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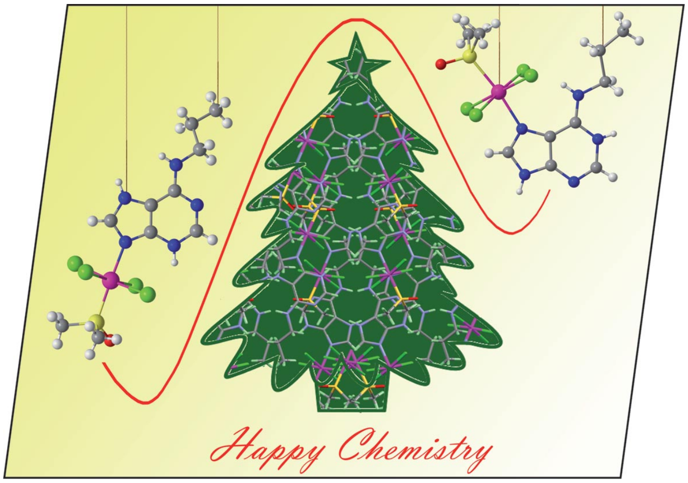
## COVER PICTURE

**The cover picture shows** two $Ir^{III}$ complexes with adenine derivatives that have been synthesized and characterized by spectroscopic techniques and by single-crystal X-ray diffraction studies. The interaction of $Ir^{III}$-adenine complexes and plasmidic DNA pBR322 has been analyzed. In all cases, iridium shows an octahedral geometry and is coordinated to four chlorido ligands, dimethyl sulfoxide (DMSO-κCS) and an adenine derivative. Two different coordination modes for adenine are observed, one through the $N^7$ (kinetic product, right side of the picture) and the other one through the $N^9$ atom (thermodynamic product, left side of the picture). Both mechanisms, which yield the different coordination products, have been studied by means of theoretical DFT calculations. Details are discussed in the article by A. García-Raso, A. Frontera et al. on p. 5617ff. The Christmas tree, which symbolizes the activation energy, is decorated with the crystal structure of an $Ir^{III}$-adenine complex, where the iridium atoms represent the Christmas ball ornaments.



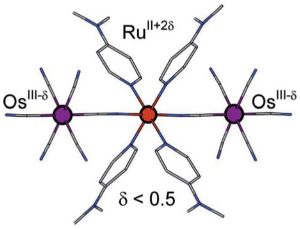
# SHORT COMMUNICATION

## Mixed Valency

**M. B. Rossi, K. A. Abboud, P. Alborés, L. M. Baraldo* ...................... 5613–5616**

Structural and Spectroscopic Evidence of Strong Electronic Delocalization through a Cyanido Bridge in a Mixed-Valence Os–Ru Complex

**Keywords:** Mixed-valent compounds / Cyanido bridge / Delocalization / Ruthenium / Osmium



Matching the energy of metal fragments bonded by a cyanido bridge results in a system that is better described as having partial $Ru^{II/III}$ and $Os^{II}/^{III}$ character as evidenced by its structure and its spectroscopic analysis.

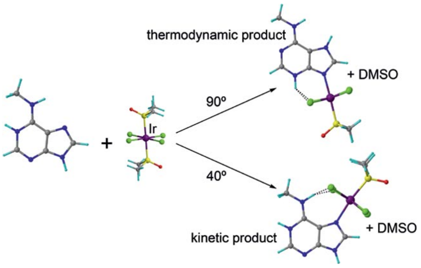
# FULL PAPERS

## Adenine–Iridium Complexes

**A. García-Raso,* J. J. Fiol, F. M. Albertí, Y. Lagos, M. Torres, M. Barceló-Oliver, M. J. Prieto, V. Moreno, I. Mata, E. Molins, C. Estarellas, A. Frontera,* D. Quiñonero, P. M. Deyà ...... 5617–5628**

New Chlorido(dimethyl sulfoxide)iridium(III) Complexes with $N^6$-Substituted Adenines – Kinetic N(7) versus Thermodynamic N(9) Coordinated Adenine Isomers

