

# AUSTRALIAN JOURNAL OF CHEMISTRY

AN INTERNATIONAL JOURNAL FOR CHEMICAL SCIENCE

## RESEARCH FRONT: UQ-NUS Joint Symposium

### Foreword

#### University of Queensland–National University of Singapore Joint Symposium

Craig Williams

*Aust. J. Chem.* **2009**, 62, 949–950.

This special issue of the Australian Journal of Chemistry includes reviews and research papers from the University of Queensland–National University of Singapore joint symposium held on the 15th and 16th of December 2008. There are a variety of topics covered including heterocyclic carbene, dicarbene complexes, vaccine candidates and delivery, molecular modelling, drug delivery and natural product total synthesis.

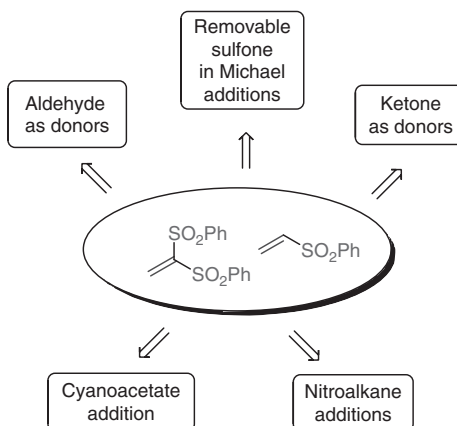
### Reviews

#### Chiral Amine-Mediated Asymmetric Conjugate Additions to Vinyl Sulfones

Qiang Zhu, Yixin Lu

*Aust. J. Chem.* **2009**, 62, 951–955.

Chiral molecules containing sulfone groups are useful intermediates and have found wide applications in organic synthesis. In this account, recent progress in the use of vinyl sulfones as Michael acceptors in the asymmetric organocatalytic conjugate addition is summarized.

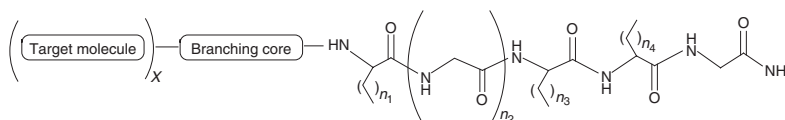


#### Lipid Core Peptide System for Gene, Drug, and Vaccine Delivery

Wei Zhong, Mariusz Skwarczynski, Istvan Toth

*Aust. J. Chem.* **2009**, 62, 956–967.

Lipidation has been demonstrated to be a convenient and useful approach to improve the stability and delivery of potential drug molecules. This review discusses the development of a lipid core peptide system to improve the pharmaceutical properties of drugs, gene products and vaccines.

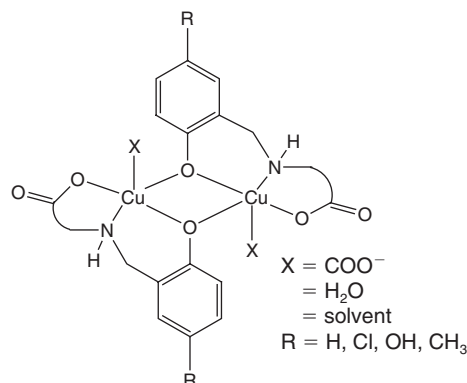


### Diphenoxo-Bridged Copper(II) Complexes of Reduced Schiff Base Ligands as Functional Models for Catechol Oxidase

Bellam Sreenivasulu

*Aust. J. Chem.* **2009**, 62, 968–979.

Several dicopper(II) complexes, derived from different series of reduced Schiff base ligands and investigated as functional models for catecholase activity, have been reviewed. The catecholase activity of different series of dicopper(II) complexes has been discussed with respect to the various ligand properties such as the length and chelating ability of the amino acid side-arm of the ligands, conformation of the ligand, nature of the donor groups on the amino acid backbone and role of different *para*-substituents.



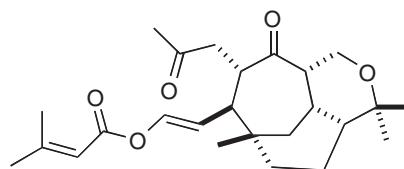
### Communication

#### Total Synthesis of (±)-Vibsanin E

Brett D. Schwartz, Justin R. Denton,  
Huw M. L. Davies, Craig M. Williams

*Aust. J. Chem.* **2009**, 62, 980–982.

Vibsanin E (**1**), a structurally rare complex diterpene, consisting of a compact 3-oxatricyclo[6.3.2.0<sup>5,10</sup>] tridecane core and an unprecedented 3,3-dimethylacroyl enol ester functional group, formulate a considerable synthetic challenge. Williams and Davies failed to independently synthesize this nemesis, however, a ‘two heads are better than one’ approach delivered the first total synthesis of the molecule, since its diamond anniversary isolation.



Vibsanin E (**1**)

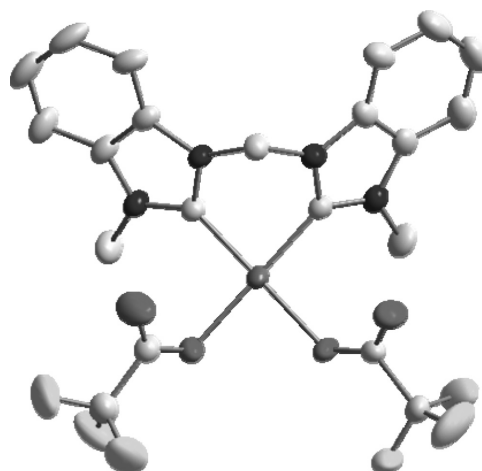
### Full Papers

#### Synthesis and Structural Characterization of Palladium Dicarbene Complexes Bearing Labile Co-Ligands

Han Vinh Huynh,  
Hui Xian Seow

*Aust. J. Chem.* **2009**, 62, 983–987.

