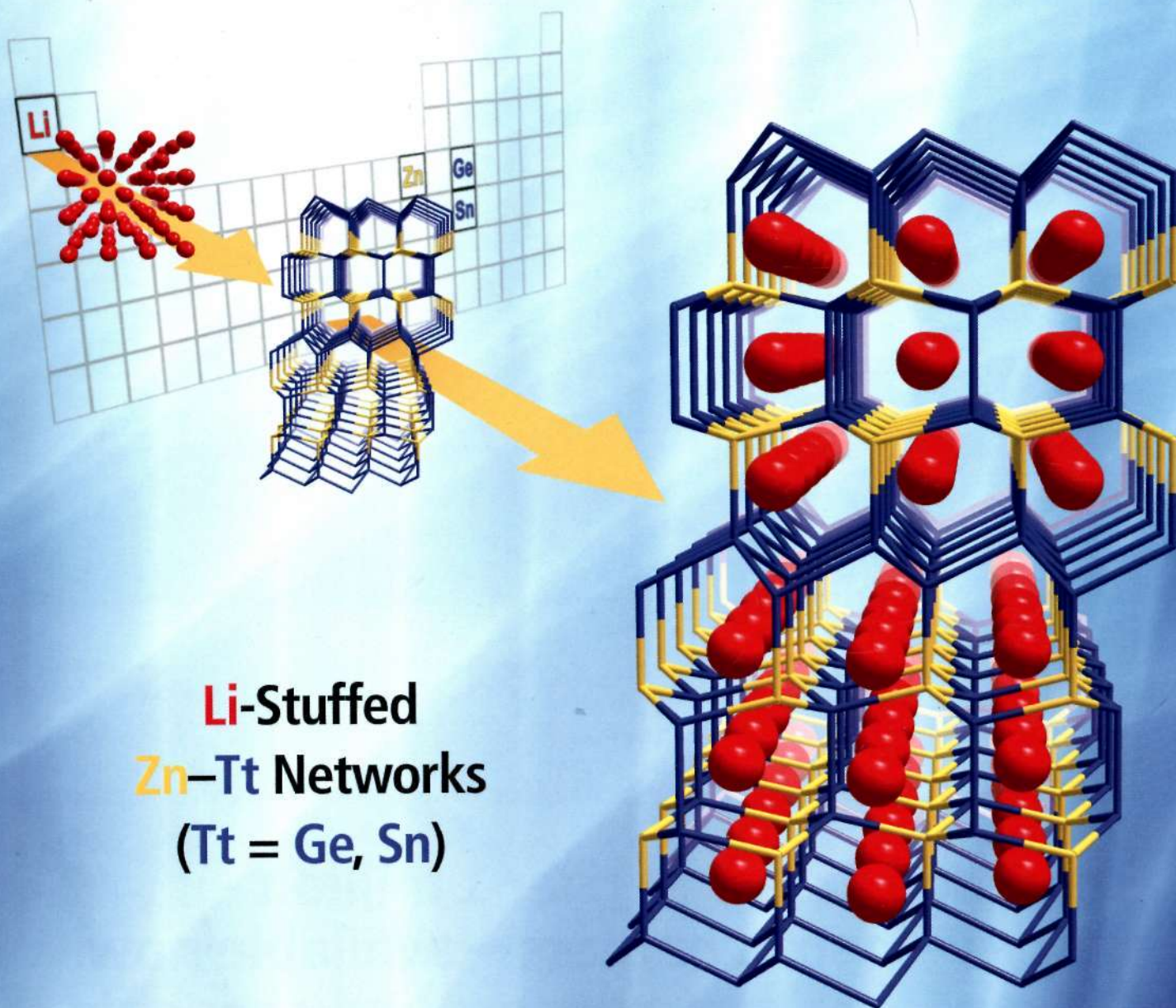


ПН
I-65

inorganic Chemistry

including bioinorganic chemistry

March 18, 2013
Volume 52, Number 6
pubs.acs.org/IC



Li-Stuffed
Zn-Tt Networks
(Tt = Ge, Sn)



ACS Publications
MOST TRUSTED. MOST CITED. MOST READ.

www.acs.org

ON THE COVER: Ternary Li–Zn–Tt (Tt = Ge, Sn) phases with Li-stuffed diamond polytype like Zn–Tt network structures are obtained by the reaction of Li with Zn and Ge or Sn. See S. Stegmaier and T. F. Fässler, p 2809.

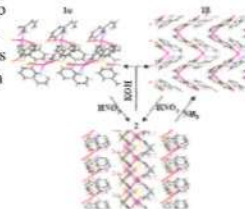
Communications

 2787 
[dx.doi.org/10.1021/ic3008415](https://doi.org/10.1021/ic3008415)

Solid-State Structural Transformations of Two Ag^I Supramolecular Polymorphs to Another Polymer upon Absorption of HNO₃ Vapors

Kamran Akhbari and Ali Morsali*

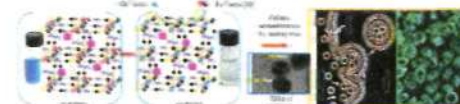
Solid-state structural transformation of two polymorphs of a Ag^I supramolecular polymer to {[Ag(8-HqH)₂]NO₃}_n (2) has been observed upon solid–gas reaction of two polymorphs with HNO₃ vapors. Solid–gas reaction of compound 2 with hydrated vapors of NH₃ results in the formation of only one polymorph because solid–solid reaction of compound 2 with KOH forms a mixture of two polymorphs.


 2790 
[dx.doi.org/10.1021/ic302262g](https://doi.org/10.1021/ic302262g)

Gallium Analogue of Soluble Prussian Blue KGa[Fe(CN)₆]·nH₂O: Synthesis, Characterization, and Potential Biomedical Applications

Murthi S. Kandanapitiye, Benjamin Valley, Liu D. Yang, Allyson M. Fry, Patrick M. Woodward,* and Songping D. Huang*

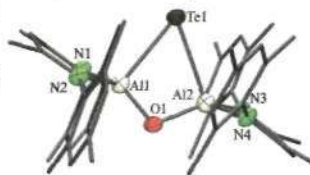
The cellular uptake of Ga(III) closely parallels that of Fe(III) and occurs by a transferrin-receptor (TfR)-mediated endocytosis, a tightly regulated process that can hamper the cellular delivery of gallium for a variety of diagnostic and therapeutic applications. The nanoparticles of the gallium analog of the soluble Prussian blue can penetrate cells via a TfR-independent endocytosis, thus providing a novel intracellular drug delivery system (DDS) for gallium.



Preparation of Telluro- and Selenoalumoxanes under Mild Conditions

Sandra González-Gallardo, Aracely S. Cruz-Zavala, Vojtech Jancik, Fernando Cortés-Guzmán, and Mónica Moya-Cabrera*

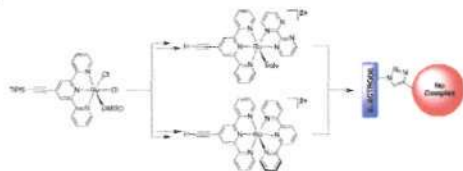
Syntheses of the heavy chalcogen-containing alumoxanes $[\text{M}^{\text{e}}\text{Al}(\text{SeH})_2](\mu\text{-O})$ (4) and $(\text{M}^{\text{e}}\text{LAl})_2(\mu\text{-Te})(\mu\text{-O})$ (7) can be easily accomplished when $(\text{M}^{\text{e}}\text{LAlH})_2(\mu\text{-O})$ (2) is reacted with either red selenium or metallic tellurium. These compounds represent the first examples of aluminum compounds bearing O–Al–E (E = Se, Te) moieties.



