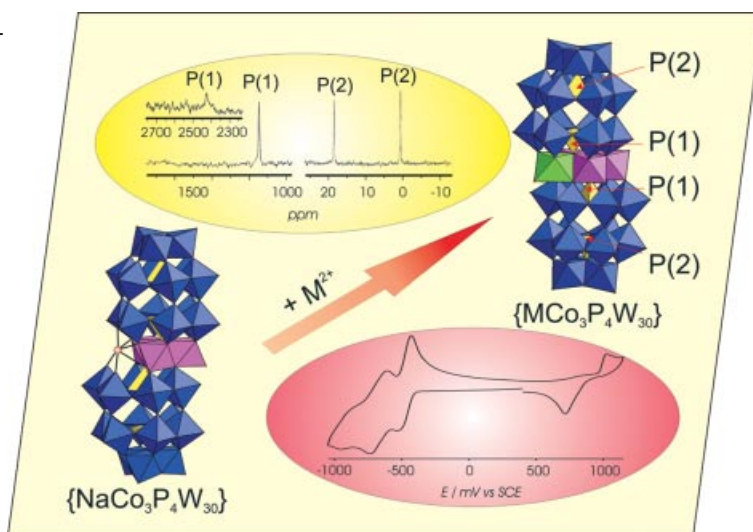




The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry*. Three further EUChemSoc Societies (Austria, Czech Republic and Sweden) are Associates of the two journals.

## COVER PICTURE

The cover picture shows the synthesis of the mixed-metal Dawson sandwich complexes  $[\text{MCo}_3(\text{H}_2\text{O})_2(\text{P}_2\text{W}_{15}\text{O}_{56})]^{16-}$  by the addition of the transition metal cation  $\text{M}^{2+}$  to the “lacunary” sandwich complex  $[\text{NaCo}_3(\text{H}_2\text{O})_2(\text{P}_2\text{W}_{15}\text{O}_{56})]^{17-}$ . This “lacunary” species is a good precursor for the preparation mixed-metal sandwich complexes, with promising interesting catalytic, electrocatalytic and magnetic properties. Details of the synthesis and the structural characterization in solution are discussed in the article by L. Ruhlmann and R. Touvenot on p. 1493 ff.



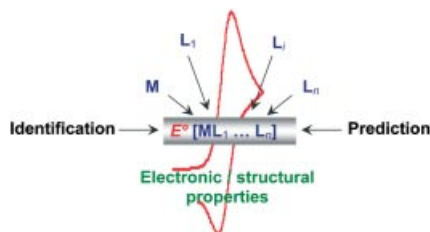
## MICROREVIEW

### Molecular Electrochemistry

A. J. L. Pombeiro\* ..... 1473–1482

Characterization of Coordination Compounds by Electrochemical Parameters

**Keywords:** Electrochemistry / Redox potential / Additivity models / Ligand parameters / Ligand effects



Attention is drawn to the interest shown in the redox potential and derived electrochemical parameters that are used for the characterization and identification of coordination compounds.

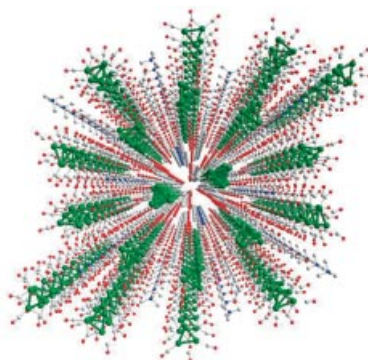
## SHORT COMMUNICATIONS

### Molecular Wires

C. Femoni, F. Kaswalder, M. C. Iapalucci, G. Longoni,\* S. Zacchini ..... 1483–1486

Infinite Molecular  $\{[\text{Pt}_{3n}(\text{CO})_{6n}]^{2-}\}_{\infty}$  Conductor Wires by Self-Assembly of  $[\text{Pt}_{3n}(\text{CO})_{6n}]^{2-}$  ( $n = 5-8$ ) Cluster Dianions Formally Resembling CO-Sheathed Three-Platinum Cables

**Keywords:** Carbonyl ligands / Cluster compounds / Platinum / Structure elucidation / Conducting materials



Self-assembly of  $[\text{Pt}_{3n}(\text{CO})_{6n}]^{2-}$  ( $n = 5-8$ ) cluster dianions into infinite semicontinuous or continuous  $\{[\text{Pt}_{3n}(\text{CO})_{3n}(\mu\text{-CO})_{3n}]^{2-}\}_{\infty}$  conductor wires is obtained upon crystallization. Pellets of these salts exhibit conductor behavior that roughly depends on the interdianion gap along the wires.

