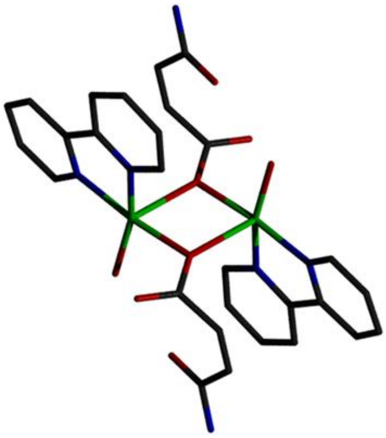
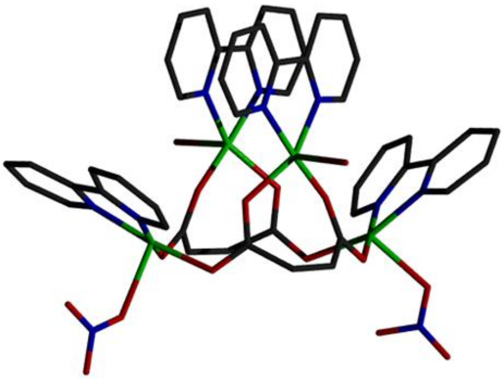
The use of maleamic acid (HO_2C-CH=CH-$CONH_2$, H_2L) in copper(II) chemistry in the presence of *N*,*N*'-chelates (1,10-phen, 2,2'-bpy) and *N*,*N*',*N*''-chelates (terpy, bppy, tptz) afforded mononuclear, dinuclear and tetranuclear complexes and 1D coordination polymers, which represent the first structurally characterized maleamate complexes of any metal. The influence of various synthetic parameters, such as the reaction solvent, the presence or absence of externally added hydroxides, the inorganic anion in the copper(II) salt, the stoichiometry of the reactants and the crystallization method, to the chemical and structural identity of the products has been investigated. H_2L adopts various coordination modes including the novel O-amide ligation. Interesting Cu^{II}-assisted/promoted transformations of HL^- to L'^- (^-O_2C-CH=CH=COOMe, monomethyl maleate(-1) ligand) and L''^{2-} (^-O_2C-CH=CH-CO_2^-, maleate(-2) ligand) were observed under certain reaction conditions. The crystal structures of the complexes are stabilized by intra- and inter-molecular hydrogen bonding and π-π stacking interactions to interesting supramolecular patterns.





How Protein Structure Controls Chemistry in Mn(II)-Dependent Oxalate-Degrading Enzymes

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The molecular mechanisms by which “second sphere” functional groups in metalloenzyme active sites can modulate transition metal reactivity are only just beginning to become understood[1]. This lecture will describe current ideas about how the protein environment controls the intrinsic chemistry of the high-spin Mn(II) center(s) in the enzyme oxalate decarboxylase (Figure)[2]. Experimental and computational strategies to investigate these hypotheses will be briefly outlined, together with a discussion of how our findings provide new information on the extent to which active site residues must be modified in an existing enzyme to evolve a “new” activity.

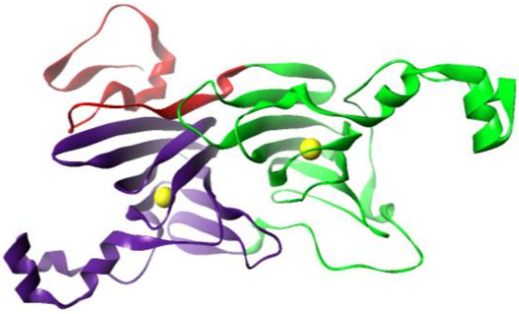

Figure: Cartoon representation of the oxalate decarboxylase monomer showing the location of the bound Mn(II) ions (yellow spheres).

[1] Miller, A. F., *Accounts of Chemical Research*, **2008**, *41*, 501

[2] Svedruzic, D., Jonsson, S., Toyota, C. G., Reinhardt, L. A., Lindqvist, Y., and Richards, N. G. J., *Archives of Biochemistry & Biophysics*, **2005**, *433*, 176

Zero Field Splitting and Non-Heisenberg interactions studied by Electron Paramagnetic Resonance.