**Keywords:** Iridium / Coordination modes / Amino acids / Structure elucidation / Density functional calculations



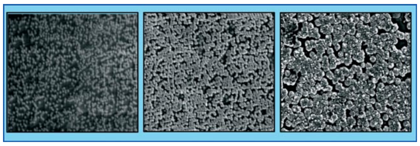
New chlorido(dimethyl sulfoxide)iridium(III) complexes with $N^6$-substituted adenine derivatives, $[Ir^{III}Cl_4(DMSO\text{-}\kappa S)\{H\text{-}AdeC_x-\kappa N(7)\}]$·and $[Ir^{III}Cl_4(DMSO\text{-}\kappa S)\{H\text{-}AdeC_x-\kappa N(9)\}]$, were synthesized and characterized. The kinetic/thermodynamic mechanisms yielding the different coordination products were studied by DFT. Their interaction with plasmid pBR322 DNA was studied by electrophoretic mobility and AFM.

## TiAs Thin Films

**T. Thomas, C. S. Blackman, I. P. Parkin, C. J. Carmalt* ........................ 5629–5634**

Atmospheric Pressure Chemical Vapour Deposition of $TiCl_4$ and $t$BuAs$H_2$ to Form Titanium Arsenide Thin Films

**Keywords:** Titanium / Arsenic / Thin films / Chemical vapour deposition



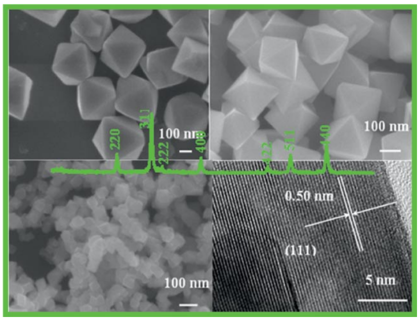
Atmospheric-pressure chemical vapour deposition of $TiCl_4$ and $t$BuAs$H_2$ using substrate temperatures between 450 and 550 °C resulted in the deposition of TiAs thin films. The film depositions, compositions and properties have been investigated.

## Magnetite Octahedra

**L. Zhao,* L. Duan .................. 5635–5639**

Uniform $Fe_3O_4$ Octahedra with Tunable Edge Length – Synthesis by a Facile Polyol Route and Magnetic Properties

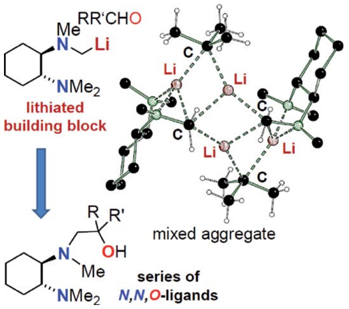
**Keywords:** Iron / Nanoparticles / Polyol synthesis / Tunable size / Magnetic properties



$Fe_3O_4$ octahedra having tunable size, sharp edge length distribution, and uniform shape were prepared by a polyol route. The influence of the dose of $N_2H_4·H_2O$ on size and shape was investigated. $Fe_3O_4$ octahedra with edge length in the range 70–1000 nm were synthesized. Interestingly, it is not the edge length but the angles of the octahedra that have the greatest effect on the magnetic properties.

## Organolithium Chemistry

(*R*,*R*)-TMCDA and its racemic mixture can be directly deprotonated at its methyl group. With 2 equiv. of the deprotonation reagent a mixed aggregate **8** of the lithiated amine **7** and *t*BuLi was formed. By addition of α-lithiated (*R*,*R*)-TMCDA onto carbonyl compounds a series of novel N,N,O ligands of type **4** with different substituents and a further stereocentre are accessible.