Modular Synthesis of Alkyne-Substituted Ruthenium Polypyridyl Complexes Suitable for "Click" Coupling

James B. Gerken, Matthew L. Rigsby, Rose E. Ruther, Riviam J. Pérez-Rodríguez, Iliá A. Guzei, Robert J. Hamers,* and Shannon S. Stahl*

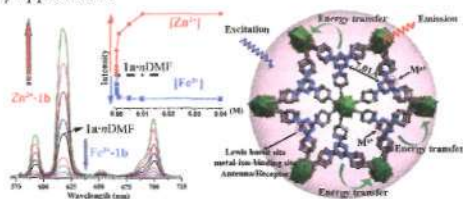
A modular synthetic route is described for the preparation of alkyne-functionalized terpyridinylRu complexes. The suitability of these complexes for "click" coupling reactions is demonstrated in the functionalization of boron-doped diamond electrodes bearing tethered azide groups.



Cation Sensing by a Luminescent Metal–Organic Framework with Multiple Lewis Basic Sites

Qun Tang, Shuxia Liu,* Yiwei Liu, Jun Miao, Shujun Li, Li Zhang, Zhan Shi, and Zhiping Zheng*

Adding metal ions to the lanthanide metal–organic frameworks containing multiple Lewis basic triazinyl N sites led to significant enhancement or quenching of luminescence because of the different nature of the metal guest–ligand interactions and suggesting potential sensory applications.



Articles

Bis(oxazolonyl)phenyl-Ligated Rare-Earth-Metal Complexes: Highly Regioselective Catalysts for *cis*-1,4-Polymerization of Isoprene

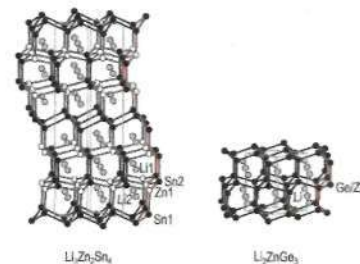
Yu Pan, Tieqi Xu,* Guan-Wen Yang, Kun Jin, and Xiao-Bing Lu*

The oxazolonyl NCN-pincer ligated rare-earth complexes exhibited high *cis*-1,4-selectivity for isoprene polymerization.

Lithium-Stuffed Diamond Polytype Zn–Tt Structures (Tt = Sn, Ge): The Two Lithium–Zinc–Tetrelides $\text{Li}_3\text{Zn}_2\text{Sn}_4$ and Li_2ZnGe_3

Saskia Stegmaier and Thomas F. Fässler*

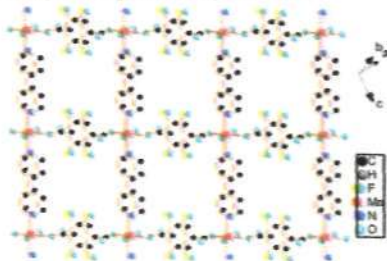
Li-stuffed diamond polytype like Zn–Tt networks (Tt = Ge, Sn) with tetrahedrally four-coordinated Zn and Tt atoms appear in $\text{Li}_3\text{Zn}_2\text{Sn}_4$ and Li_2ZnGe_3 . In case of the new phase, $\text{Li}_3\text{Zn}_2\text{Sn}_4$, Zn and Sn atoms are ordered and constitute a 6H diamond polytype like network. The Zn–Ge substructure of Li_3ZnGe_3 is a hexagonal diamond (2H polytype) like network. The Li–Zn–Tt phases were obtained by high-temperature syntheses from the elements, and their crystal structures were determined with single-crystal X-ray diffraction methods. DFT calculations (TB-LMTO-ASA) reveal metallic properties for $\text{Li}_3\text{Zn}_2\text{Sn}_4$.



Manganese-Based Layered Coordination Polymer: Synthesis, Structural Characterization, Magnetic Property, and Electrochemical Performance in Lithium-Ion Batteries

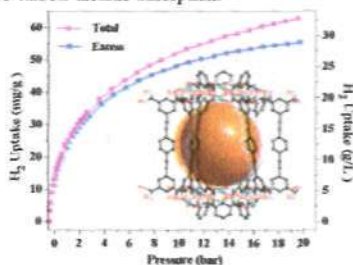
Qi Liu,* Lili Yu, Ying Wang, Yunzhou Ji, Josip Horvat, Mei-Ling Cheng, Xiaoyan Jia, and Guoxiu Wang*

Manganese-based layered coordination polymer ($[\text{Mn}(\text{tfbdc})(4,4'\text{-bpy})(\text{H}_2\text{O})_2]$, Mn-LCP) with microporous structure was synthesized by reaction of 2,3,5,6-tetrafluoroterephthalic acid (H_2tfbdc) and 4,4'-bipyridine (4,4'-bpy) with manganese(II) acetate tetrahydrate in water solution. Mn-LCP was characterized by elemental analysis, IR spectra, thermogravimetric analysis, X-ray single-crystal structure analysis, and powder X-ray diffraction.

**Expanded Porous MOF-505 Analogue Exhibiting Large Hydrogen Storage Capacity and Selective Carbon Dioxide Adsorption**

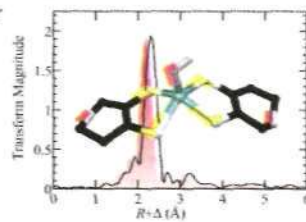
Baishu Zheng,* Ruirui Yun, Junfeng Bai,* Zhiyong Lu, Liting Du, and Yizhi Li

An expanded NbO-type copper metal-organic framework (NJU-Bai12) has been successfully constructed from a nanosized rectangular alkyne-bridging tetracarboxylate ligand and copper(II) paddlewheel secondary building unit, exhibiting large hydrogen storage capacity and selective carbon dioxide adsorption.

**X-ray Absorption Spectroscopy of a Quantitatively Mo(V) Dimethyl Sulfoxide Reductase Species**

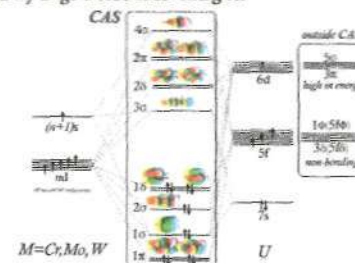
M. Jake Pushie, Julien J. H. Cotelesage, Ganna Lyashenko, Russ Hille, and Graham N. George*

X-ray absorption spectroscopy of an extensively studied Mo(V) form of *Rhodobacter sphaeroides* dimethylsulfoxide reductase (the high-g split species) shows that previously suggested structures for the active site are likely incorrect.