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The significance of zero field splitting and non Heisenberg interactions in the determination of the electronic and magnetic properties of inorganic (mono- and poly-nuclear) complexes is well recognized. We will present examples in which the presence and the role of such factors are revealed by Electron Paramagnetic Resonance (EPR) studies.

High order zero field splitting terms. Usually, for a paramagnetic system with S>1/2, the zero field splitting arises mainly from $\mathbf{S_i}^2$ (i = x,y, z) terms. We will present EPR studies from a mononuclear Fe(III)(S=5/2) complex in which the contribution of $\mathbf{S_i}^4$ terms in the zero field splitting is manifested.

Distributions on zero field splitting parameters. Usually, the line-broadening characterizing the EPR spectra originates from distributions of the parameters which the signals depend upon. We will present EPR studies in combination with DFT calculations from a mononuclear Mn(II)(S=5/2) complex in which the line broadening observed in the EPR spectra is correlated with distributions of geometrical configurations of the molecule.

Non Heisenberg interactions in dimers. We will present EPR studies from an anti-ferromagnetic Fe(III) dimer. EPR signals were observed from the S = 1 and S = 2 excited states. Analysis of these signals leads to determination of the zero field splitting parameters.

Non Heisenberg interactions in trinuclear Cu(II) complexes. Many trinuclear Cu(II) complexes exhibit antiferromagnetic interactions with an S = 1/2 ground state. In many cases EPR spectroscopy of the S=1/2 state reveals the presence of non Heisenberg interactions such as antisymmetric exchange. We will present examples of ferromagnetic trinuclear Cu(II) complexes in which non Heisenberg interactions are revealed by EPR studies from the ground S = 3/2 state.

Dimers of weakly magnetically coupled molecules

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It has been proposed that a two qu-bit quantum gate could be built from two spin clusters held together by a linker[1]; to function, the two units must interact, i. e. magnetic exchange, and the interaction should be switchable from the 'on' state to the 'off' state. Right now there are not any examples of molecules that fulfill all of the requirements and the synthesis of a suitable system is a challenge. One way of synthesizing such a dimer of complexes with a magnetic ground state is the use of ligands with two distinct coordination 'pockets'. By using the ligand 1,3-bis-(3-oxo-3-(2-hydroxyphenyl)-propionyl)-2-methoxybenzene alone or in combination with pyrazine we have succeeded in isolating a series of dimers of tetranuclear and trinuclear complexes which will be presented here, along with a study of their magnetic properties. The dimers with a pyrazine bridge are shown to display the weak magnetic coupling expected.

[1] *Phys. Rev. Lett.* **2003**, *90*, 47901.

Charge-Transfer Excitons in Strongly Coupled Organic Semiconductors

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In organic semiconductors, molecules or polymers are the building blocks of desired architectures, instead of atoms as in traditional semiconductors. This has the advantage that individual motifs can be tailored synthetically for specific electronic properties. However, electronic interactions between building blocks are often complex due to energetic disorder. Here, we address the nature of photoexcitations in chiral, near-cofacial stacks of a sexithiophene derivative that exhibits strong supramolecular π electronic coupling [1]. Time-resolved and temperature-dependent photoluminescence measurements on these one-dimensional lattices reveal intrinsic branching of photoexcitations to two distinct species: self-trapped excitons and dark charge-transfer excitons (CTX; >5% yield), with radii spanning 2-3 sites. The significant CTX yield results from the strong chargetransfer character of the Frenkel exciton band due to the large free exciton bandwidth (400 meV) in these supramolecular nanostructures. We have demonstrated that in organic semiconductors, the supramolecular coupling energy dominates the nature of the primary photoexcitations. The large free-exciton bandwidth is significantly larger than attainable in the most highly organised semiconductor polymer microstructures, but the primary photoexcitations are highly localised. The Frenkel exciton band mixes with CT states, which play an important role in the primary photophysics.

[1] Sebastian Westenhoff, Agnese Abrusci, W. James Feast, Oliver Henze, Andreas F. M. Kilbinger, Albertus P. H. J. Schenning, and Carlos Silva, *Advanced Materials,* **2006**, *18,* 1281.