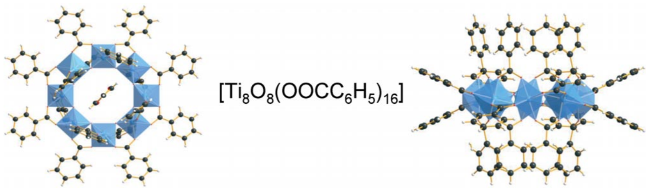


**V. H. Gessner, B. Fröhlich, C. Strohmann*** ...................... **5640−5649**

α-Lithiated (*R*,*R*)-TMCDA as an Efficient Building Block for the Preparation of Chiral N,N,O Ligands by Asymmetric 1,2-Addition

**Keywords:** Lithium / Organolithium compounds / Structure elucidation / N ligands / Addition reactions

## Titanium−Oxo Clusters



New titanium−oxo clusters have been synthesized. The clusters [$Ti_8O_8(OOCR)_{16}$], consisting of an octameric oxo core surrounded by 16 carboxylate ligands, are obtained under solvothermal conditions in high yields. For the first time, the ability of these nanoobjects to be post-modified by other organic acids with the preservation of the octameric oxo core is demonstrated.

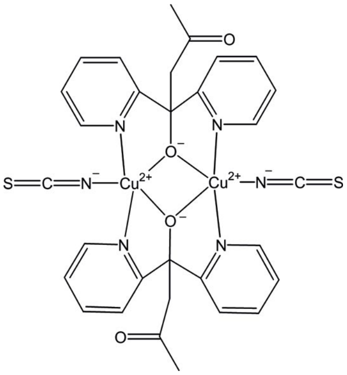
**T. Frot, S. Cochet, G. Laurent, C. Sassoye, M. Popall, C. Sanchez, L. Rozes*** ............................. **5650−5659**

$Ti_8O_8(OOCR)_{16}$, a New Family of Titanium−Oxo Clusters: Potential NBUs for Reticular Chemistry

**Keywords:** Metal−organic frameworks / Nanostructures / Titanates / Cluster compounds

## Mixed-Aldol Condensation

The conversion of a $Cu^I$ polymer to a $Cu^{II}$ dimer incorporating a transition-metal-promoted mixed-aldol condensation.

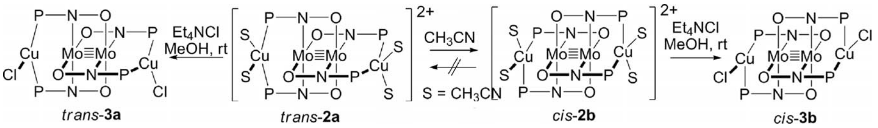


**K. B. Szpakolski, K. Latham,* C. J. Rix, J. M. White** ........................... **5660−5667**

Di(2-pyridyl) Ketone Complexes of $Cu^I$- and $Cu^{II}$-Containing Iodide and Thiocyanate Ligands: An Unusual Case of a Mixed-Aldol Condensation

**Keywords:** Copper / Aldol reactions / Magnetic properties / Polymorphism

## Molybdenum Cluster Compounds



We have demonstrated the solvent-dependent synthesis and structural characterization of *cis* and *trans* isomers of linear tetranuclear clusters [$Mo_2\{Cu(CH_3CN)_2\}_2(pyphos)_4]^{2+}$ (pyphos = 6-diphenylphosphanyl-2-pyridonato). The *trans* isomer was readily converted into its *cis* isomer by an intramolecular rearrangement of the paddle-wheel $Mo_2$ core upon dissolution in a coordinating solvent such as acetonitrile.

**K. Pal, K. Nakao, K. Mashima*** ......................... **5668−5674**

Solvent-Dependent *cis*/*trans* Isomerism at the Paddlewheel $Mo_2$ Core of Linear Tetranuclear Clusters of $Mo^{II}$ and $Cu^I$ Supported by 6-(Diphenylphosphanyl)pyridin-2-olate (pyphos)