**Molecules with High Bond Orders and Ultrashort Bond Lengths: CrU, MoU, and WU**

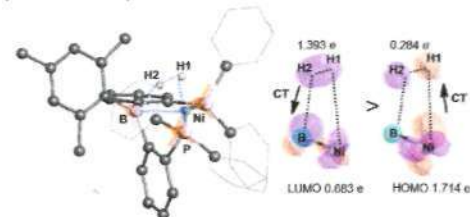
Fernando Ruipérez, Gabriel Merino, Jesus M. Ugalde, and Ivan Infante*

The effective bond order of the MoU dimer (5.5) is higher than that of the tungsten dimer (5.2), known to date as the molecule with the highest bond order in the whole periodic table. The MU (M = Cr, Mo, W) heterodimers present also ultrashort bond distances and remarkably large dissociation energies.

**Unexpected Electronic Process of H₂ Activation by a New Nickel Borane Complex: Comparison with the Usual Homolytic and Heterolytic Activations**

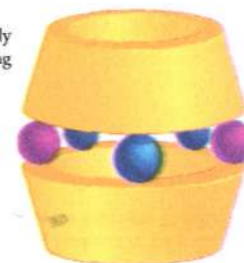
Guixiang Zeng and Shigeyoshi Sakaki*

The H-H σ -bond was cleaved under the cooperation of the electron-rich nickel center and the electron-deficient borane to form an unprecedented hydridoborohydrido complex through a four-center transition state. The electronic process is different from those of the usual homolytic and heterolytic H₂ activation reactions.

 **γ -Cyclodextrin Cuprate Sandwich-Type Complexes**

Abdulaziz A. Bagabas,* Marco Frascioni, Julien lehl, Brad Hauser, Omar K. Farha, Joseph T. Hupp, Karel J. Hartlieb, Youssry Y. Botros, and J. Fraser Stoddart*

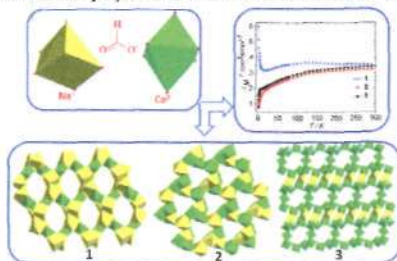
Sandwich-type complexes based on γ -cyclodextrin (orange) and Cu²⁺ (purple) ions, with alkali-metal (blue) ions (Li⁺, Na⁺, and Rb⁺), have been prepared and characterized structurally by single-crystal X-ray diffraction, with the identity of the alkali-metal ion strongly influencing the precise nature of the solid-state structures. Gas uptake studies reveal promising CO₂ sorption properties, particularly for the Cu²⁺/Rb⁺ complex.



Tuning the Structure and Magnetism of Heterometallic Sodium(1+)–Cobalt(2+) Formate Coordination Polymers by Varying the Metal Ratio and Solvents

Jiong-Peng Zhao, Song-De Han, Ran Zhao, Qian Yang, Ze Chang, and Xian-He Bu*

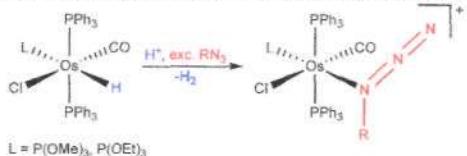
Through variation of the metal ratio and solvents, the structure and magnetism of three new heterometallic sodium(1+)–cobalt(2+) formate coordination polymers with different ratios of Co^{2+} and Na^+ ions have been well tuned.



Azo Complexes of Osmium(III): Preparation and Reactivity of Organic Azide and Hydrazine Derivatives

Gabriele Albertin,* Stefano Antoniutti, Laura Bonaldo, Alessandra Botter, and Jesús Castro

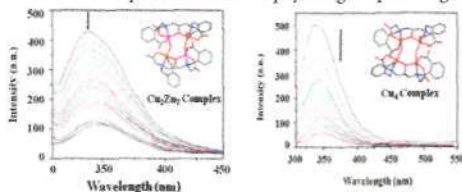
The preparation of unprecedented organic azide complexes of osmium $[\text{OsCl}(\eta^1\text{-N}_3\text{R})(\text{CO})(\text{PPh}_3)_2\text{L}]\text{BPh}_4$ is described. The reaction of the benzylazide derivative leading to the *N*-protio imine complex $[\text{OsCl}(\text{CO})\{\eta^1\text{-NH}=\text{C}(\text{H})\text{C}_6\text{H}_4\text{-4-CH}_3\}(\text{PPh}_3)_2\{\text{P}(\text{OEt})_3\}]\text{BPh}_4$ is also reported. Mixed-ligand hydrazine and arylidiazene complexes of the types $[\text{OsCl}(\text{CO})(\text{RNHNH}_2)(\text{PPh}_3)_2\text{L}]\text{BPh}_4$ and $[\text{OsCl}(\text{CO})(\text{ArN}=\text{NH})(\text{PPh}_3)_2\text{L}]\text{BPh}_4$ were also prepared.



Synthesis, Structure, Spectroscopic Characterization, and Protein Binding Affinity of New Water-Soluble Hetero- and Homometallic Tetranuclear $[\text{Cu}^{\text{II}}_2\text{Zn}^{\text{II}}_2]$ and $[\text{Cu}^{\text{II}}_4]$ Clusters

Ayan Patra, Tamal K. Sen, Atanu Ghorai, Ghezai T. Musie,* Swadhin K. Mandal, Utpal Ghosh, and Manindranath Bera*

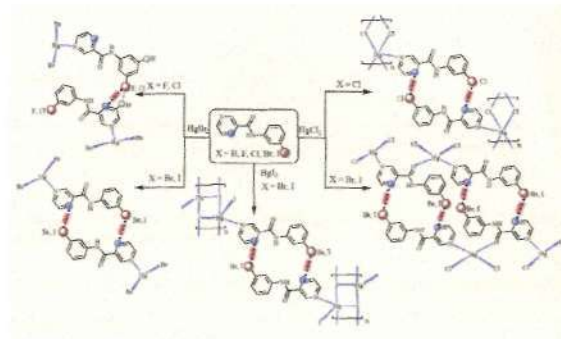
Two new water-soluble hetero- and homometallic tetranuclear clusters, $\text{Na}_4[\text{Cu}_2\text{Zn}_2(\text{ccdp})_2(\mu\text{-OH})_2]\cdot\text{CH}_3\text{OH}\cdot 6\text{H}_2\text{O}$ (**1**) and $\text{K}_3[\text{Cu}_4(\text{ccdp})_2(\mu\text{-OH})(\mu\text{-OH}_2)]\cdot 14\text{H}_2\text{O}$ (**2**), have been synthesized and characterized by exploiting the flexibility, chelating ability, and bridging potential of a carboxylate-rich dinucleating ligand. These clusters are investigated for their binding affinity with the protein bovine serum albumin in an aqueous medium at physiological pH using fluorescence spectroscopy.



Influence of Halogen Bonding Interaction on Supramolecular Assembly of Coordination Compounds; Head-to-Tail *N*→*X* Synthons Repetitively

Hamid Reza Khavasi* and Alireza Azhdari Tehrani

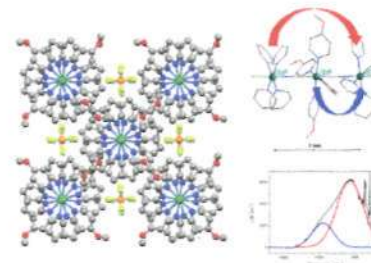
One of the common features in the crystal structures of these complexes is that there is a strong tendency to form halogen bonding synthons. The second common feature of crystal structures of complexes studied here, is the selectivity of metal ion coordination site.