New Pd<sup>II</sup> dicarbene complexes bearing labile co-ligands have been prepared and fully characterized. A preliminary study reveals that the thermal stability of such complexes under hydroamination conditions is strongly influenced by these co-ligands.

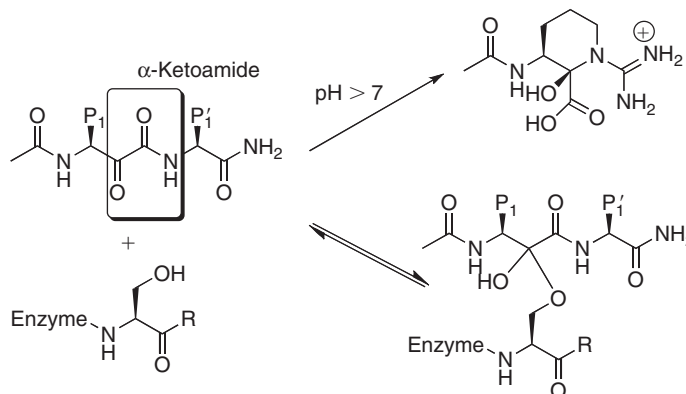


### Base-Sensitivity of Arginine Alpha-Ketoamide Inhibitors of Serine Proteases

Martin J. Stoermer,  
Donmienne Leung, Paul R. Young,  
David P. Fairlie

*Aust. J. Chem.* **2009**, 62, 988–992.

$\alpha$ -Ketoamide electrophilic isosteres are frequently used in compounds to confer potent inhibition of serine proteases. This major class of inhibitors for trypsin-like serine proteases have a preference for arginine adjacent to the N-terminus of the cleavable amide bond. We report that  $\alpha$ -ketoamides are unstable above pH 7, where many inhibitors are assayed, undergoing hydrolysis to a six-membered cyclic hemiaminal.

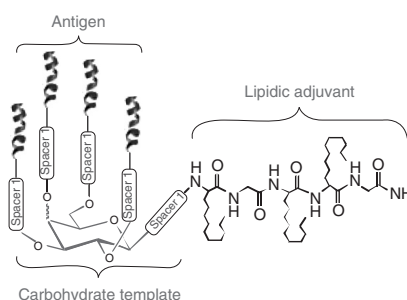


### Design and Synthesis of Lipopeptide–Carbohydrate Assembled Multivalent Vaccine Candidates Using Native Chemical Ligation

Wei Zhong, Mariusz Skwarczynski,  
Yoshio Fujita, Pavla Simerska,  
Michael F. Good, Istvan Toth

*Aust. J. Chem.* **2009**, 62, 993–999.

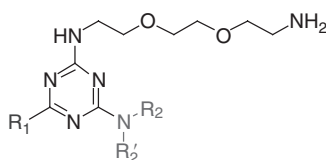
We have synthesized two lipopeptide conjugated carbohydrate templates and assembled peptide antigens on them using native chemical ligation. The template-assembled peptides formed four  $\alpha$ -helix bundles.



### Novel Orthogonal Synthesis of a Tagged Combinatorial Triazine Library via Grignard Reaction

Jae Wook Lee, Jacqueline T. Bork,  
Hyung-Ho Ha, Animesh Samanta,  
Young-Tae Chang

*Aust. J. Chem.* **2009**, 62, 1000–1006.



To expand 1,3,5-substituted triazine libraries to include aryl- and alkyl-functionalities through the C–C bond formation, we have employed a new synthetic route via Grignard monoalkylation or monoarylation of cyanuric chloride in solution. We have demonstrated a novel orthogonal synthesis of tagged aryl- and alkyl-triazine libraries on solid support utilizing a building block prepared via Grignard reaction in solution. The approach to aryl- and alkylated triazine libraries is further expanded by incorporation of a triethylene glycol linker at one of the alternate sites of the triazine scaffold, ultimately allowing for synthesis of an intrinsic tagged library.

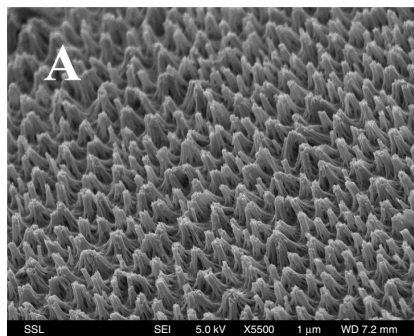
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**Fabrication and Field Emission Properties of Poly-CuTAPc Nanowires and Nanotubes**

*Feng Gu, Chorng Haur Sow,  
Guo Qin Xu, Siau Gek Ang*

*Aust. J. Chem.* **2009**, 62, 1007–1013.

Poly-CuTAPc nanowires and nanotubes were successfully fabricated on porous alumina templates by electropolymerization and characterized. These nanostructures were studied for investigation of potential application as field emitters. Interesting turn-on field, maximum current density, and enhancement factor were obtained which are comparable to many other organic nanomaterials.