**Keywords:** Copper / Molybdenum / Cluster compounds / Multinuclear clusters / Solvent effects / Isomerization

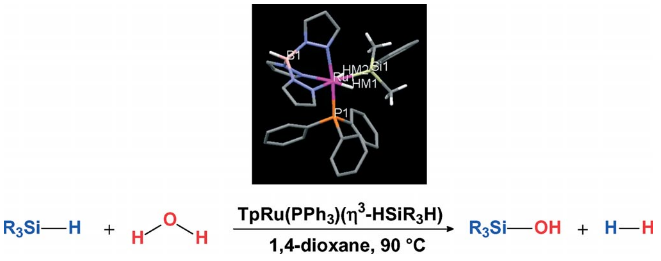
# CONTENTS

## Silane Hydrolysis

**T. Y. Lee, L. Dang, Z. Zhou, C. H. Yeung, Z. Lin,* C. P. Lau* ................. 5675–5684**

Nonclassical Ruthenium Silyl Dihydride Complexes TpRu(PPh$_3$)($\eta^3$-HSiR$_3$H) [Tp = Hydridotris(pyrazolyl)borate]: Catalytic Hydrolytic Oxidation of Organosilanes to Silanols with TpRu(PPh$_3$)($\eta^3$-HSiR$_3$H)

**Keywords:** Silanes / Hypervalent compounds / Oxidation / Reaction mechanisms / Density functional calculations



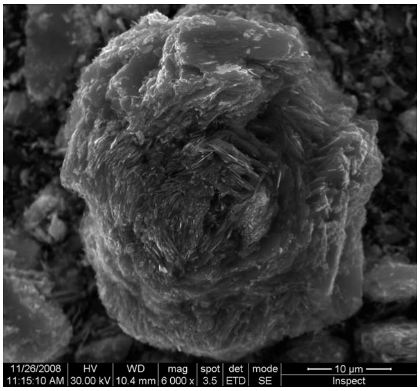
An X-ray crystallographic study showed that the previously reported complexes TpRu(PPh$_3$)(H$_a$)($\eta^2$-H$_b$SiR$_3$) and TpRu(PPh$_3$)(H$_b$)($\eta^2$-H$_a$SiR$_3$) should be formulated as TpRu(PPh$_3$)($\eta^3$-HSiR$_3$H), a structure containing a hypervalent Si center. One of these complexes was used for the catalytic hydrolytic oxidation of organosilanes to silanols. A mechanism, supported by theoretical calculation, is proposed.

## Rare Earth Oxysulfides and -selenides

**R. Kalai Selvan, A. Gedanken* ......................... 5685–5690**

Synthesis and Characterization of Hierarchically Structured La$_2$O$_2$M@C:Eu$^{3+}$ (M = S, Se) Microflowers by a Single-Step RAPET Method

**Keywords:** Hierarchical structures / RAPET / Lanthanum / X-ray diffraction / HRTEM / UV/Vis spectroscopy



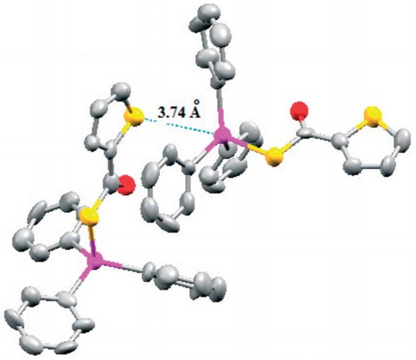
Hierarchically structured La$_2$O$_2$M@C:Eu$^{3+}$ (M = S, Se) microflowers have been successfully prepared by a facile one-pot synthesis at a low temperature of 950 °C by the RAPET technique. The structural (XRD, Raman), morphological (HRSEM, TEM and HRTEM) and optical (UV/Vis) properties of the materials have been studied.

## Organotin and -lead Thiocarboxylates

**S. Singh, S. Bhattacharya,* H. Nöth ................................. 5691–5699**

Synthesis and Structural Studies of Organotin(IV) and Organolead(IV) Thiophene-2-thiocarboxylate