Communication between Remote Moieties in Linear Ru–Ru–Ru Trimetallic Cyanide-Bridged Complexes

German E. Pieslinger, Pablo Albores, Leonardo D. Slep, Benjamin J. Coe, Cliff J. Timpson, and Luis M. Baraldo*

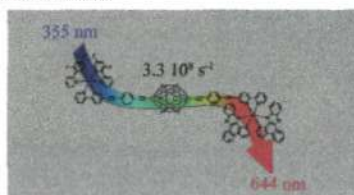
The mixed-valence complexes $\text{trans}[\text{Ru}(\text{L})_4\{\mu\text{-CN}\}\text{Ru}(\text{py})_4\text{Cl}_2]^{3+}$ (*L* = pyridine or 4-methoxypyridine) show an intense transition assignable to a charge transfer between the remote ruthenium units. This is more intense when *L* = 4-methoxypyridine, which gives evidence of the role of the bridging ruthenium unit in promoting mixing between the *d π* orbitals of the terminal fragments.



p-Carborane-Bridged Bipyridine Ligands for Energy Transfer between Two Iridium Centers

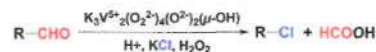
M. Teresa Indelli,* Thomas Bura, and Raymond Ziessel*

Two disparate Ir(III) complexes displaying different optical properties were linked via ethynyl-bipyridine ligands to a closo-*para*-carborane spacer. The electronic levels of the Ir chromophores were modulated by changing the peripheral ligand from 2',4'-difluoro-2-phenylpyridine to dibenzo[*a,c*]phenazine. Slow energy transfer is occurring between both Ir(III) subunits due to the absence of extensive electronic delocalization.

**Decarbonylative Halogenation by a Vanadium Complex**

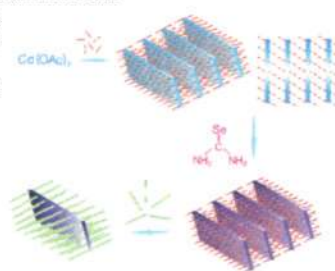
Sujoy Rana, Rameezul Haque, Ganji Santosh, and Debabrata Maiti*

The first metal-mediated decarbonylative halogenation reaction starting from the divanadium oxoperoxo complex $K_3V_2^{5+}(O_2^{2-})_4(O_2^{2-})_2(\mu-OH)$ has been reported. A concerted decarbonylative halogenation reaction is proposed based on experimental observations.

**Preparation of Primary Amine Derivatives of the Magic-Size Nanocluster (CdSe)₁₃**

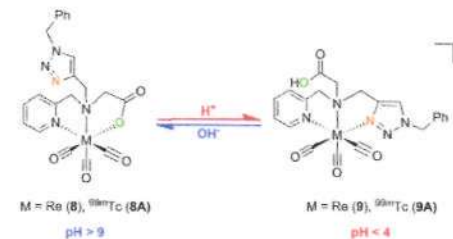
Yuanyuan Wang, Yi-Hsin Liu, Ying Zhang, Paul J. Kowalski, Henry W. Rohrs, and William E. Buhro*

Compounds [(CdSe)₁₃(RNH₂)₁₃] (R = *n*-propyl, *n*-pentyl, *n*-octyl, and oleyl) are conveniently prepared by a common amine-bilayer-template synthesis and exhibit a common stoichiometry. These are the first derivatives of magic-size CdSe nanoclusters to be isolated in purity. Analysis of low-angle XRD data provides an experimental estimate of the diameter of the (CdSe)₁₃ nanocluster at 0.8 nm, which matches theory. [(CdSe)₁₃(*n*-propylamine)₁₃] is obtained as a yellowish-white solid in gram quantities.

**pH-Controlled Coordination Mode Rearrangements of "Clickable" Huisgen-Based Multidentate Ligands with [M(CO)₃]⁺ (M = Re, ^{99m}Tc)**

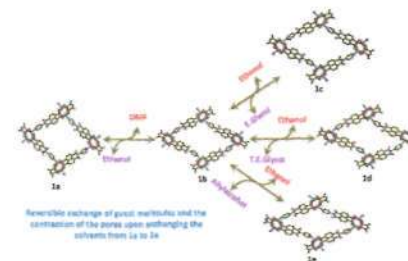
Shalina C. Bortorff, Adam L. Moore, Ariana R. Wemple, Dejan-Krešimir Bučar, Leonard R. MacGillivray, and Paul D. Benny*

An alkyne-functionalized 2-[(pyridin-2-ylmethyl)amino]acetic acid (PMAA) ligand was investigated using two strategies (*click, then chelate* and *chelate, then click*) with *fac*-[M'(OH)₂(CO)₃]⁺ (M = Re, ^{99m}Tc) and the Cu^I-catalyzed Huisgen click reaction to determine the influence of assembly on the coordination species observed. Of three possibilities, two coordination modes were observed in the reaction based on solution pH, which could reversibly intraconvert upon addition of acid (N₁N₂N₃-N₄) or base (O, N₁N₂N₃). Coordination mode rearrangement was studied on the macroscopic Re and radiotracer ^{99m}Tc level.

**Solvent-Induced Structural Dynamics in Noninterpenetrating Porous Coordination Polymeric Networks**

Raghavender Medishetty, Daram Jung, Xiaokai Song, Dongwook Kim, Shim Sung Lee,* Myoung Soo Lah,* and Jagadeesha J. Vittal*

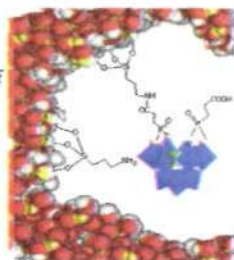
Flexible MOFs have been synthesized, and in Zn-MOF solvent, molecules reversibly exchange with four different solvents via SCSC manner suggesting dynamic nature of framework, whereas the Cd-MOF shows selective adsorption of CO₂ over other gases.



Covalent Grafting of Organic–Inorganic Polyoxometalates Hybrids onto Mesoporous SBA-15: A Key Step for New Anchored Homogeneous Catalysts

Richard Villanneau,* Asma Marzouk, Yan Wang, Aicha Ben Djamaa, Guillaume Laugel, Anna Proust, and Franck Launay*

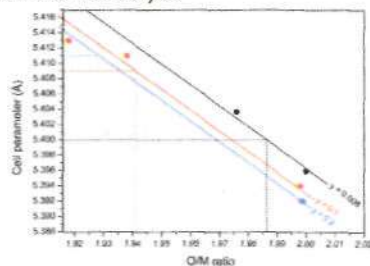
Covalent grafting of the polyoxometalate (POM) hybrid $[\text{AsW}_9\text{O}_{33}[\text{P}(\text{O})(\text{CH}_2\text{CH}_2\text{CO}_2\text{H})_2]_2]^{5-}$ on mesoporous NH_2 -functionalized SBA-15 is the first example of anchored vacant POMs in which nucleophilic oxygen atoms are still available after incorporation into the supports. Such systems are interesting candidates for the preparation of anchored homogeneous catalysts in which the POMs would play the role of polydentate inorganic ligands for the active centers.