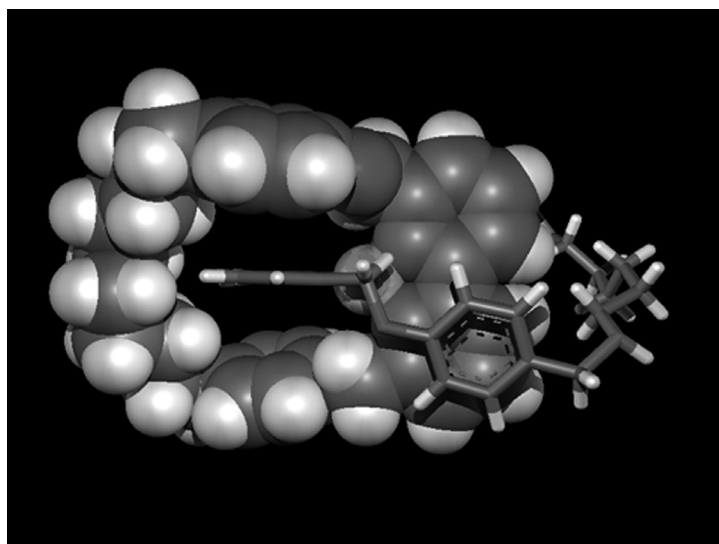
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**Copper(I) Templated Synthesis of a 2,2'-Bipyridine Derived 2-Catenane: Synthetic, Modelling, and X-ray Studies**

*Jason R. Price, Jack K. Clegg,  
Ronald R. Fenton, Leonard F. Lindoy,  
John C. McMurtrie,  
George V. Meehan, Andrew Parkin,  
David Perkins, Peter Turner*

*Aust. J. Chem.* **2009**, 62, 1014–1019.

A metal template reaction involving Schiff base condensation followed by sodium borohydride reduction has been employed to produce a new [2]-catenane incorporating a bis-bipyridyl copper(I) core – the first example of this catenane type so far reported.



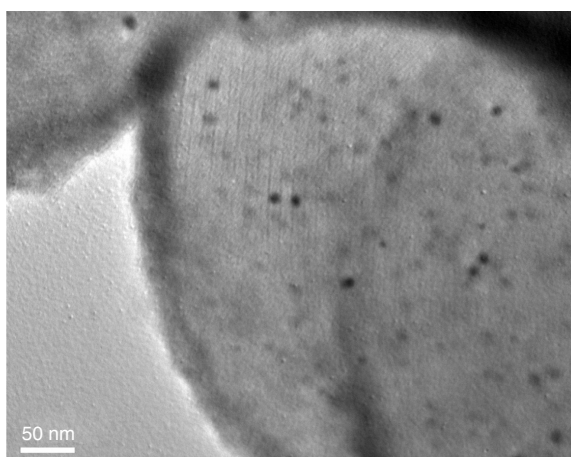
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**Hydrogenation of Glucose over Ru Nanoparticles Embedded in Templated Porous Carbon**

*Jiajia Liu, Xiao Ning Tian,  
Xiu Song Zhao*

*Aust. J. Chem.* **2009**, 62, 1020–1026.

Ruthenium nanoparticles incorporated into the pore walls of porous carbon was used as a catalyst in glucose hydrogenation to produce sorbitol. The Ru-C nanostructured catalyst displayed higher catalytic activity and stability compared with other catalysts. These effects were associated with the enhanced contact between the Ru nanoparticles and carbon matrix, as well as the unblocked pores of the catalyst.

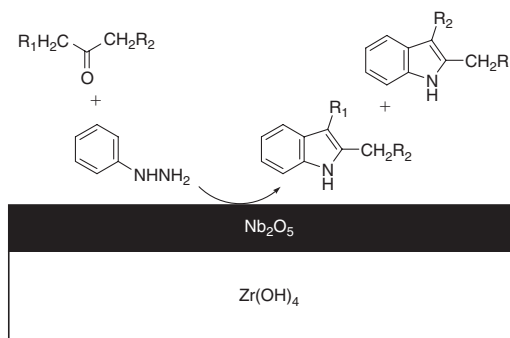


### Fischer Indole Synthesis over Hydrous Zirconia-Supported Niobium Oxide

Liang Zhong, Gaik-Khuan Chuah

*Aust. J. Chem.* **2009**, 62, 1027–1033.

Supported niobium oxide is an active reusable catalyst in the Fischer indole reaction of phenylhydrazine with either 3-heptanone or with cyclohexanone. The samples are easily prepared by wet impregnation of hydrous zirconia and MCM-41 with niobium chloride. The activity increased with loading to reach a maximum at monolayer coverage.

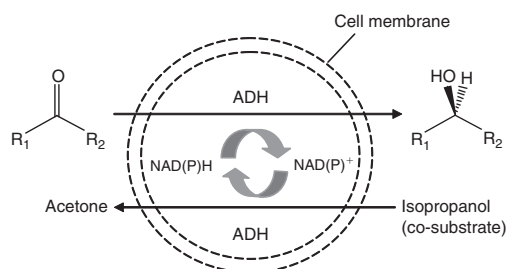


### Immobilized Whole Cells as Effective Catalysts for Chiral Alcohol Production

Jeck Fei Ng, Stephan Jaenicke

*Aust. J. Chem.* **2009**, 62, 1034–1039.

Recombinant *E. coli* over-expressing alcohol dehydrogenase from *Lactobacillus brevis* catalyzes the reduction of pro-chiral ketones with high conversion and ee >99%. Immobilizing the cells improves the stability. The system gave a stable productivity of  $1.4 \text{ g}_{\text{EHB}} \text{g}_{\text{wcv}}^{-1} \text{h}^{-1}$ .

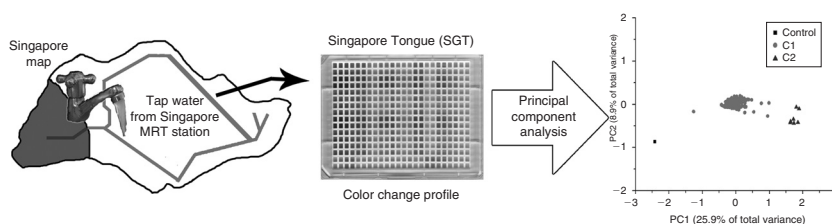


### Colorimetric Sensor Array for Qualitative Water Analysis

Shu Ann Chan, Jun-Seok Lee, Young-Tae Chang

*Aust. J. Chem.* **2009**, 62, 1040–1046.

