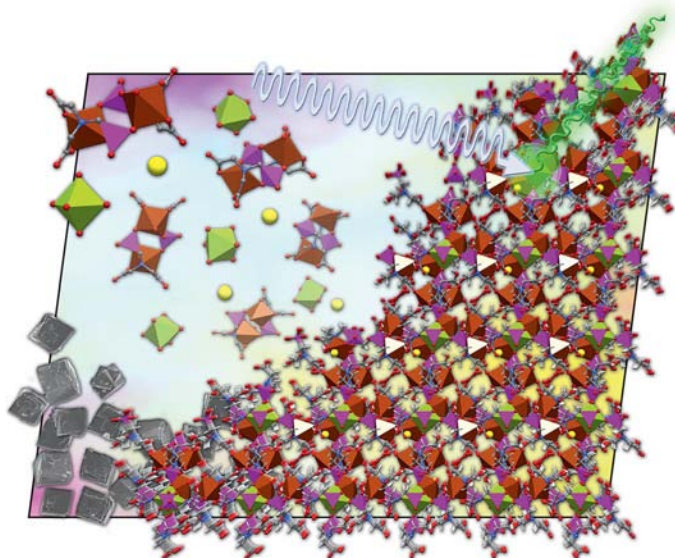


**EurJIC** is a journal of ChemPubSoc Europe, a union of 16 European chemical societies formed for the purpose of publishing high-quality science. All owners merged their national journals to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry*.

Other ChemPubSoc Europe journals are *Chemistry – A European Journal*, *ChemBioChem*, *ChemPhysChem*, *ChemMedChem*, *ChemSusChem* and *ChemCatChem*.

## COVER PICTURE

The cover picture shows the self-assembly of modular porous  $[\text{LnFe}^{\text{III}}\text{Fe}^{\text{II}}_6(\text{Hpmida})_6] \cdot n\text{H}_2\text{O}$  [ $\text{Ln}^{3+} = \text{Nd}^{3+}, \text{Gd}^{3+}, \text{Tb}^{3+}$  and  $\text{Er}^{3+}$ ] frameworks (isolated as large single crystals) from individual  $\{\text{LnO}_6\}$  octahedra,  $[\text{Fe}_2(\text{Hpmida})_2]^{2-}$  dimeric units and charge-balancing  $\text{Fe}^{3+}$  cations. The simultaneous presence of d- and f-block elements promotes multifunctionality: whereas the magnetic properties of the  $\text{Gd}^{3+}$ -based framework are highly sensitive to the local structural disorder, the emission lifetime of the  $\text{Tb}^{3+}$ -based material is increased three-fold when the temperature is lowered. Details of the synthesis and characterization of this series of porous frameworks are given in the article by J. Rocha, F. A. Almeida Paz et al. on p. 2035ff.



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## SHORT COMMUNICATIONS

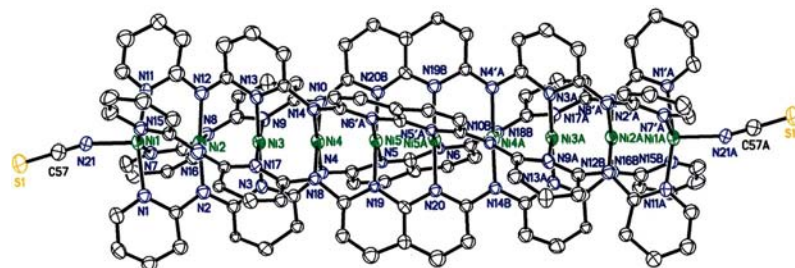
### Decanickel Chains

J.-H. Kuo, T.-B. Tsao,  
G.-H. Lee, H.-W. Lee, C.-Y. Yeh,  
S.-M. Peng\* ..... 2025–2028



An Extended Metal Chain with the 2,7-Bis(dipyridyldiamino)-1,8-naphthyridine ( $H_4bdpdany$ ) Ligand – The Longest Even-Numbered Metal Chain Complex

**Keywords:** Metal–metal interactions / N ligands / Nickel / Magnetic properties



A new pyridyl- and naphthyridyl-modulated ligand ( $H_4bdpdany$ ) and a linear decanickel chain complex were synthesized. We report the molecular structure and the

magnetic and electrochemical properties of the decanickel chain complex, which is the longest even-numbered metal chain complex known to date.