Pseudohalogen Groups in Higher Oxidation State Manganese Cluster Chemistry

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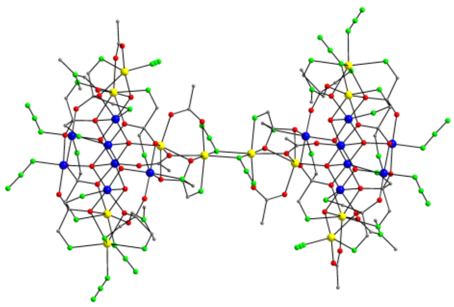
The present talk overviews the recent amalgamation of two long established areas, manganese/oxo coordination cluster chemistry involving the higher Mn^{II}-Mn^{IV} oxidation states, and transition metal pseudohalogen [azide (N_3^-), cyanate (OCN^-)] chemistry[1]. The combination of azide or cyanate and alkoxide- or carboxylate-containing ligands in Mn chemistry has led to a variety of new polynuclear clusters, high-spin molecules, and single-molecule magnets (SMMs), with metal nuclearities ranging from Mn_4 to Mn_{32}, and with ground state spin values as large as $S = 83/2$. The large structural diversity of the resulting complexes stems from the combined ability of the pseudohalogen and organic ligands to adopt a variety of bridging ligation modes. Indeed, one of the most satisfying aspects of this chemistry with respect to the magnetic properties has been the commonly observed μ-1,1 or μ_3-1,1,1 (end-on) bridging mode of the pseudohalogen group, since this is the one that favors ferromagnetic exchange interactions and thus can facilitate products with a high ground state S value[2]. This has undoubtedly been one of the main reasons that this area of Mn/pseudohalogen chemistry is proving such a rich source of molecules with high S values[3].



The combined work demonstrates the synthetic novelty that arises when pseudohalogens are used in conjunction with alcohol-based chelates, the aesthetic beauty of the resulting molecules, and the often fascinating magnetic properties these compounds possess. This continues to emphasize the extensive and remarkable ability of Mn chemistry to satisfy a variety of different tastes.

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[2] O. Kahn, *Molecular Magnetism*; VCH Publishers: New York, **1993**.

[3] (a) Th. C. Stamatatos, K. A. Abboud, W. Wernsdorfer, G. Christou, *Angew. Chem. Int. Ed.*, **2007**, *46*, 884; (b) Th. C. Stamatatos, K. A. Abboud, W. Wernsdorfer, G. Christou, *Angew. Chem. Int. Ed.*, **2006**, *45*, 4134; (c) Th. C. Stamatatos, K. A. Abboud, W. Wernsdorfer, G. Christou, *Angew. Chem. Int. Ed.*, **2008**, *47*, 6694.

Synthesis, structure, magnetic properties and aqueous solution characterization, of *p*–hydroquinone and phenol iminodiacetate copper (II) complexes

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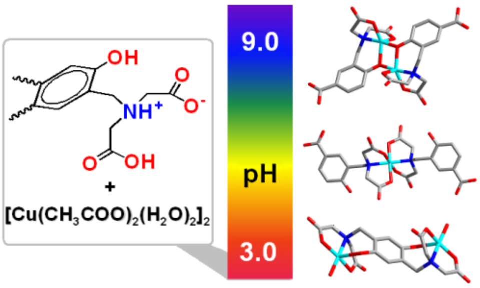
Reaction of copper(II) acetate monohydrate with each of the 2–[*N*,*N*–bis(carboxymethyl)aminomethyl]–4–carboxyphenol (H_4cacp), 2–[*N*,*N*–bis(carboxymethyl)aminomethyl]hydroquinone (H_4cah) and the dinucleating 2,5-bis[*N*,*N*–bis(carboxymethyl) aminomethyl]hydroquinone (H_6bicah) in water results in the formation of several Cu(II) species which are in dynamic equilibrium in aqueous solution and their stability is pH dependent. A systematic crystallographic study of these species was pursued resulting in the characterization of most of them. Additional techniques were employed to characterize the molecules in solid state (infrared spectroscopy) and in solution (UV–vis spectroscopy and electrochemistry). These measurements show that the Cu(II) ions are ligated mainly to the iminodiacetate at pHs below 6, whereas exhibit only weak interactions with the phenol oxygen. At pHs above 6, phenol oxygen was deprotonated and dinuclear bridged from the phenolate oxygen complexes exhibiting a $Cu(II)_2O_2$ core were isolated. The coordination environment around the copper ions varies between trigonal bipyramidal, tetragonal pyramidal and octahedral distorted geometries. The two unpaired electrons of the Cu(II) ions found to be antifferomagnetically coupled. A survey of the magnetic and structural properties of dinuclear phenoxide bridged Cu(II) complexes shows that the strength of the antifferomagnetic coupling is linear dependent on the Cu–$O_{phenolate}$ bond lengths, at bond distances below 1.98 Å. The effect of the Cu–O–Cu angles at the magnetic properties of the complexes is also discussed.[1]