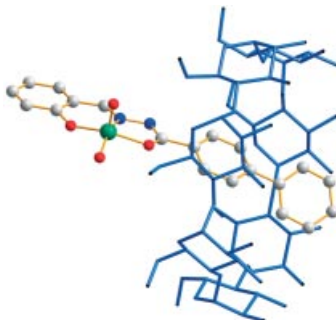
### Inclusion Compounds

I. Lippold, H. Görls, W. Plass\* ..... 1487–1491



New Aspects for Modeling Supramolecular Interactions in Vanadium Haloperoxidases:  $\beta$ -Cyclodextrin Inclusion Compounds of *cis*-Dioxovanadium(V) Complexes

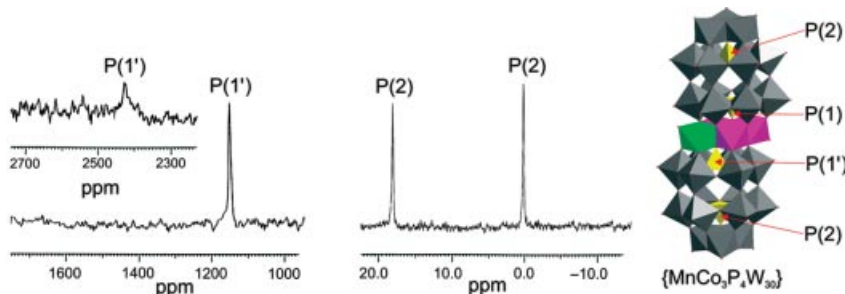
**Keywords:** Cyclodextrins / Host–guest systems / Inclusion compounds / Vanadium / X-ray diffraction



A novel  $\beta$ -cyclodextrin inclusion compound of the *cis*-dioxovanadium(V) complex derived from biphenyl-4-carboxylic acid salicylidene hydrazide has been synthesized. The isolated inclusion compound  $\text{K}[\text{VO}_2(\text{salhybiph})@ \beta\text{-CD}]$  has been characterized in solution by NMR spectroscopy and in the solid state by X-ray crystallography. The latter reveals a channel-type packing of head-to-head  $\beta$ -cyclodextrin dimers.

## FULL PAPERS

### Dawson Sandwich Complexes



Mixed-metal Dawson sandwich complexes  $[\text{MCo}_3(\text{H}_2\text{O})_2(\text{P}_2\text{W}_{15}\text{O}_{56})_2]^{16-}$  have been synthesized by the reaction of  $\text{M}^{2+}$  (where  $\text{M} = \text{Mn}, \text{Co}, \text{Ni}, \text{Zn}$  and  $\text{Cd}$ ) with the “lacunary” sandwich complex

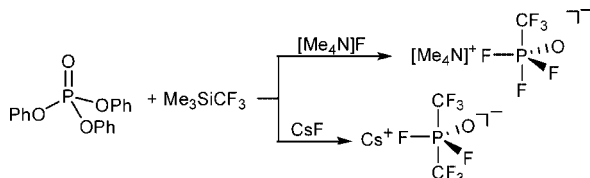
$\alpha\beta\text{-}[\text{NaCo}_3(\text{H}_2\text{O})_2(\text{P}_2\text{W}_{15}\text{O}_{56})_2]^{17-}$ . The  $\{\text{MCo}_3\text{P}_4\text{W}_{30}\}$  species were characterized by IR spectroscopy, elemental analysis,  $^{31}\text{P}$  NMR spectroscopy and electrochemistry.