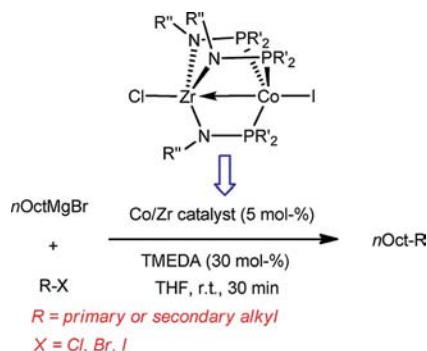
### Heterobimetallic Catalysts

W. Zhou, J. W. Napoline,  
C. M. Thomas\* ..... 2029–2033



A Catalytic Application of Co/Zr Heterobimetallic Complexes: Kumada Coupling of Unactivated Alkyl Halides with Alkyl Grignard Reagents

**Keywords:** Heterometallic complexes / Cobalt / Radical reactions / Metal-metal interactions / Cross-coupling



Tris(phosphanylamide) early/late heterobimetallic Zr/Co complexes have been utilized as catalysts for the cross-coupling of alkyl halides, including alkyl chlorides, with *n*-octylmagnesium bromide. Corresponding monometallic complexes are inert towards alkyl chlorides, suggesting that each metal in the heterobimetallic catalyst is playing an essential role.

## FULL PAPERS

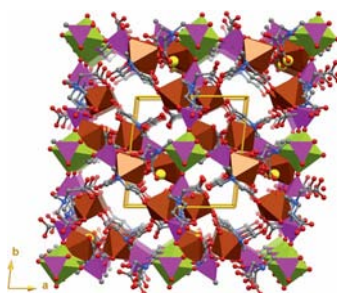
### Mixed-Metal Frameworks

J. Rocha,\* F. A. Almeida Paz,\* F.-N. Shi,  
D. Ananias, N. J. O. Silva, L. D. Carlos,  
T. Trindade ..... 2035–2044

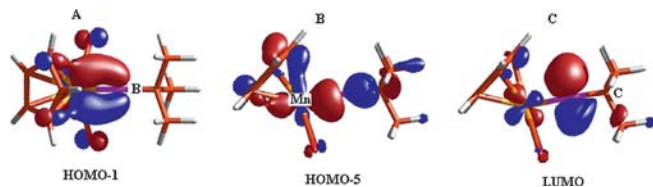


Mixed-Metal d-f Phosphonate Frameworks – Photoluminescence and Magnetic Properties

**Keywords:** Metal–organic frameworks / Lanthanides / Iron / Photoluminescence / Magnetic properties



Mixed-metal d-f, highly symmetric  $[LnFe^{III}-Fe^{II}_6(Hpmida)_6]_n \cdot nH_2O$  metal–organic frameworks [ $Ln = Nd^{3+}, Gd^{3+}, Tb^{3+}, Er^{3+}$ ] have been prepared by hydrothermal synthesis and their photoluminescent and magnetic properties have been investigated at room and low temperatures.