The Singapore Tongue (SGT), a novel chemosensor array that is comprised of 45 off-the-shelf colorimetric dyes, is successfully used to discriminate and identify 12 kinds of bottled water (even up to 100 times dilution) and 63 tap waters in Singapore. As such the SGT is proven to be a simple robust portable tool for water analysis.

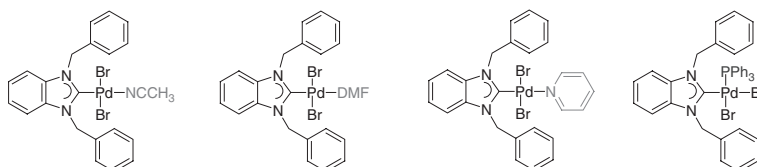


### Structures and Suzuki-Coupling of *N*-Heterocyclic Carbene Complexes of Pd<sup>II</sup> with Coordinated Solvent and PPh<sub>3</sub>

Swee Kuan Yen, Lip Lin Koh, Han Vinh Huynh, T. S. Andy Hor

*Aust. J. Chem.* **2009**, 62, 1047–1053.

A series of mononuclear *N,N*-heterocyclic carbene (NNHC) complexes of Pd<sup>II</sup> with 1,3-dibenzylbenzimidazoly-2-ylidene and solvent ligand (CH<sub>3</sub>CN, DMF, pyridine, and DMSO) or PPh<sub>3</sub> were prepared and characterized by X-ray single-crystal diffraction analysis. Their structural and catalytic activity are compared directly with their *N,S*-heterocyclic carbene analogues.

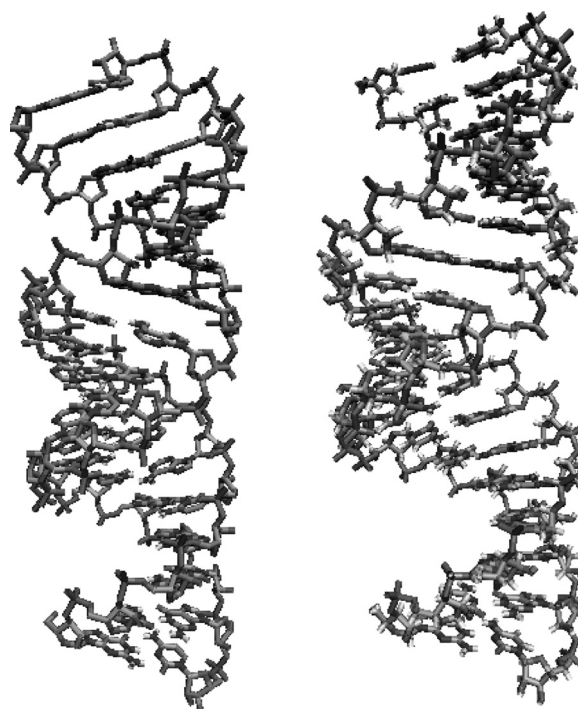


**Flexibility of Short-Strand RNA in Aqueous Solution as Revealed by Molecular Dynamics Simulation: Are A-RNA and A'-RNA Distinct Conformational Structures?**

Defang Ouyang, Hong Zhang,  
Dirk-Peter Herten, Harendra  
S. Parekh, Sean C. Smith

*Aust. J. Chem.* **2009**, 62, 1054–1061.

Analysis of three structural descriptors commonly used to differentiate between A-RNA and A'-RNA conformers over 30 ns MD simulations in aqueous solution with counter-ions, reveals a flexible structure and suggests that the identification of distinct structures, while relevant in the crystalline form, may not be generally relevant in the aqueous phase.

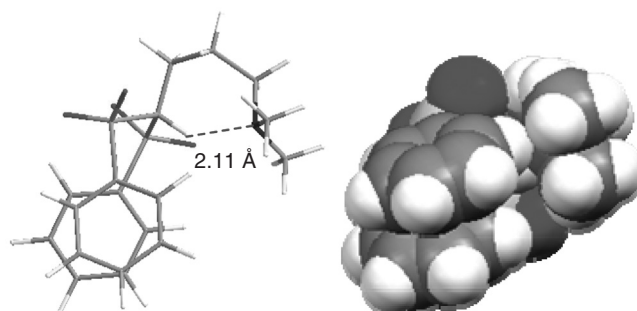


**Structure of 4,4-Bisphenylsulfonyl-*N,N*-dimethylbutylamine: Interplay of Intramolecular C–H···N, C–H···O=S, and  $\pi$ ··· $\pi$  Interactions**

Jiong Ran, Ming Wah Wong

*Aust. J. Chem.* **2009**, 62, 1062–1067.

*Ab initio* calculations show that the structure of 4,4-bisphenylsulfonyl-*N,N*-dimethylbutylamine is stabilized by intramolecular C–H···N, C–H···O=S, and  $\pi$ ··· $\pi$  interactions. This finding is supported by charge density analysis based on the theory of atoms in molecules. The intramolecular C–H···N hydrogen bond is estimated to have a significant interaction energy of 25 kJ mol<sup>–1</sup>.

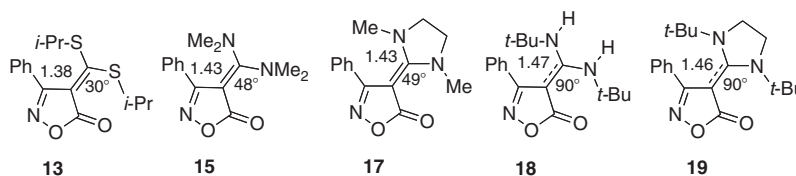


**Highly Twisted C=C Double Bonds in 4-Methyleneisoxazolones**

David Kvaskoff, Paul V. Bernhardt,  
Rainer Koch, Curt Wenstrup

*Aust. J. Chem.* **2009**, 62, 1068–1078.