**Keywords:** Tin / Lead / Thiocarboxylate / Thiophene / Density functional calculations / Structure elucidation



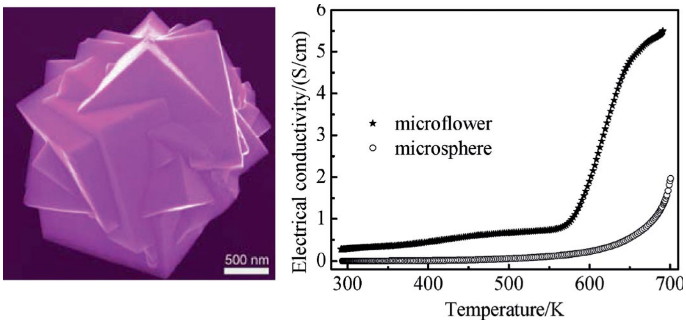
Organotin ([R$_2$SnCl$_2$], [R$_3$SnCl]; R = Me, Ph, *n*Pr, and *n*Bu) and organolead ([Ph$_2$PbCl$_2$], [Ph$_3$PbCl]) compounds that contain the thiophene-2-thiocarboxylate ligand have been synthesized and characterized by spectral and crystallographic studies. Structures and electronic transitions have been explained on the basis of DFT calculations.

## Hierarchical Lead Sulfide

**R. Jin, G. Chen,* Q. Wang, J. Pei, G. Wang, L. Wang ................. 5700–5708**

Flowerlike PbS Microcrystals: Citric Acid Assisted Synthesis, Shape Evolution, and Electrical Conductivities

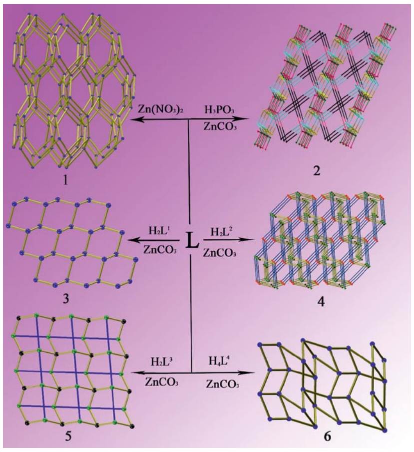
**Keywords:** Lead sulfide / Hydrothermal synthesis / Facet-selective growth / Dissolution–recrystallization / Electrical conductivity



Flowerlike PbS has been synthesized by means of a simple solution route, which shows a higher electrical conductivity relative to other morphologies.

## Zinc Coordination Polymers

Six $Zn^{II}$ containing coordination polymers based on tetrakis(imidazol-1-ylmethyl)methane and different anions have been synthesized successfully under hydrothermal conditions. The thermal and photoluminescent properties of the complexes were also investigated.

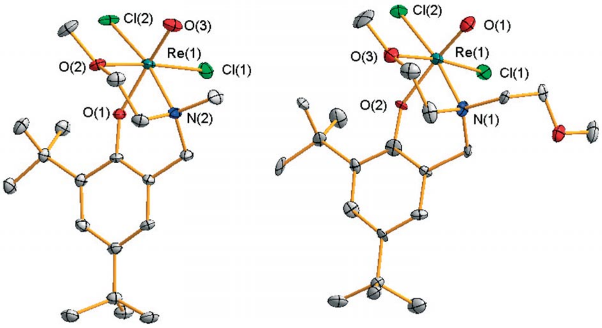


**H.-Y. Bai, J.-F. Ma,* J. Yang,* B. Liu, L.-P. Zhang, J.-C. Ma, Y.-Y. Liu ............................... 5709–5717**

Syntheses, Structures and Properties of a Series of $Zn^{II}$ Complexes Constructed from a Tetrakis(imidazole) Ligand and Various Anions 💻

**Keywords:** Coordination polymers / Zinc / N ligands / Carboxylate ligands / Hydrothermal synthesis

## Oxidorhenium(V) Complexes



Oxidorhenium(V) complexes of the type $[ReOX_2L]$ (X = Cl, Br) that contain tridentate and tetradentate phenolate-based ligands were prepared and tested for their catalytic activity in epoxidation reactions.

**P. Traar, A. Schröckeneder, M. E. Judmaier, F. Belaj, J. Baumgartner, A. Sachse, N. C. Mösch-Zanetti* ............ 5718–5727**

Oxidorhenium(V) Complexes with Tridentate and Tetradentate Phenol-Based Ligands

**Keywords:** Rhenium / Polydentate ligands / Epoxidation / Phenols

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* Author to whom correspondence should be addressed.

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*Happy New Year.*

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