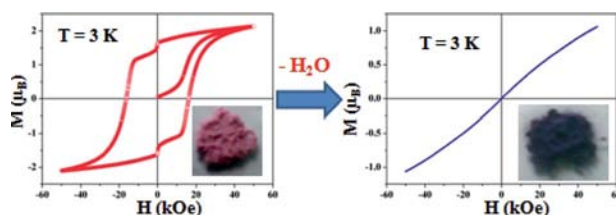
Theoretical calculations have been performed for the terminal alkylborylene complexes  $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{M}(\text{BR})]$  and halo-borylene complexes  $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{M}(\text{BX})]$  ( $\text{M} = \text{Mn, Re}$ ;  $\text{R} = \text{Me, Et, } i\text{Pr, } t\text{Bu}$ ;  $\text{X} = \text{F, Cl, Br, I}$ ) using the exchange correlation functionals BP86/TZ2P. The contributions of the electrostatic interactions  $\Delta E_{\text{elstat}}$

are significantly larger in all borylene complexes than the covalent bonding  $\Delta E_{\text{orb}}$ , that is, the  $\text{M}=\text{BR}$  bonding in the borylene complexes has a greater degree of ionic character. It is significant to note that the  $\pi$ -bonding contribution is, in all complexes, smaller (22.6–25.8% of total orbital contributions) than the  $\sigma$  bonding contribution.

**K. K. Pandey,\* H. Braunschweig,\*  
R. D. Dewhurst ..... 2045–2056**

DFT Study on Alkyl- and Haloborylene Complexes of Manganese and Rhenium: Structure and Bonding Energy Analysis in  $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{M}(\text{BR})]$  and  $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{M}(\text{BX})]$  ( $\text{M} = \text{Mn, Re}$ ;  $\text{R} = \text{Me, Et, } i\text{Pr, } t\text{Bu}$ ;  $\text{X} = \text{F, Cl, Br, I}$ )

**Keywords:** Manganese / Rhenium / Boron / Boron ligand / Borylene complex / Density functional calculations



An amine-templated 2D  $\text{Co}^{\text{II}}$  coordination polymer,  $\{[\text{EDA}]\text{H}_2[\text{Co}_2\text{F}_2(\text{SO}_4)_2(\text{H}_2\text{O})_2]\}_n$  (**1**) (EDA = ethylenediamine), has been synthesised and structurally characterised. Magnetic measurements reveal the pres-

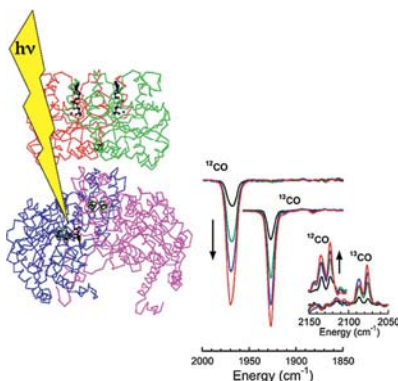
ence of spin-canted antiferromagnetism and hard-magnet-like behaviour with a large magnetic hysteresis with a coercive field ( $H_c$ ) of 16.2 kOe and a remnant magnetisation ( $M_R$ ) of 1.64  $\mu_B$ .

**C. M. Nagaraja, N. Kumar, T. K. Maji,  
C. N. R. Rao\* ..... 2057–2063**

Amine-Templated  $\text{Co}^{\text{II}}$  Coordination Polymer Exhibiting Novel Magnetic Properties: Effect of Dehydration

**Keywords:** Coordination polymers / Magnetic properties / Cobalt / Hard magnets / Canted antiferromagnets / Hydration

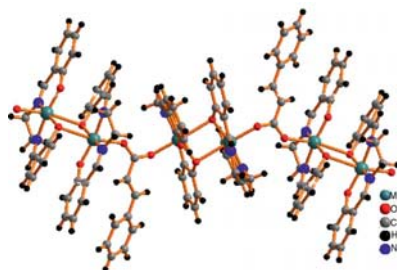
Fourier transform infrared spectroscopy (FT-IR) has been used to study the photochemistry at cryogenic temperatures of CO-inhibited *Azotobacter vinelandii* nitrogenase MoFe protein as well as  $\alpha$ -H195Q and  $\alpha$ -H195N variant proteins. The observed spectra allow the identification of 11 distinct CO-bound species. The spectra can be interpreted in terms of a combination of terminal, multiply bridged and possibly protonated CO species bound to the FeMo cofactor active site.