**L. Ruhlmann,\* C. Costa-Coquelard, J. Canny, R. Thouvenot\* ..... 1493–1500**

Mixed-Metal Dawson Sandwich Complexes: Synthesis, Spectroscopic Characterization and Electrochemical Behaviour of  $\text{Na}_{16}[\text{M}^{\text{II}}\text{Co}_3(\text{H}_2\text{O})_2(\text{P}_2\text{W}_{15}\text{O}_{56})_2]$  ( $\text{M} = \text{Mn}, \text{Co}, \text{Ni}, \text{Zn}$  and  $\text{Cd}$ )

**Keywords:** Dawson complexes / Paramagnetic  $^{31}\text{P}$  NMR spectroscopy / Electrochemistry

### Anions of Pentacoordinate P



The competitive nucleophilic trifluoromethylation/fluorination of  $(\text{PhO})_3\text{P}(\text{O})$

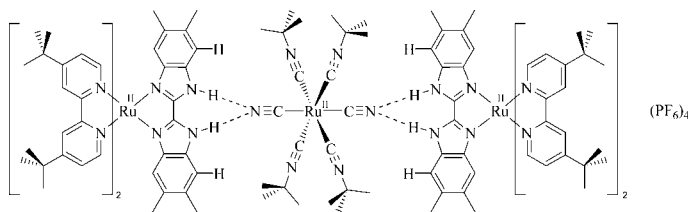
with  $\text{Me}_3\text{SiCF}_3$  and  $[\text{Me}_4\text{N}]\text{F}$  or  $\text{CsF}$  was investigated.

**N. V. Pavlenko, L. A. Babadzhanova, I. I. Gerus, Y. L. Yagupolskii,\* W. Tyrre, D. Naumann ..... 1501–1507**

New Anions of Pentacoordinate Phosphorus Containing Fluorine and Trifluoromethyl Groups

**Keywords:** Phosphorus / Fluorides / Silanes / Pentacoordinate anions

### Supramolecular Photochemistry



*cis*- or *trans*- $[\text{Ru}(\text{C}\equiv\text{N}-t\text{Bu})_4(\text{CN})_2]$  and photochemically active [bis(bipyridyl)bis(benzimidazole-ruthenium(II))] complexes form supramolecular adducts via hydrogen

bond association. Stoichiometry, molecular structure, photophysical properties and association constants of the adducts are reported.

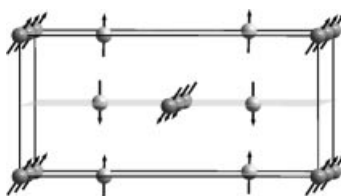
**K. Halbauer, A. Göbel, A. Sterzik, H. Görls, S. Rau, W. Imhof\* ..... 1508–1514**

Ruthenium Complex Fragments as Constituents of Trinuclear Photoactive Supramolecular Assemblies Based on Hydrogen Bond Association

**Keywords:** Supramolecular Photochemistry / Bibenzimidazole ligands / Hydrogen bonds / Ruthenium

### Olivine – Magnetic Structure

The antiferromagnetic structure on the olivine-type  $\text{Mn}_2\text{GeSe}_4$  is discussed as a potentially canted structure.



**H. Mikus, H.-J. Deiseroth,\* K. Aleksandrov, C. Ritter, R. K. Kremer ..... 1515–1518**

The Magnetic Structure of  $\text{Mn}_2\text{GeSe}_4$

**Keywords:** Olivine / Magnetic structure / Manganese / Germanium / Selenium / Antiferromagnetism

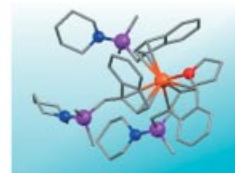
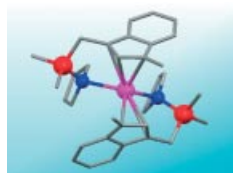
# CONTENTS

## Organolanthanide Complexes

S. Zhou, S. Wang,\* E. Sheng,  
L. Zhang, Z. Yu, X. Xi, G. Chen,  
W. Luo, Y. Li ..... 1519–1528

Synthesis, Characterization, and Catalytic Activity of Some Neodymium(III), Ytterbium(II), and Europium(II) Complexes with Pyrrolidinyl- and Piperidinyl-Functionalized Indenyl Ligands

**Keywords:** Homolysis / Catalysts / Polymerization / Lanthanoids



Studies on the reactivity of pyrrolidinyl- and piperidinyl-functionalized indene compounds with the lanthanide(III) amides have led to synthesis and characterization of a series of new organolanthanide(II)

complexes and a new neodymium(III) complex. All complexes exhibited moderate to good catalytic activities for the ring-opening polymerization of  $\epsilon$ -caprolactone.