The X-ray crystal structures for several isoxazolone derivatives reveal highly twisted exocyclic double bonds, with twist angles of 20–90°, and bond lengths approaching that of singles bonds. X-ray and NMR data match well to theoretical (DFT) data. Barriers to rotation as low as 7–10 kcal mol<sup>–1</sup> were calculated for **17** and **19**.



## Foreword

**Supramolecular Magnetic Materials**

Cameron J. Kepert

*Aust. J. Chem.* **2009**, 62, 1079–1080.

Supramolecular materials come in a variety of shapes and sizes and can be made to display a rich array of magnetic properties through judicious design. In this special issue of *Australian Journal of Chemistry* this area is reviewed and a number of important new discoveries are presented, with particular focus on systems that exhibit magnetic ordering, single molecule magnetism, and electronic switching.

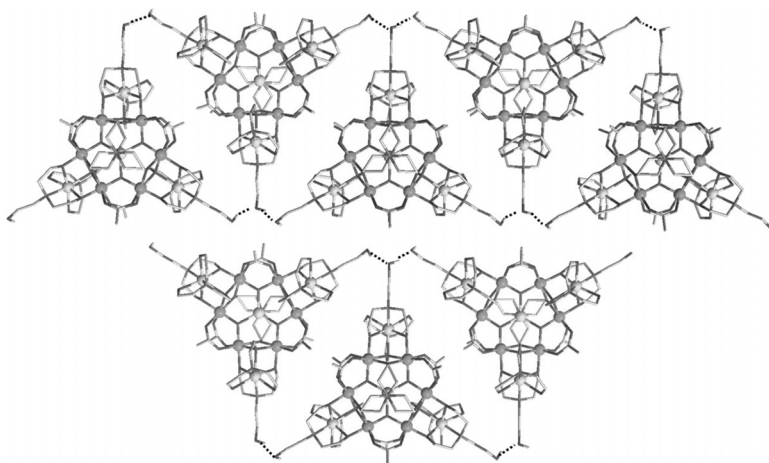
## Review

**Recent Advances in Molecular Magnetic Materials**

Keith S. Murray

*Aust. J. Chem.* **2009**, 62, 1081–1101.

Molecular magnetic materials of the extended framework, large cluster, ( $n \times n$ ) grid and spin-crossover types continue to attract great attention. This review focuses on the work in these areas of the author and colleagues and of other groups. Recent advances are compared to those made by other groups in understanding the single molecule magnetic properties of Mn clusters and of spin switching mechanisms in dinuclear and multidimensional Fe<sup>II</sup> polynuclear materials. Future applications in memory and other devices are outlined.



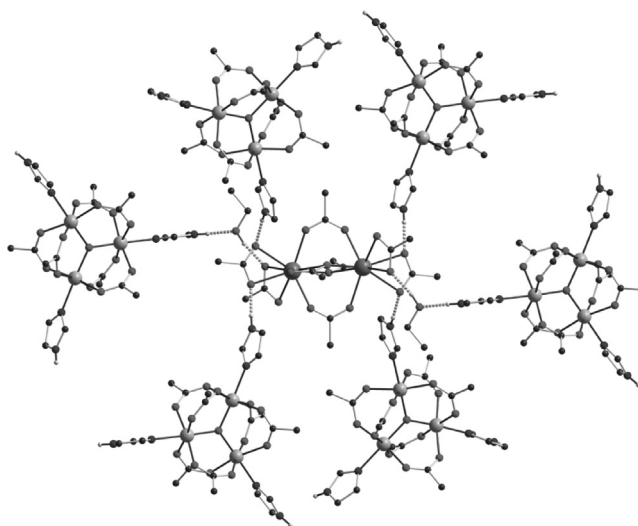
## Communication

**A Three-Dimensional Hydrogen-Bonded Network of Triiron(III) and Dilanthanum(III) Pivalate Complexes**

 Süreyya Isilak, Valeriu Mereacre,  
Yanhua Lan, Christopher E. Anson,  
Annie K. Powell

*Aust. J. Chem.* **2009**, 62, 1102–1107.

A cationic tri-nuclear iron(III) complex and an anionic di-nuclear lanthanum(III) complex assemble to form a three-dimensional hydrogen-bonded supramolecular 3d-4f network  $[\text{Fe}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CBu}^t)_6(\text{im})_3]_2$   $[\text{La}_2(\mu\text{-O}_2\text{CBu}^t)_4(\eta\text{-O}_2\text{CBu}^t)_4] \cdot 2\text{C}_2\text{H}_5\text{OH}$  (im = imidazole).



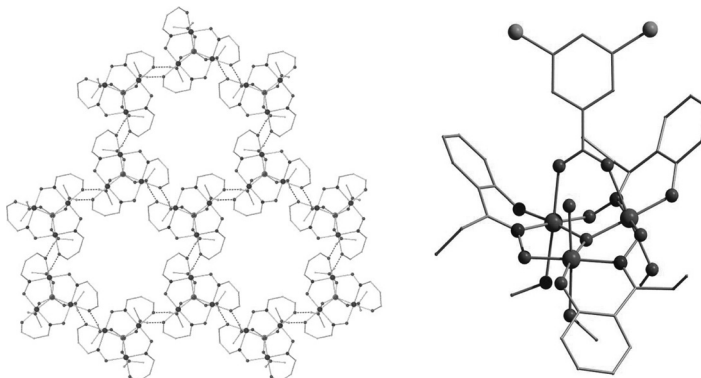
## Full Papers

**Ferromagnetic [Mn<sub>3</sub>] Single-Molecule Magnets and Their Supramolecular Networks**

Ross Inglis, Giannis S. Papaefstathiou,  
Wolfgang Wernsdorfer,  
Euan K. Brechin

*Aust. J. Chem.* **2009**, 62, 1108–1118.