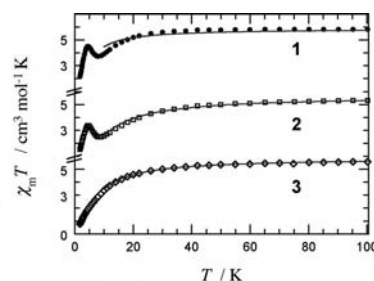
**L. Yan, C. H. Dapper, S. J. George,  
H. Wang, D. Mitra, W. Dong, W. E. Newton,  
S. P. Cramer\* ..... 2064–2074**

Photolysis of Hi-CO Nitrogenase – Observation of a Plethora of Distinct CO Species Using Infrared Spectroscopy

**Keywords:** Nitrogen fixation / Nitrogenases / Enzyme catalysis / Carbon monoxide / IR spectroscopy / Photolysis / *Azotobacter vinelandii*



Three new alternating phenoxo-carboxylato-bridged  $\text{Mn}^{\text{III}}$  complexes with a Schiff base salen have been synthesized and characterized. Two of the complexes that form 1D infinite chains exhibit spin-canted



antiferromagnetic phase transitions, whereas the third complex that has a tetranuclear structure, also shows antiferromagnetic coupling, but remains paramagnetic down to 2 K.

## Spin-Canted Manganese(III)

**P. Kar, P. M. Guha, M. G. B. Drew,  
T. Ishida,\* A. Ghos ..... 2075–2085**

Spin-Canted Antiferromagnetic Phase Transitions in Alternating Phenoxo- and Carboxylato-Bridged  $\text{Mn}^{\text{III}}$ -Salen Complexes

**Keywords:** Manganese complexes / Salen / Magnetic properties / Spin canting



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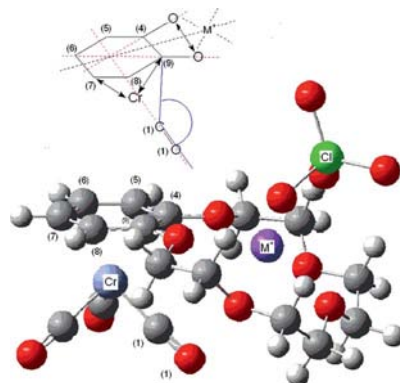
## Differential Metal Cation Sensing

G. R. Stephenson,\* C. E. Anson,  
C. S. Creaser, C. A. Daul ..... 2086–2097



Spectroscopic, Structural and DFT Study of the Responses of Carbonylmethyl Crown Ether Complexes to Alkali Metal Cations

**Keywords:** Crown compounds / Alkali metal ions / IR spectroscopy / Density functional calculations / Molecular sensors / Carbonyl ligands



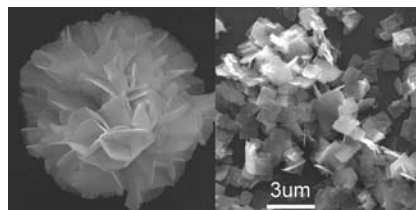
FTIR spectroscopy and DFT calculations are used to differentiate  $1\cdot\text{Li}^+$ ,  $1\cdot\text{Na}^+$  and  $1\cdot\text{K}^+$  coordination complexes. The geometry and bonding in the  $\text{C}(4)\text{--}\text{C}(9)\cdots\text{C}(1)\text{--}\text{O}(1)$  region of the  $(\eta^6\text{-C}_6\text{H}_4\text{O}_2)\text{-Cr}(\text{CO})$  portion of the complex is sensitive to the nature of  $\text{M}^+$ , and influences the vibrational stretching frequencies of  $\nu(\text{CO})$ .