[1] Stylianou M., Drouza C., Viskadourakis Z., Giapintzakis J., Keramidas A. D., *J. Chem. Soc., Dalton Trans.*, **2008**,*44*, 6188.

Classical and Quantum Monte Carlo Magnetic Simulation Techniques: Important tools for understanding large magnetic systems.

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Monte Carlo (MC) simulations are powerful numerical tools for high-precision studies of many-body systems, both in the classical and quantum regime. Especially near second-order phase transitions, where physical length scales diverge, it is essential to simulate large systems, which has become possible due to significant algorithmic advances within the last 15 years. In classical simulations, conventional MC algorithms sample the canonical partition function by making local configurational updates. While being straightforward, this approach turns to slow down simulations near phase transitions and gives rise to long autocorrelation times in the measurement of the relevant physical observables. For classical spin-like systems, this critical slowing down can be overcome using cluster algorithms which update large clusters of spins in a single MC step.

The generalization of these non-local update schemes to the case of quantum Monte Carlo (QMC) simulations was initiated by the development of the loop algorithm in the world-line representation. This very efficient method has been used in many studies, where it allowed the simulation of large systems at very low temperatures. In the original formulation (either in discrete or continuous imaginary time), the loop algorithm however has a major drawback: to work efficiently, its application is restricted to specific parameter regimes. In the case of quantum spin models for example, it suffers from severe slowing down upon turning on a magnetic field.

Various quantum Monte Carlo studies (QMC) using the (SSE) algorithm were carried out instead of the usual ITO (Irreducible Tensor Operators) method in order to simulate the magnetic behaviour of complex magnetic systems and will be presented. Also for the case of classical spins several (CMC) studies were carried out for large classical systems.

Trianionic pincer ligands: a d^1 Cr(V)=O aerobic oxidation catalyst.

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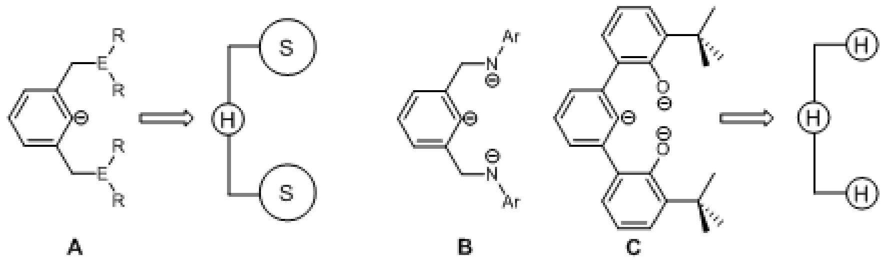
Classic pincer ligands (**A**, E = P, N, O, S) are complementary to late transition. Our approach is to match the harder early transition metals with a harder pincer ligand. We have synthesized a series of new pincer ligands based on amido–arylide–amido (**B**, Ar = 2,6–^{i}PrC$_6$H$_3$, and 3,5–MeC$_6$H$_3$$^{)}$ and alkoxide–arylide–alkoxide linkages (**C,** OCO^{3-} = 1,3-C$_6$H$_4$(6-^{t}BuC$_6$H$_3$OH)$_2$).

Ligand Attributes



1. occupy three coordination sites but contribute maximum of 10e- (access electronically unsaturated species)
2. rigid backbone allows only meridional coordination (access constrained, high- energy species)
3. tridentate trianionic versus three individual monodentate monoanionic ligands (increased stability, resistant to protonation)
4. easily adjust electronics, sterics, rigidity, and chelate ring size
5. can stabilize unusual high oxidation states

Restricting three anionic donor ligands to meridional positions generates reactive metal fragments. As proof, an [OCO]Mo-nitrido complex readily adds mild electrophiles and completes N-atom transfer to acid chlorides to synthesize nitriles. A reactive d^1 Cr(V)=O complex completes the O-atom transfer to PPh$_3$ with O$_2$ as the terminal oxidant.