Role of Cation Interactions in the Reduction Process in Plutonium–Americium Mixed Oxides

Renaud C. Belin,* Philippe M. Martin, Jacques Lechelle, Muriel Reynaud, and Andreas C. Scheinost

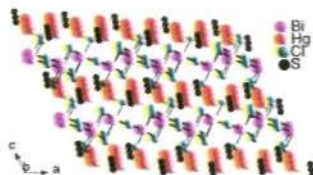
This paper describes the synthesis of three hypo-stoichiometric $\text{Pu}_{1-x}\text{Am}_x\text{O}_{2-x}$ compounds and their X-ray diffraction and X-ray absorption spectroscopy characterization. A quantitative determination of Pu and Am valences is provided and compared to the average O/M ratio deduced from XRD data analysis.



Mercury Bismuth Chalcogenides, $\text{Hg}_3\text{Q}_2\text{Bi}_2\text{Cl}_8$ (Q = S, Se, Te): Syntheses, Crystal Structures, Band Structures, and Optical Properties

Arief C. Wibowo, Christos D. Malliakas, Duck Young Chung, Jino Im, Arthur J. Freeman, and Mercuri G. Kanatzidis*

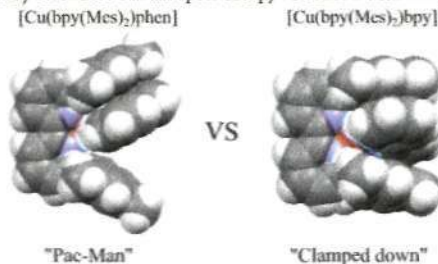
The $\text{Hg}_3\text{Q}_2\text{Bi}_2\text{Cl}_8$ (Q = S, Se, Te) compounds have layered structures where a hole perforated sheet network of $[\text{Hg}_3\text{Q}_2]^{2+}$ alternates with another two-dimensional network of anions of $[\text{Bi}_2\text{Cl}_6]^{2-}$. They exhibit wide band gaps and incongruent melt behavior.



Heteroleptic Cu(I) Bis-diimine Complexes of 6,6'-Dimesityl-2,2'-bipyridine: A Structural, Theoretical and Spectroscopic Study

Michael G. Fraser, Holly van der Salm, Scott A. Cameron, Allan G. Blackman, and Keith C. Gordon*

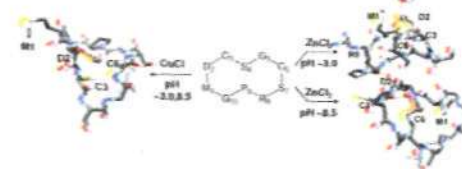
A series of heteroleptic Cu(I) complexes containing 6,6'-dimesityl-2,2'-bipyridine and phenanthroline-, bipyridine-, and biquinoline-based ligands is studied. The X-ray crystal structures of the complexes are presented. The Cu(I) MLCT transitions of the complexes are investigated by resonance Raman spectroscopy in concert with TD-DFT calculations.



Peptide Models of Cu(I) and Zn(II) Metallochaperones: The Effect of pH on Coordination and Mechanistic Implications

Michal S. Shoshan, Deborah E. Shalev, and Edit Y. Tshuva*

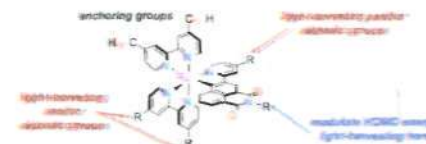
NMR structures of Cu(I)- and Zn(II)-bound peptides as models for metallochaperone proteins were determined under acidic and basic conditions. Unlike Cu(I), Zn(II) bound the D-mutant peptide with different ligation under different pH conditions, further supporting possible role of pH in metal transport and release. Participation of particular residues including Met and Asp is some metal coordination spheres and their absence from others shed light on the source of metal selectivity and other transport mechanistic aspects.



Ruthenium(II) Complexes Bearing a Naphthalimide Fragment: A Modular Dye Platform for the Dye-Sensitized Solar Cell

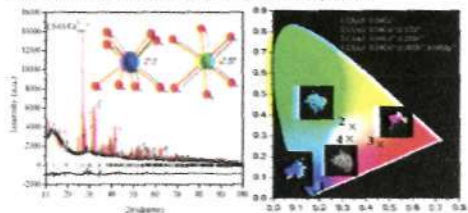
Dmitry V. Pogoshev, Máté J. Bezdek, Phil A. Schauer, and Curtis P. Berlinguette*

A series of cycloruthenated dyes bearing a naphthalimide unit is reported. The distinctively weaker σ -donating character of this unit relative to other cyclometalating ligands offers the opportunity to indiscriminately modify the anionic fragment of the ligand while maintaining a highest occupied molecular orbital at a sufficiently positive potential for regeneration by the electrolyte in the dye-sensitized solar cell. Consequently, device efficiencies in excess of 7% can be attained with this family of dyestuff.



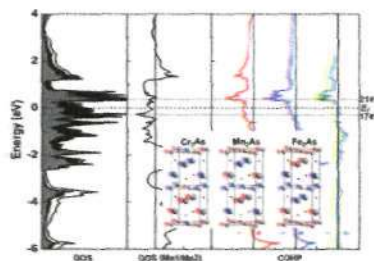
3007 [dx.doi.org/10.1021/ic3024666](https://doi.org/10.1021/ic3024666)
Tunable Color of Ce³⁺/Tb³⁺/Mn²⁺-Coactivated CaScAlSiO₆ via Energy Transfer: A Single-Component Red/White-Emitting Phosphor
 Wei Lü, Ning Guo, Yongchao Jia, Qi Zhao, Wenzhen Lv, Mengmeng Jiao, Baiqi Shao, and Hongpeng You*

Novel tunable red/white-emitting CaScAlSiO₆:Ce³⁺,Tb³⁺,Mn²⁺ phosphors have been synthesized for UV-pumped light-emitting diodes. White light can be achieved by combining the four emission colors (a blue band of 380 nm, a green band of 542 nm, a yellow band of 574 nm, and a red band of 670 nm) in this system.



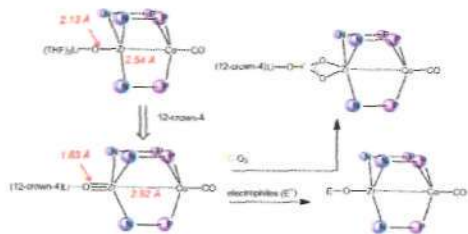
3013 [dx.doi.org/10.1021/ic3024716](https://doi.org/10.1021/ic3024716)
Magnetic Ordering in Tetragonal 3d Metal Arsenides M₂As (M = Cr, Mn, Fe): An Ab Initio Investigation
 Yuemei Zhang, Jakoah Brogich, and Gordon J. Miller*

The electronic and magnetic structures of the tetragonal 3d metal arsenides, Cr₂As, Mn₂As, and Fe₂As, were examined on the basis of density functional calculations to identify chemical influences on their respective patterns of antiferromagnetically (AFM) ordered local moments at the 3d metal sites. Moreover, a magnetostrictive tetragonal-to-orthorhombic distortion was predicted to occur in Cr₂As.