## Iron Selenide Nanoplates

L. Q. Chen, X. F. Yang, X. H. Fu,  
C. M. Wang, C. L. Liang,  
M. M. Wu\* ..... 2098–2102

Facile Solvothermal Synthesis of Uniform Iron Selenide Nanoplates

**Keywords:** Iron / Selenium / Nanostructures / Solvothermal synthesis



Dispersed nanoplates and their flowerlike aggregates of stoichiometric FeSe have been grown from safe and simple inorganic sources by a diol thermal synthesis in the presence of PVP. Both the nanostructures and chemical phase can be controlled by selecting the use of diol and the amount of PVP, respectively.

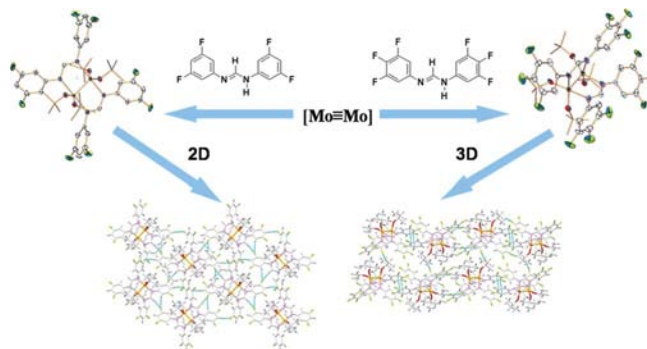
## Atom Networks

S. Krackl, S. Inoue, M. Driess,  
S. Enthaler\* ..... 2103–2111



Intermolecular Hydrogen–Fluorine Interaction in Dimolybdenum Triply Bonded Complexes Modified by Fluorinated Formamidine Ligands for the Construction of 2D- and 3D-Networks

**Keywords:** Molybdenum / Fluorine / Fluorinated ligands / N ligands / Heteroleptic complexes / Multiple bonds / Crystal engineering / Hydrogen-fluorine interactions



Modification of *N*-aryl-substituted formamidine ligands by simple introduction of fluorine atoms into the ligand sphere of

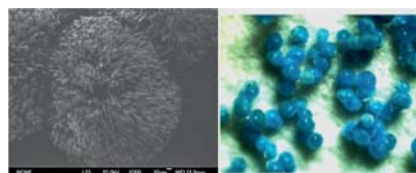
metal-organic complexes and the resulting hydrogen–fluorine interactions can be used for crystal engineering.

## Synthesis of Pure-Phase AV-23

Q. Z. Jiang, Q. Shi, H. Xu\*, J. P. Li,  
J. X. Dong\* ..... 2112–2117

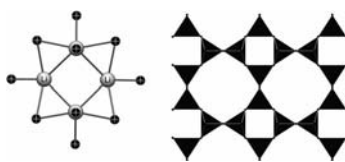
Hydrothermal Synthesis of Pure-Phase Copper Silicate  $\text{Na}_2\text{Cu}_2\text{Si}_4\text{O}_{11}\cdot 2\text{H}_2\text{O}$  with Ammonia as Complexing Agent

**Keywords:** Hydrothermal synthesis / Silicates / Copper / Pure phases / Competitive balance



Pure-phase copper silicate AV-23 was synthesized with aqueous ammonia as a complexing agent for  $\text{Cu}^{2+}$ . The key to the preparation of pure-phase AV-23 is the control of  $\text{Cu}(\text{OH})_2$  precipitation from the solution.

The new quaternary nitridosilicate nitride  $\text{Li}_2\text{Sr}_4[\text{Si}_2\text{N}_5]\text{N}$  with loop-branched  $[\text{Si}_2\text{N}_5]^{7-}$  dreier single layers derived from the apophyllite structure type has been synthesized in lithium melts in weld-shut tantalum ampoules. The single-crystal structure has been analyzed by Madelung (MAPLE) and DFT (VASP) calculations.