Composite Filing Materials: The Chemistry behind Drill and Fill

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The development of filling materials derived from synthetic polymers has been initiated by two major driving forces in addition to the obvious commercial ones. First, there was a requirement to produce a material which could overcome the major deficiencies of the earlier silicate materials, namely erosion, brittleness, acidity and a moisture sensitivity which demanded very careful manipulation. Secondly, developments in polymer technology produced resins which could be readily cured at mouth temperature and, with the aid of pigments and fillers, could be made to resemble the natural tooth in appearance.

This presentation will focus on modern composite materials and the difficulties faced by clinicians associated with bonding to tooth tissue. The composition of tooth tissue will be explained to gain an understanding of the substrate in which bonding occurs. Dentine bonding will be the focus with insight into “smear layers” and “hybrid layers” and how polymers such as 4-methacryloxyethyltrimelliticanhydride (4 META) are used to bond to dentine. The advantages and disadvantages of composite materials will be highlighted and an insight into the future of tooth colour materials will be presented.

"Where are the (valence) electrons in Coordination Complexes? Chemistry with Ligand π-Radicals"

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Coordination compounds of transition metal ions containing α-diimine, α-iminoketone, or 1,2-diketone type ligands have been synthesized in the past and their electronic structures have almost invariably been described as species with closed shell, neutral ligands. We show that this is an unduly oversimplification: these ligands are redox-noninnocent and can exist in three oxidation levels, namely neutral ligands $(L^{ox})^{\circ}$, π radical monoanions $(L\bullet)^{1-}$ and closed shell dianions $(L^{Red})^{2-}$. We will discuss how these forms may be identified by spectroscopy and broken symmetry DFT calculations. Remember, the correct electronic structure matters when you want to understand reactivity – in catalysis and elsewhere.

Building Multi-Functional Nanomaterials: From Therapeutics to Magneto-Optics and Energy.

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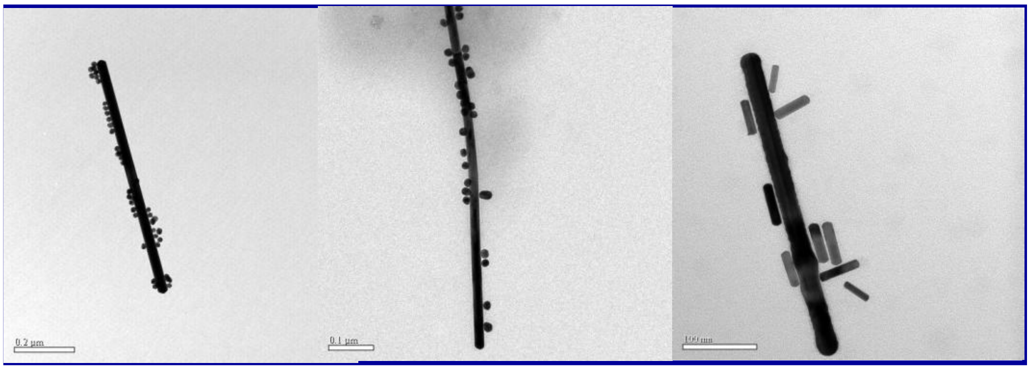
The development of bi- and multi-functional nanomaterials has changed the way researchers think about the development of chemical systems for applied fields such as medicine and energy, as well as magneto-optical technologies. The assembly of such constructs requires a thoughtful, modular design and approach that often entails fusion of several different chemistries not typically used in concert. The end result is a unique material both in composition and size, that leads to unique physio-chemical properties that provide bi- or multi-dimensional function. Examples include magnetically or optically visible nanomaterials targeted toward specific biological substrates with particular therapeutic payloads that can be released (so called therognostic materials).

The synthetic strategy for developing these materials, as well as specific examples that include magnetic systems for medical, energy, and materials applications, as well as optical nanomaterials for imaging or sensing will be discussed.



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