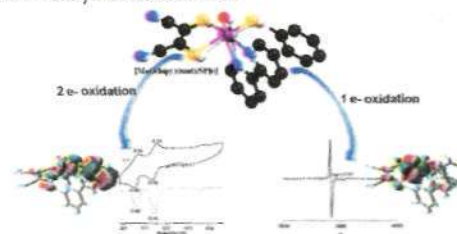
3022 [dx.doi.org/10.1021/ic302473j](https://doi.org/10.1021/ic302473j)
Synthesis, Structure, and Reactivity of an Anionic Zr–Oxo Relevant to CO₂ Reduction by a Zr/Co Heterobimetallic Complex
 Jeremy P. Krogman, Mark W. Bezpalko, Bruce M. Foxman, and Christine M. Thomas*

Synthesis and structural parameters of a CO₂-derived Zr–oxo anion is described in the context of a hypothetical CO₂ reduction scheme. This anionic oxo species reacts readily with electrophiles and also reversibly reacts with CO₂ to generate a Zr-bound carbonate species.



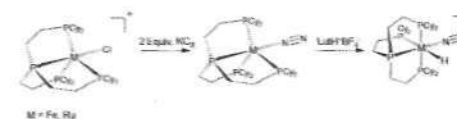
3032 [dx.doi.org/10.1021/ic302485c](https://doi.org/10.1021/ic302485c)
Oxo–Mo(IV)(dithiolene)thiolato Complexes: Analogue of Reduced Sulfite Oxidase
 Joyee Mitra and Sabyasachi Sarkar*

Sulfite oxidase on reduction to the Mo^{IV} state retains the minimum structural feature [Mo^{IV}O(S–S)(SR)][–] (with S–S = ene–dithiolene, SR = Scys) moiety that responds to two sequential one-electron oxidations at low potential via an EPR-active intermediate Mo^V species. The role of redox-active dithiolene as an electron transfer gate between the molybdenum center and the external oxidants has been shown here. The transient sulfur-based radical generated at the initial oxidation phase is monitored by EPR, which has been supported by DFT calculation, showing a ligand-based SOMO. The bite angle of the stabilizing ligand and dihedral angle of thiolato controls the nature of the SOMO. This is relevant to protein breathing with the change in the oxidation state of the molybdenum active site.



3043 [dx.doi.org/10.1021/ic3024953](https://doi.org/10.1021/ic3024953)
Low Oxidation State Iron(0), Iron(II), and Ruthenium(0) Dinitrogen Complexes with a Very Bulky Neutral Phosphine Ligand
 Ryan Gilbert-Wilson, Leslie D. Field,* Stephen B. Colbran, and Mohan M. Bhadbhade

A series of dinitrogen complexes on Ru and Fe containing the tripodal phosphine ligand P²P₃^{Cl}. These include the Ru(0), Fe(0), and Fe(II) dinitrogen complexes. The first Ru(II) chloro complex was also synthesized and characterized. Protonation of the Ru(0) and Fe(0) dinitrogen complexes gave the Ru(II) and Fe(II) hydrido dinitrogen complexes.



3054 [dx.doi.org/10.1021/ic302513c](https://doi.org/10.1021/ic302513c)
Stable Plumbylene Dichalcogenolate Monomers with Large Differences in Their Interligand Angles and the Synthesis and Characterization of a Monothiolato Pb(II) Bromide and Lithium Trithiolato Plumbate
 Brian D. Rekken, Thomas M. Brown, Marilyn M. Olmstead, James C. Fetting, and Philip P. Power*

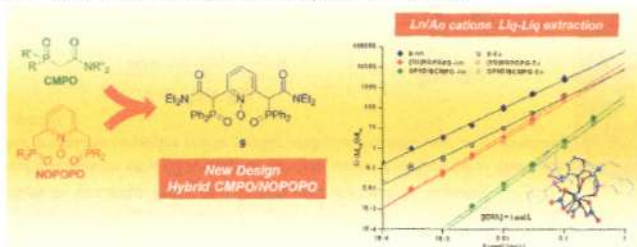
The plumbylenes, Pb(ChAr²)₂ (Ch = O (1), S (2); Ar² = C₆H₁₁-2,6-(C₆H₃-2,6-Prⁱ)₂) are the first fully characterized monomeric, two-coordinate, lead dichalcogenolates in the solid state. They were synthesized by alcoholysis and salt metathesis routes. Structural studies showed that the acute S–Pb–S angle (ca. 77.2°) is significantly narrower than the corresponding O–Pb–O angle (ca. 99.9°). Based on the ²⁰⁹Pb NMR and electronic spectroscopy, the HOMO–LUMO energy separation is shown to decrease from the bisaryloxo plumbylene to the bithiolato derivative.



Synthesis, Lanthanide Coordination Chemistry, and Liquid–Liquid Extraction Performance of CMPO-Decorated Pyridine and Pyridine *N*-Oxide Platforms

Daniel Rosario-Amorin, Sabrina Ouizem, Diane A. Dickie, Yufeng Wen, Robert T. Paine,* Jian Gao, John K. Grey, Ana de Bettencourt-Dias, Benjamin P. Hay, and Lætitia H. Delmau

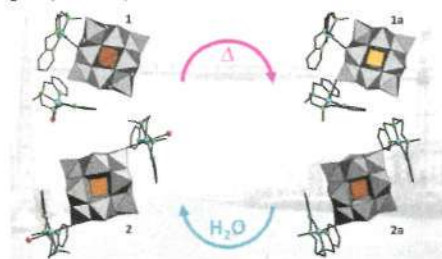
Syntheses for four hybrid CMPO decorated pyridine *N*-oxide ligands and selected coordination chemistry with lanthanide cations as well as liquid–liquid extraction analyses for the ligands are described.



Copper(II) Complexes of Tetradentate Pyridyl Ligands Supported on Keggin Polyoxometalates: Single-Crystal to Single-Crystal Transformations Promoted by Reversible Dehydration Processes

Amaia Iturrospe, Beñat Artetxe, Santiago Reinoso, Leire San Felices, Pablo Vitoria, Luis Lezama, and Juan M. Gutiérrez-Zorrilla*

Single-crystal to single-crystal transformations promoted by reversible dehydration processes have been studied for two new hybrid compounds constructed from Keggin type polyoxometalates and copper(II) complexes of tetradentate ligands containing amine and pyridyl groups, [Cu(bpmen)(H₂O)]₂[SiW₁₂O₄₀{Cu(bpmen)}] (1) and [SiW₁₂O₄₀{Cu(bmpmn)-(H₂O)}₂]-3H₂O (2). Structural transformations to the high-temperature, crystalline 1a and 2a anhydrous phases have been followed by both powder and single-crystal X-ray diffraction.