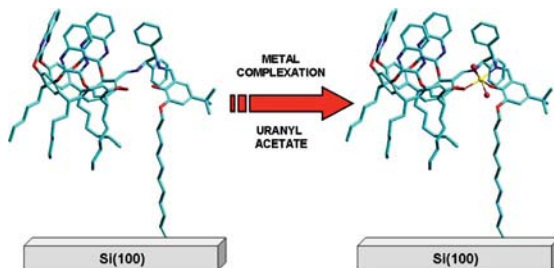


S. Lupart, S. Pagano, O. Oeckler,  
W. Schnick\* ..... 2118–2123

$\text{Li}_2\text{Sr}_4[\text{Si}_2\text{N}_5]\text{N}$  – A Layered Lithium Nitridosilicate Nitride

**Keywords:** Solid-state structures / Lithium / Silicon / Nitridosilicates / Density functional calculations

## Modified Silicon Surface



A cavitand-modified salen receptor was covalently grafted onto porous and monocrystalline silicon. The uranyl complex of the modified salen was also obtained directly

on the surface. The observed salen-uranyl interaction suggests that the surface anchored molecules are intact and, therefore, retain their complexation properties.

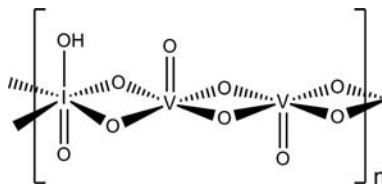
C. Tudisco, G. T. Sfrassetto,  
A. Pappalardo, A. M., G. A. Tomaselli,  
I. L. Fragale, F. P. Ballistreri,  
G. G. Condorelli\* ..... 2124–2131

Covalent Functionalization of Silicon Surfaces with a Cavitand-Modified Salen

**Keywords:** Silicon / Surface chemistry / Monolayers / Metalation / Cavitands

## Vanadium Periodates

Compounds  $[\text{M}_5\text{V}_4\text{I}_{20}(\text{OH})] n\text{H}_2\text{O}$  ( $\text{M} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ ) were prepared by precipitation from aqueous solutions of  $\text{V}^{\text{V}}$ , and their edge-linked polymeric structure was demonstrated by using V and I K-edge extended X-ray absorption fine structure (EXAFS) spectroscopy.



A. L. Hector,\* W. Levason .... 2132–2137

Synthesis, Spectroscopic and Structural Studies on Vanadium(V) Periodates

**Keywords:** Vanadium / Periodate / EXAFS spectroscopy

## Aerobic White Phosphorus Chemistry

A zero-waste, one-step synthetic route to triaryl phosphates from elemental white phosphorus is reported. White phosphorus is combined with phenols under aerobic conditions and in the presence of iron catalysts and iodine, facilitating full conversion to various phosphates without the use of chlorine or chlorinated solvents.



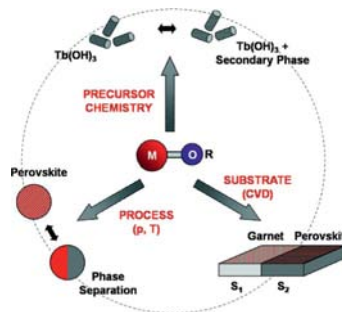
K. M. Armstrong, P. Kilian\* ... 2138–2147

Catalytic Synthesis of Triaryl Phosphates from White Phosphorus

**Keywords:** Homogeneous catalysis / Phosphorus / Flame retardants / Triaryl phosphates / Green chemistry

## Terbium Containing Nanostructures

Homo- and heterometallic terbium alkoxides were synthesized and used as molecular precursors in solvothermal synthesis, sol-gel and CVD processes to prepare Tb-containing hydroxide and oxide nanostructures and thin films. The observation of different phases and morphologies reveals the strong influence of precursor chemistry on material properties.