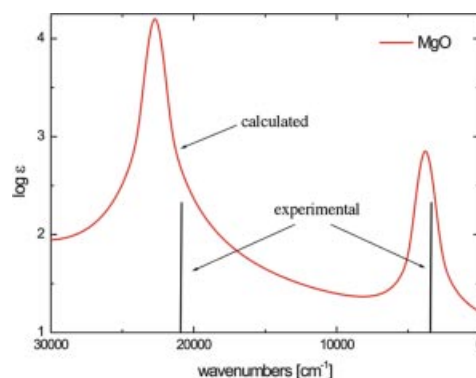
## Microclusters

M. Srnec,\* R. Zahradník ..... 1529–1543



Small Group IIa–VIa Clusters and Related Systems: A Theoretical Study of Physical Properties, Reactivity, and Electronic Spectra

**Keywords:** Ab initio calculations / Cluster compounds / Structural elucidation



The group IIa–VIa diatomics exhibit electronic transitions in the visible region and the longest wavelength bands are located in

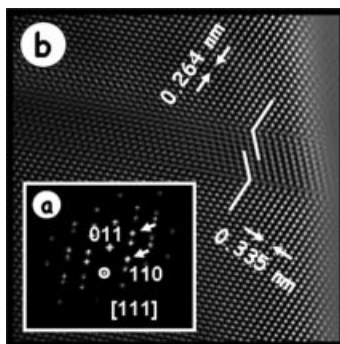
the near-infrared region. MgO represents an extreme.

## Semiconducting Oxides

D. Maestre, J. Ramírez-Castellanos,  
P. Hidalgo, A. Cremades,  
J. M. González-Calbet,  
J. Piqueras\* ..... 1544–1548

Study of the Defects in Sintered SnO<sub>2</sub> by High-Resolution Transmission Electron Microscopy and Cathodoluminescence

**Keywords:** Semiconductors / Luminescence / Microstructure / Resistivity



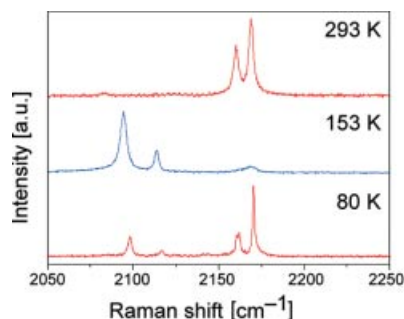
High-resolution images of sintered SnO<sub>2</sub> samples annealed under an oxygen atmosphere show structural defects that seem to be related to changes in both the cathodoluminescence spectra and electrical resistivity.

## Nonstoichiometric Compounds

S. Cobo, R. Fernández, L. Salmon,  
G. Molnár, A. Bousseksou\* ... 1549–1555

Correlation between the Stoichiometry and the Bistability of Electronic States in Valence-Tautomeric Rb<sub>x</sub>Mn[Fe(CN)<sub>6</sub>]<sub>y</sub>·zH<sub>2</sub>O Complexes

**Keywords:** Prussian blue analogues / Magnetic properties / Phase transitions / Raman spectroscopy

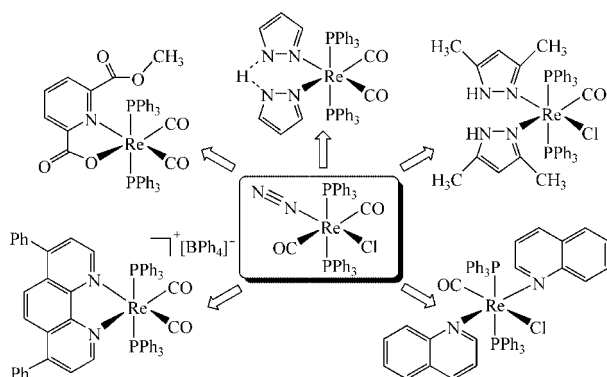


A series of Prussian blue analogues Rb<sub>x</sub>Mn[Fe(CN)<sub>6</sub>]<sub>y</sub>·zH<sub>2</sub>O with different stoichiometries was synthesized; some of the samples exhibit a first-order phase transition between the Mn<sup>II</sup>–Fe<sup>III</sup> and Mn<sup>III</sup>–Fe<sup>II</sup> electronic states accompanied by large entropy changes that are mainly of vibrational origin.