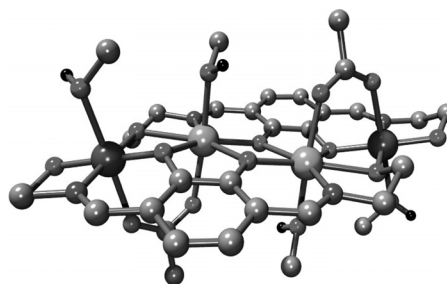
Ferromagnetic Mn<sup>III</sup><sub>3</sub> single-molecule magnets are H-bonded in the crystal lattice creating supramolecular networks with various dimensionalities, causing a field-bias in magnetization versus field hysteresis loops.

**A Tetranuclear Mixed-Valence Manganese Complex of a Diimine Ligand Derived from 1,4-Diformyl-2,3-dihydroxybenzene: Synthesis, Structure, and Magnetic Properties**

Humphrey L. C. Feltham,  
Rodolphe Clérac, Sally Brooker

*Aust. J. Chem.* **2009**, 62, 1119–1123.

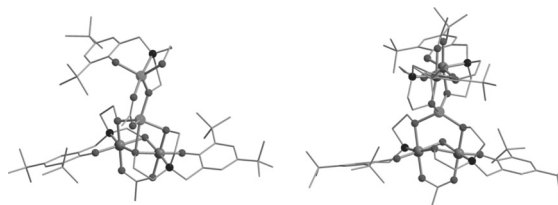
A diimine ligand (H<sub>4</sub>L<sup>1</sup>) derived from the title dialdehyde gave crystals of [Mn<sup>II</sup><sub>2</sub>Mn<sup>III</sup><sub>2</sub>(L<sup>1</sup>)<sub>2</sub>(OAc)<sub>2</sub>(MeOH)<sub>4</sub>]-2MeOH. Magnetic studies on an air-dried sample, [Mn<sup>II</sup><sub>2</sub>Mn<sup>III</sup><sub>2</sub>(L<sup>1</sup>)<sub>2</sub>(OAc)<sub>2</sub>(MeOH)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]-3H<sub>2</sub>O, showed that antiferromagnetic interactions dominate between the metal ions.

**Mixed-Valent Polynuclear Cobalt Complexes Incorporating Tetradentate Phenoxyamine Ligands**

Joo Chuan Ang, Yanyan Mulyana,  
Chris Ritchie, Rodolphe Clérac,  
Colette Boskovic

*Aust. J. Chem.* **2009**, 62, 1124–1129.

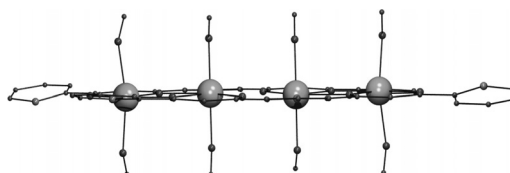
New mixed-valent tetra- and pentanuclear cobalt complexes bearing tetradentate phenoxyamine ligands have been synthesized and characterized. Unusual trigonal bipyramidal and tetrahedral coordination geometries are observed for the divalent cobalt centres in these complexes, allowing a spin-only treatment of the magnetic properties of the tetranuclear complex.

**A Molecular Chain of Four Co<sup>II</sup> Ions Stabilized by a Tris-Pyridyl/Bis-β-Diketonate Ligand**

Leoní A. Barrios, David Aguilà,  
Olivier Roubeau, Keith S. Murray,  
Guillem Aromí

*Aust. J. Chem.* **2009**, 62, 1130–1136.

A major challenge of the emerging field of supramolecular magnetic materials is the design of molecular species with predetermined structures and properties. The assembly of four Co<sup>II</sup> atoms into a tetranuclear molecular chain, [Co<sub>4</sub>L<sub>2</sub>(MeOH)<sub>8</sub>](NO<sub>3</sub>)<sub>4</sub> (**1**), has been achieved using a newly synthesized tris-pyridyl/bis-β-diketone ligand. Ligand exchange at the labile axial positions may allow structuring the [Co<sub>4</sub>] chains into elaborate supramolecular architectures.

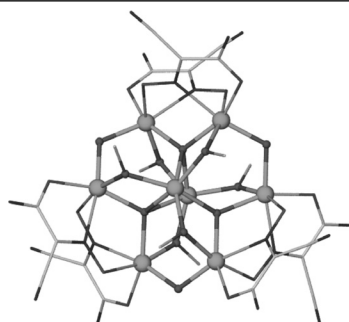




**An Octanuclear Iron(III) Cluster Complex Containing the Nitroso Bridging Ligand Carbamoylcyanonitrosomethanide**

Anthony S. R. Chesman,  
David R. Turner, Boujemaa Moubaraki,  
Keith S. Murray, Glen B. Deacon,  
Stuart R. Batten

*Aust. J. Chem.* **2009**, 62, 1137–1141.