E. Hemmer, V. Huch, M. Adlung,  
C. Wickleder, S. Mathur\* ..... 2148–2157

Homo- and Heterometallic Terbium Alkoxides – Synthesis, Characterization and Conversion to Luminescent Oxide Nanostructures

**Keywords:** Lanthanides / Terbium / Aluminium / Alkoxides / Nanostructures / Luminescence / Sol-gel process / Optical materials

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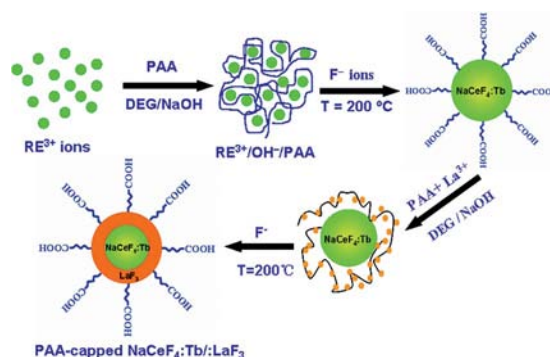
## Carboxyl-Functionalized Nanocrystals

X. Wu, Q. Zhang, X. Wang,\* H. Yang,  
Y. Zhu ..... 2158–2163



One-Pot Synthesis of Carboxyl-Functionalized Rare Earth Fluoride Nanocrystals with Monodispersity, Ultrasmall Size and Very Bright Luminescence

**Keywords:** Rare earths / Fluorides / Nanoparticles / Luminescence



A one-pot synthesis of carboxyl-functionalized rare earth (RE) fluoride nanocrystals has been developed by introducing poly(acrylic acid) (PAA). PAA strongly coordinated to the surface of the  $\text{NaCeF}_4:\text{Tb}^{3+}$  nanocrystals to form a trans-

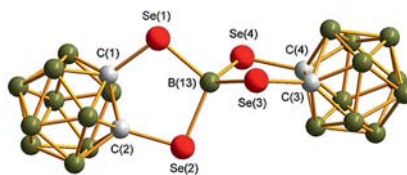
parent colloidal aqueous solution. The PAA-capped  $\text{NaCeF}_4:\text{Tb}^{3+}/\text{LaF}_3$  core/shell nanostructure was successfully synthesized and demonstrated superior optical properties.

## Selenaborates

B. Wrackmeyer\*, E. V. Klimkina,  
W. Milius ..... 2164–2171

A Spirocyclic Borate and a Dihydroborate Derived from the 1,2-Diselenolato-1,2-dicarba-*closo*-dodecaborane(12) Dianion  $[\text{1,2-(1,2-C}_2\text{B}_{10}\text{H}_{10})\text{Se}_2]^{2-}$ : Structures, NMR Spectroscopy, and DFT Calculations

**Keywords:** Borates / Carboranes / Selenium / NMR spectroscopy / X-ray diffraction



The synthesis and structures of a spirocyclic bis(1,2-dicarba-*closo*-dodecaborane-1,2-diselena)borate and of a 1,2-dicarba-*closo*-dodecaborane-1,2-diselenadihydroborate are reported. Their solution-state structures were studied by multinuclear magnetic resonance spectroscopy ( $^1\text{H}$ ,  $^{11}\text{B}$ ,  $^{13}\text{C}$ , and  $^{77}\text{Se}$ ).

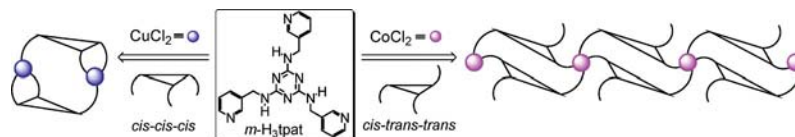
## Tripodal Semi-Rigid Ligand

M.-R. Tsai, J.-Y. Wu,\*  
L.-L. Lai\* ..... 2172–2178



Discrete and Infinite Metallacyclic Coordination Architectures Based on a Conformationally Flexible Tripodal Aminotriazine-Derived Polypyridyl Ligand

**Keywords:** Heterocycles / Cobalt / Copper / Metallacycles / Tripodal ligands



Discrete and infinite metallacycles have been synthesized by self-assembly from a

conformationally flexible tripodal aminotriazine-derived polypyridyl ligand.

\* Author to whom correspondence should be addressed.



Supporting information on the WWW (see article for access details).



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