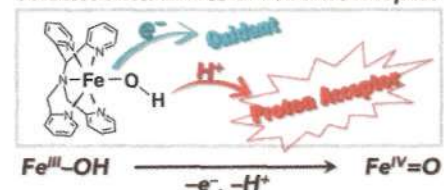


Effects of Proton Acceptors on Formation of a Non-Heme Iron(IV)–Oxo Complex via Proton-Coupled Electron Transfer

Yusuke Nishida, Yuma Morimoto, Yong-Min Lee, Wonwoo Nam,* and Shunichi Fukuzumi*

Rates of formation of a non-heme iron(IV)–oxo complex, [Fe^{IV}(O)(N4Py)]²⁺, via electron-transfer oxidation of [Fe^{III}(OH)(N4Py)]²⁺ in acetonitrile containing H₂O were accelerated as much as 390-fold by addition of proton acceptors. The one-electron oxidation potential of [Fe^{III}(OH)(N4Py)]²⁺ was shifted by −0.28 V in the presence of TsO[−] (10 mM). The electron-transfer oxidation occurred following the deprotonation equilibrium with proton acceptors in which deuterium kinetic isotope effects were observed when H₂O was replaced by D₂O.

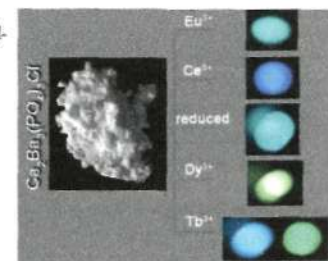
Acceleration Effect of Proton Acceptor



Luminescence and Energy Transfer Properties of Ca₂Ba₃(PO₄)₃Cl and Ca₂Ba₃(PO₄)₃Cl:A (A = Eu²⁺/Ce³⁺/Dy³⁺/Tb³⁺) under UV and Low-Voltage Electron Beam Excitation

Mengmeng Shang, Dongling Geng, Dongmei Yang, Xiaojiao Kang, Yang Zhang, and Jun Lin*

Ca₂Ba₃(PO₄)₃Cl:A (A = Eu²⁺/Ce³⁺/Dy³⁺/Tb³⁺) phosphors with multicolor emissions have been prepared as efficient phosphors for solid-state light and field-emission displays.



Reactions of a Cyclodimethylsiloxane (Me₂SiO)₆ with Silver Salts of Weakly Coordinating Anions; Crystal Structures of [Ag(Me₂SiO)₆][Al] ([Al] = [FAHOC(CF₃)₃]₃, [Al{OC(CF₃)₃}]₄) and Their Comparison with [Ag(18-Crown-6)]₂[SbF₆]₂

T. Stanley Cameron, Andreas Decken, Ingo Krossing, Jack Passmore,* J. Mikko Rautiainen,* Xinping Wang, and Xiaoqing Zeng

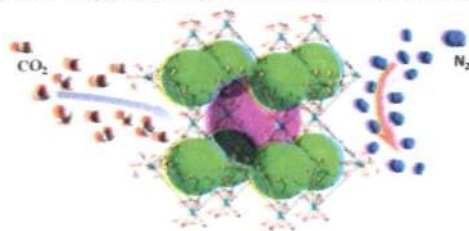
Salts [AgD₆][Al] ([Al] = [Al{OC(CF₃)₃}]₄, [AlF{OC(CF₃)₃}]₄) are the first examples of a preparation of transition metal ion host–guest complexes of cyclic dimethylsiloxanes directly from the components. Bonding and energetics of [AgD₆]⁺ have been compared to analogous [Ag(18-crown-6)]⁺ and other [MD_n]⁺ (M = Ag, Li, n = 4–8) complexes with theoretical calculations.



Construction of a Polyhedral Metal–Organic Framework via a Flexible Octacarboxylate Ligand for Gas Adsorption and Separation

Zu-Jin Lin, Yuan-Biao Huang, Tian-Fu Liu, Xiang-Ying Li, and Rong Cao*

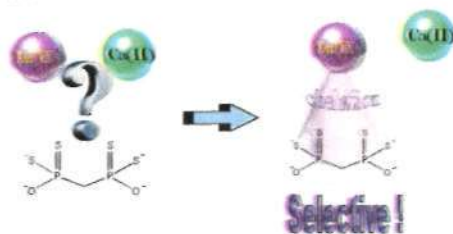
A flexible octacarboxylate ligand, tetrakis[(3,5-dicarboxyphenyl)oxamethyl]methane (H_8X), has been used to construct a porous metal–organic framework, which is comprised of octahedral and cuboctahedral cages and shows a rare (4,8)-connected scu topology. Gas adsorption measurements and ideal adsorbed solution theory (IAST) calculations demonstrate that the framework has high selectivities of CO_2 over CH_4 and N_2 . Remarkably, the resulting material represents a MOF with the highest gas uptakes and gas selectivities (CO_2 from CH_4 and N_2) constructed by the flexible ligand.



Methylenediphosphonotetrathioate: Synthesis, Characterization, and Chemical Properties

Aviran Amir, Alon Haim Sayer, Alon Ezra, and Bilha Fischer*

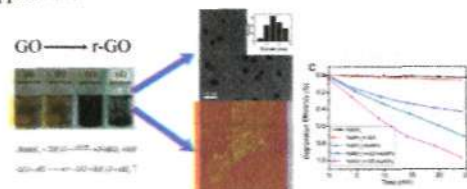
MDPT forms water-soluble complexes preferably with soft/borderline metal-ions. For instance, MDPT showed a 10,000,000-fold preference to $Zn(II)$ vs $Ca(II)$ ions.



Facile Synthesis of Graphene/Metal Nanoparticle Composites via Self-Catalysis Reduction at Room Temperature

Qiqi Zhuo, Yanyun Ma, Jing Gao, Pingping Zhang, Yujian Xia, Yiming Tian, Xiuxiao Sun, Jun Zhong, and Xuhui Sun*

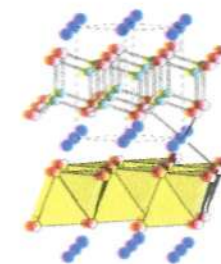
Facile synthesis of a graphene/metal NP composite with good control of size and morphology has been developed. The approach has been demonstrated to successfully synthesize graphene composites with various metal NPs in large quantity, which opens up a novel and simple way to prepare large-scale graphene/metal or graphene/metal oxide composites under mild conditions for practical applications. For example, graphene/AuNP composites synthesized by the method show excellent performance in the catalysis applications.



Quaternary Arsenides $AM_{1.5}Tt_{0.5}As_2$ ($A = Na, K, Rb; M = Zn, Cd; Tt = Si, Ge, Sn$): Size Effects in $CaAl_2Si_2$ - and $ThCr_2Si_2$ -Type Structures

Mansura Khatun, Stanislav S. Stoyko, and Arthur Mar*

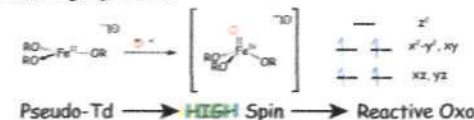
The quaternary arsenides $AM_{1.5}Tt_{0.5}As_2$ adopt either $CaAl_2Si_2$ - or $ThCr_2Si_2$ -type structures depending on the relative sizes of the A , M , and Tt components, as can be represented on a structure map.