**A. M. Kirillov, M. Haukka,**  
**M. F. C. Guedes da Silva,**  
**A. J. L. Pombeiro\* ..... 1556–1565**

Synthesis, Characterization and Redox  
 Behaviour of Mono- and Dicarboxyl  
 Phosphane Rhenium(I) Complexes Bearing  
 N-, N,N- and N,O-Type Ligands

**Keywords:** Carbonyl ligands / Electro-  
 chemistry / N ligands / Rhenium



Pyrazole, quinoline, phenanthroline, picolinate or dipicolinate complexes with  $\{\text{Re}(\text{CO})_x\}$  ( $x = 1, 2$ ) sites were prepared from a dinitrogen-complex precursor. The

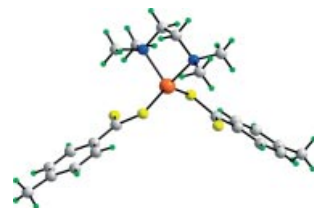
redox behaviour of the complexes was studied and the Lever electrochemical ligand parameter  $E_L$  was determined for 4,7- $\text{Ph}_2$ -phen.

## Metal Sulfide Nanoparticles

**G. Kedarnath, V. K. Jain,\* S. Ghoshal,**  
**G. K. Dey, C. A. Ellis,**  
**E. R. T. Tiekink\* ..... 1566–1575**

Zinc, Cadmium and Mercury Dithiocarbonylates: Synthesis, Characterization, Structure and Their Transformation to Metal Sulfide Nanoparticles

**Keywords:** Zinc / Cadmium / Mercury /  
 Dithiocarbonylates / Nanoparticles



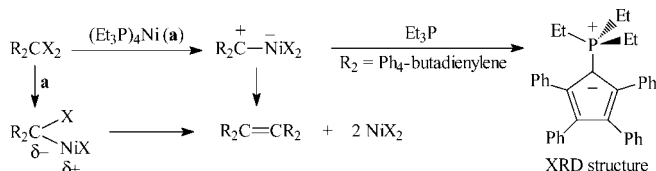
Thermolysis of  $[\text{M}(\text{S}_2\text{CPh})_2(\text{tmeda})]$  gave metal sulfide nanoparticles which were characterized by XRD, EDAX and TEM. Both hexagonal and cubic phases of metal sulfide nanoparticles can be prepared by changing experimental conditions.

## Nickel(II)-Carbene Intermediates

**J. J. Eisch,\* Y. Qian,**  
**A. L. Rheingold ..... 1576–1584**

Nickel(II)-Carbene Intermediates in Reactions of Geminal Dihalides with Nickel(0) Reagents and the Corresponding Carbene Capture as the Phosphonium Ylide

**Keywords:** Nickel(0) reagents / Nickel(II)-carbenes / Phosphonium ylides /  $\alpha$ -Elimination / Carbon-carbon bond formation



Coupling of geminal dihalides with  $(\text{Et}_3\text{P})_4\text{Ni}$  has been reinvestigated. Failure to trap assumed nickel(0)-carbenes, detection and isolation of Wittig reagents and the failed coupling of 5,5-dibromotetra-

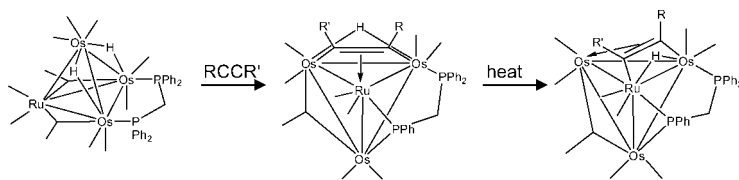
phenylcyclopentadiene led us to conclude that nickel(II)-carbenes are involved. The X-ray structure of  $\text{Ph}_4\text{Cp}=\text{PEt}_3$  is best represented as having a zwitterionic C–P bond.