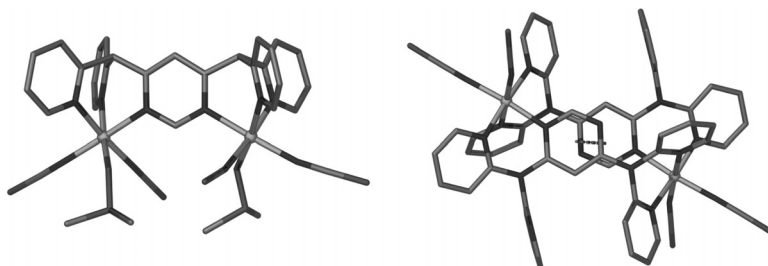
The synthesis and structure is reported for an antiferromagnetically coupled, disc-shaped cluster containing the anionic ligand carbamoylcyanonitrosomethanide (ccnm),  $[\text{Fe}_8\text{O}_6(\text{MeO})_6(\text{ccnm})_6]$ , with an  $\text{Fe}_8^{\text{III}}\text{O}_3$  core. It highlights the utility of the ccnm ligand for building large clusters of magnetic interest.

**Synthesis and Coordination Chemistry of Doubly-Tridentate Tripodal Pyridazine and Pyrimidine-Derived Ligands: Structural Interplay Between  $\text{M}_2\text{L}$  and  $\text{M}_2\text{L}_2$  ( $\text{M} = \text{Ni}$  and  $\text{Pd}$ ) Complexes and Magnetic Properties of Iron(II) Complexes**

Christopher J. Sumby, Ben A. Leita,  
Boujemaa Moubaraki, Keith S. Murray,  
Peter J. Steel

*Aust. J. Chem.* **2009**, 62, 1142–1154.

Bridging heterocyclic ligands that facilitate strong interactions between multiple metal centres play a significant role in the magnetic, electronic and photophysical properties of transition metal complexes. Suitable ligands, able to bridge two octahedral metals with tripodal tridentate coordination of each metal centre, are uncommon. Dinuclear complexes of selected ligands demonstrate the desired bridging mode is achievable, paving the way for further investigations of the properties of these compounds.

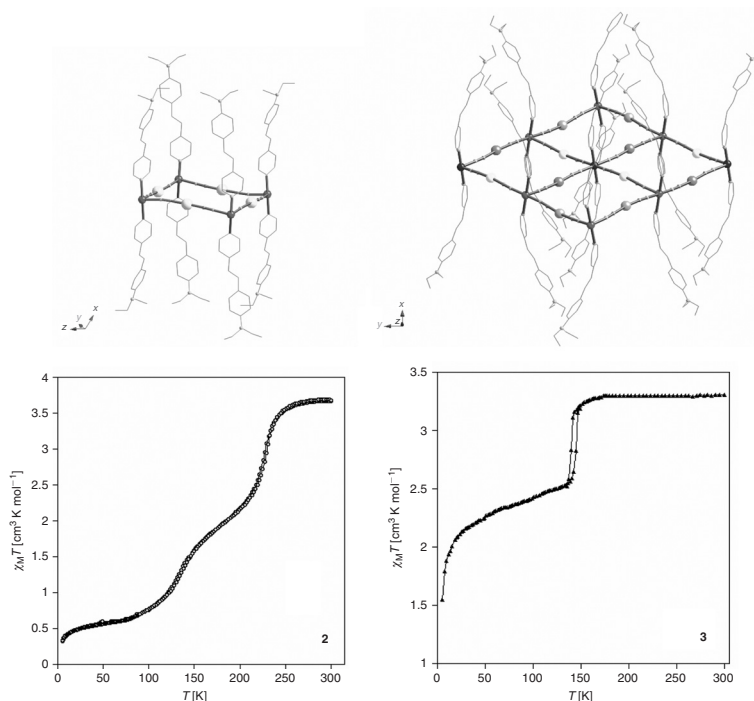


**Spin Crossover and Paramagnetic Behaviour in Two-Dimensional Iron(II) Coordination Polymers with Stilbazole Push–Pull Ligands**

Gloria Agustí, Ana Belén Gaspar,  
M. Carmen Muñoz, Pascal G. Lacroix,  
José Antonio Real

*Aust. J. Chem.* **2009**, 62, 1155–1165.

The suitability of the stilbazole push–pull ligands, 4'-dimethylaminostilbazole (DMAS) and 4'-diethylaminostilbazole (DEAS), for the construction of bimetallic  $\text{Fe}^{\text{II}}\text{--Ag}^{\text{I}}/\text{Au}^{\text{I}}$  cyanide-based coordination polymers that exhibit spin crossover properties is investigated. The structural and physical characterization of four novel two-dimensional  $\text{Fe}^{\text{II}}$  polymers is reported.

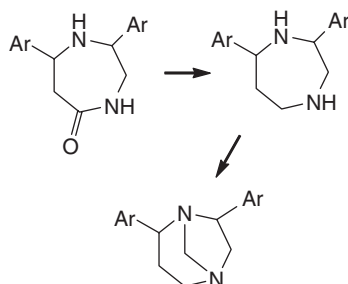


## Full Papers

**Synthesis of Novel Diazabicycles and their Antiprotozoal Activities**

Volker Wolkinger, Robert Weis,  
Ferdinand Belaj, Marcel Kaiser,  
Reto Brun, Robert Saf, Werner Seebacher

*Aust. J. Chem.* **2009**, 62, 1166–1172.



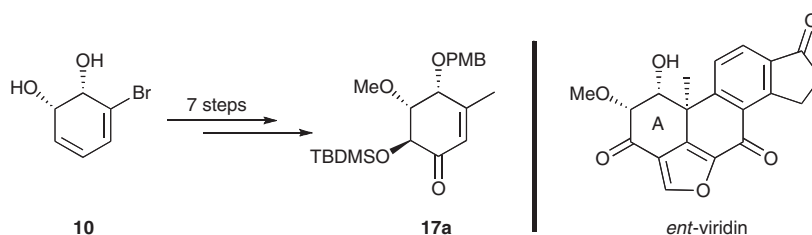
New diaryl diazabicyclo [3.2.1]octanes were synthesized from diazepanes. The formation of the bicyclic ring system was optimized via microwave irradiation. The structure of bicyclic compounds was established by NMR and crystal structure analysis. All new products were investigated for their antiprotozoal and antitrypanosomal activities.

**The Enantiocontrolled Synthesis of a Highly Functionalized Cyclohexenone Related to the A-Ring of the Furanosteroid Viridin**

Alison D. Findlay, Antje Gebert,  
Ian A. Cade, Martin G. Banwell

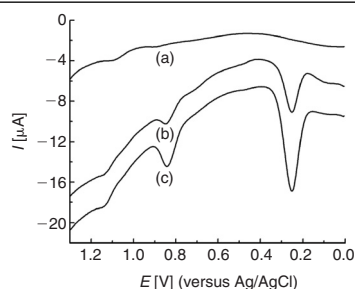
*Aust. J. Chem.* **2009**, 62, 1173–1180.

The enantiomerically pure metabolite **10** has been converted, over 7 steps, into enone **17a** embodying key elements of the A-ring of *ent*-viridin.

**Detection of DNA Damage Induced by Hydroquinone and Catechol Using an Electrochemical DNA Biosensor**

Chuanhu Wang, Jun Zhao, Dapeng Zhang,  
Zhousheng Yang

*Aust. J. Chem.* **2009**, 62, 1181–1184.



A DNA biosensor was fabricated and employed to evaluate DNA damage. Calf thymus DNA was immobilized onto the surface of the pretreated glassy carbon electrode (GCE(ox)) to form a DNA biosensor. The biosensor was incubated in buffer solution containing hydroquinone or catechol at a constant potential for the desired time. DNA damage could be electrochemically recognized via electrochemical signals of guanine and adenine bases on electrode. The prepared biosensor could be applied rapidly to detect DNA damage.

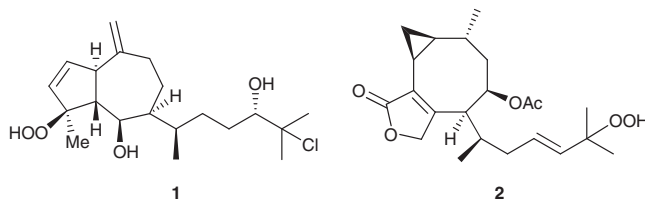
## Communications

**Diterpenoid Hydroperoxides from the Far-Eastern Brown Alga *Dictyota dichotoma***

Sophia A. Kolesnikova,  
Ekaterina G. Lyakhova,  
Anatoly I. Kalinovskiy,  
Pavel S. Dmitrenok,  
Sergei A. Dyshlovoy,  
Valentin A. Stonik

*Aust. J. Chem.* **2009**, 62, 1185–1188.

The brown algae of the genus *Dictyota* are known to be a rich source of different secondary metabolites, especially diterpenes. The present investigation of the brown alga *Dictyota dichotoma*, from the western part of the Sea of Japan, led to the isolation of two new hydroperoxyditerpenoids, dictyohydroperoxide **1** and hydroperoxyacetoxycrenulide **2**, along with fifteen known secondary metabolites. The structures and stereochemistry of these novel compounds were elucidated by 1D and 2D NMR, mass spectrometry and chemical transformations.

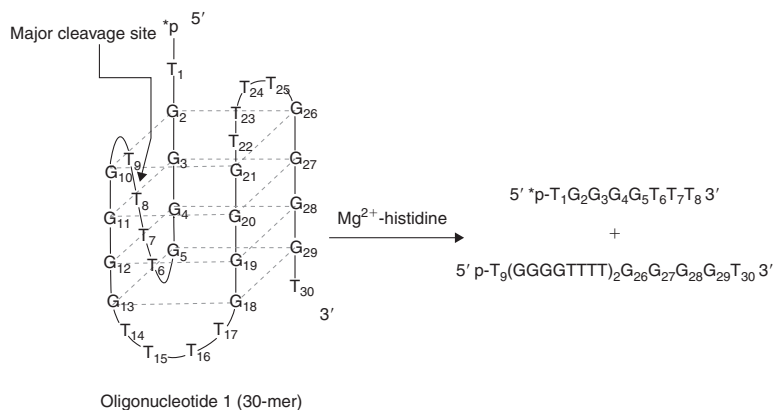


# Site-Specific Cleavage of G-quadruplexes Formed by *Oxytricha* Telomeric Repeats

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*Aust. J. Chem.* **2009**, 62, 1189–1193.

G-quadruplex structures could be formed by certain single-stranded *Oxytricha* telomeric repeats under certain physiological-like conditions. The authors demonstrated that some of such G-quadruplex structures could perform site-specific hydrolytic reactions on certain particular phosphodiester bonds.



Oligonucleotide 1: 5' \*p-T<sub>1</sub>G<sub>2</sub>G<sub>3</sub>G<sub>4</sub>G<sub>5</sub>TTTTGGGGTTTTGGGGTTTTGGGGT 3' (30-mer)

Fragment 1: 5' \*p-T<sub>1</sub>G<sub>2</sub>G<sub>3</sub>G<sub>4</sub>G<sub>5</sub>T<sub>6</sub>T<sub>7</sub>T<sub>8</sub> 3'

Fragment 2: 5' p-T<sub>9</sub>G<sub>10</sub>G<sub>11</sub>G<sub>12</sub>G<sub>13</sub>T<sub>14</sub>T<sub>15</sub>T<sub>16</sub>T<sub>17</sub>G<sub>18</sub>G<sub>19</sub>G<sub>20</sub>G<sub>21</sub>T<sub>22</sub>T<sub>23</sub>T<sub>24</sub>T<sub>25</sub>G<sub>26</sub>G<sub>27</sub>G<sub>28</sub>G<sub>29</sub>T<sub>30</sub> 3'