## Stereoselective Alkyne Binding

**Y. L. K. Tan, W. K. Leong\* ... 1585–1598**

The Ditertiary-Phosphane-Bridged Heteronuclear Cluster  $\text{RuOs}_3(\mu\text{-H})_2(\text{CO})_9(\mu\text{-CO})_2(\mu\text{-dppm})$ : Synthesis and Reactivity with Alkynes

**Keywords:** Heterometallic complexes / Ruthenium / Osmium / Ditertiary phosphanes / Alkynes



The reaction of the dppm-bridged heteronuclear cluster  $\text{RuOs}_3(\mu\text{-H})_2(\text{CO})_9(\mu\text{-CO})_2(\mu\text{-dppm})$  with alkynes afforded tetrahedral clusters in which the alkyne is aligned parallel to an Os–Os bond ( $\parallel\text{Os-Os}$

isomer). The clusters incorporating internal alkynes underwent isomerization to the  $\parallel\text{Ru-Os}$  isomer by alkyne and hydride migration.



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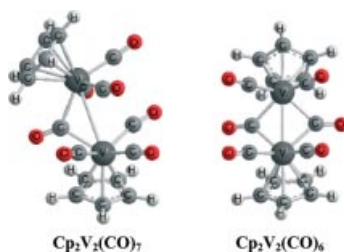
## Cyclopentadienylvanadium CO Structures

X.-H. Zhang, Q.-S. Li,\* Y. Xie,  
R. B. King,\* H. F. Schaefer III ... 1599–1605



The Binuclear Cyclopentadienylvanadium Carbonyls ( $\eta^5\text{-C}_5\text{H}_5\text{)}_2\text{V}_2(\text{CO})_7$  and ( $\eta^5\text{-C}_5\text{H}_5\text{)}_2\text{V}_2(\text{CO})_6$ : Comparison with Homoleptic Chromium Carbonyls

**Keywords:** Binuclear cyclopentadienylvanadium carbonyls / Density functional theory



The cyclopentadienylvanadium carbonyls  $\text{CpV}(\text{CO})_n$  ( $n = 4, 3, 2, 1$ ),  $\text{Cp}_2\text{V}_2(\text{CO})_7$ , and  $\text{Cp}_2\text{V}_2(\text{CO})_6$  have been studied by density functional theory using the B3LYP and BP86 functionals. Thermodynamic information from these calculations rationalize why neither  $\text{Cp}_2\text{V}_2(\text{CO})_7$  nor  $\text{Cp}_2\text{V}_2(\text{CO})_6$  have yet been synthesized whereas  $\text{Cp}_2\text{V}_2(\text{CO})_5$  is a known stable compound.

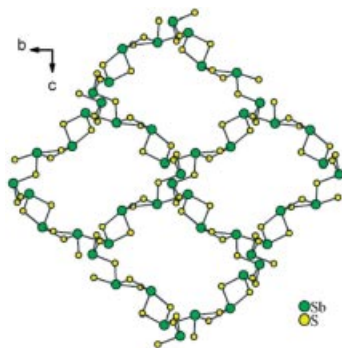
## Thioantimonates

M. Zhang, T. L. Sheng, X. H. Huang,  
R. B. Fu, X. Wang, S. M. Hu, S. C. Xiang,  
X. T. Wu\* ..... 1606–1612



Solvothermal Synthesis, Crystal Structure, and Thermal Stability of Three-Layered Thioantimonate(III) Complexes:  $[\text{Ni}(\text{C}_3\text{H}_{10}\text{N}_2)_3]\text{Sb}_4\text{S}_7$ ,  $[\text{C}_4\text{H}_{14}\text{N}_2]\text{Sb}_8\text{S}_{13} \cdot \text{H}_2\text{O}$ , and  $[\text{C}_6\text{H}_{18}\text{N}_2]\text{Sb}_{10}\text{S}_{16} \cdot \text{H}_2\text{O}$

**Keywords:** Thioantimonates / Solvothermal synthesis / Cations / Layered compounds



In the compound  $[\text{Ni}(\text{C}_3\text{H}_{10}\text{N}_2)_3]\text{Sb}_4\text{S}_7$ , a rectangle-like  $\text{Sb}_{16}\text{S}_{16}$  heteroring with dimensions of about  $8.1 \times 14.7 \text{ \AA}$  is observed. This is the largest reported pore in layered thioantimonates to date. Further condensation of the  $\text{Sb}_{16}\text{S}_{16}$  heterorings resulted in an unprecedented framework of the five-atom-thick  $\text{Sb}_x\text{S}_y^{n-}$  layer.

If not otherwise indicated in the article, papers in issue 10 were published online on March 19, 2007