Iron in a Trigonal Tris(alkoxide) Ligand Environment

Matthew B. Chambers, Stanislav Groysman, Dino Villagrán, and Daniel G. Nocera*

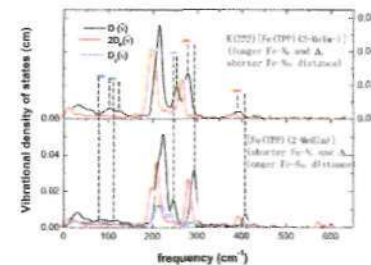
Mononuclear compounds of Fe^{2+} and Fe^{3+} supported by tris(alkoxide) ligand scaffolds, tBu_2MeCO^- (ditox), have been synthesized and characterized. Whereas tris(ditox) complexes of trivalent iron were observed to be inert toward oxygen atom transfer reagents, divalent iron tris(ditox) species were found to react readily to transiently generate high valent intermediates. Subsequent observation of facile reactivity (HAT and oxo transfer) is attributed to the weakly donating tris(alkoxide) ligand field, which is calculated to stabilize high spin states.



Effects of Imidazole Deprotonation on Vibrational Spectra of High-Spin Iron(II) Porphyrinates

Chuanjiang Hu,* Qian Peng, Nathan J. Silvermail, Alexander Barabanschikov, Jiyong Zhao, E. Ercan Alp, Wolfgang Sturhahn, J. Timothy Sage,* and W. Robert Scheidt*

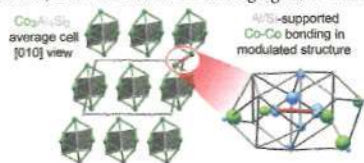
The iron vibrations in the five-coordinate high-spin iron(II) porphyrinates with imidazole and imidazolate as the axial ligands are compared. The in-plane frequencies shift to lower frequency in the imidazolate complexes, whereas the out-of-plane modes shift to higher frequency.



The Modulated Structure of $\text{Co}_3\text{Al}_4\text{Si}_2$: Incommensurability and Co–Co Interactions in Search of Filled Octadecets

Rie T. Fredrickson and Daniel C. Fredrickson*

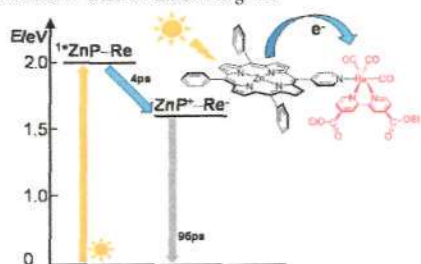
The origins of incommensurate modulations are often mysterious, but appear to be as diverse as the compounds in which they arise. We describe the crystal structure and bonding of $\text{Co}_3\text{Al}_4\text{Si}_2$, whose modulated structure can be traced to a central concept of inorganic chemistry: the 18 electron rule. Key to this compound's bonding are covalently shared electron pairs in orbitals isolobal to classical Co–Co σ and π bonds, but delocalized over bridging Si/Al atoms.



Improving the Efficiency of the Photoinduced Charge-Separation Process in a Rhenium(I)–Zinc Porphyrin Dyad by Simple Chemical Functionalization

Teresa Gatti, Paolo Cavigli, Ennio Zangrando, Elisabetta Ingo, Claudio Chiorboli, and Maria Teresa Indelli*

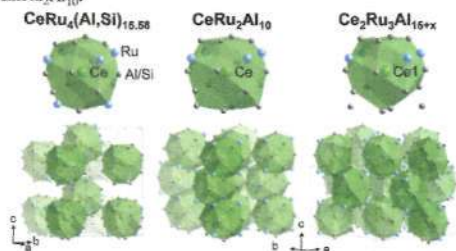
The dyad system for efficient photoinduced electron transfer is given.



Synthesis, Structure, and Properties of $\text{Ln}_2\text{Ru}_3\text{Al}_{15}$ ($\text{Ln} = \text{Ce}, \text{Gd}$): Comparison with $\text{LnRu}_2\text{Al}_{10}$ and $\text{CeRu}_2(\text{Al},\text{Si})_{15,58}$

Gregory Morrison, Neel Haldolaarachchige, Chih-Wei Chen, David P. Young, Emilia Morosan, and Julia Y. Chan*

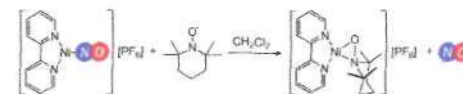
$\text{Ln}_2\text{Ru}_3\text{Al}_{15}$ ($\text{Ln} = \text{Ce}, \text{Gd}$) have been synthesized, and the competition between the growth of $\text{Ce}_2\text{Ru}_3\text{Al}_{15}$ and $\text{CeRu}_2\text{Al}_{10}$ has been studied. The structure of $\text{Ce}_2\text{Ru}_3\text{Al}_{15}$ was modified from the previously reported $\text{Ce}_2\text{Ru}_3\text{Al}_{15}$ structure, and the structure of $\text{Gd}_2\text{Ru}_3\text{Al}_{15}$ was determined for the first time. The magnetic and transport properties of $\text{Ln}_2\text{Ru}_3\text{Al}_{15}$ were measured and compared to the properties of $\text{LnRu}_2\text{Al}_{10}$.



Nitric Oxide Release from a Nickel Nitrosyl Complex Induced by One-Electron Oxidation

Ashley M. Wright, Homaira T. Zaman, Guang Wu, and Trevor W. Hayton*

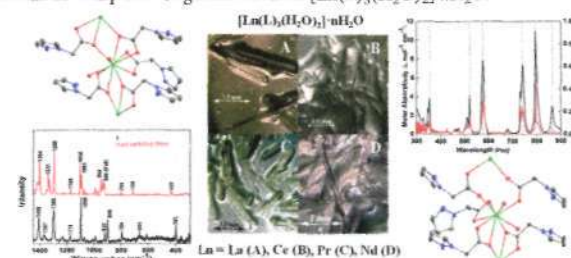
Oxidation of $[\text{Ni}(\text{NO})(\text{bipy})][\text{PF}_6]$ with a variety of one-electron ($1e^-$) oxidants, including AgPF_6 , $[\text{NO}][\text{PF}_6]$, and TEMPO, results in rapid release of NO gas. In the TEMPO reaction, the Ni-containing byproduct, $[(\text{bipy})\text{Ni}(\eta^2\text{-TEMPO})][\text{PF}_6]$, can be isolated in good yield.



Solid-State and Solution-State Coordination Chemistry of Lanthanide(III) Complexes with (Pyrazol-1-yl)acetic Acid

Xiao-Yan Chen,* George S. Goff,* Brian L. Scott, Michael T. Janicke, and Wolfgang Runde

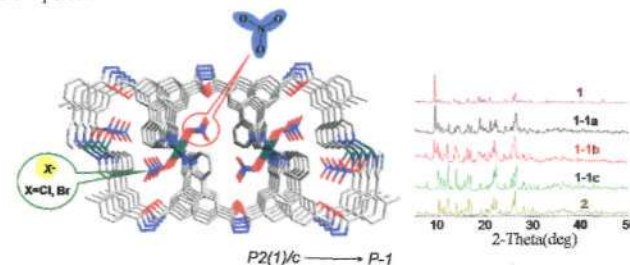
As a precursor of carboxyl-functionalized task-specific ionic liquids (TSILs) for f-element separation, (pyrazol-1-yl)acetic acid (**L**) can be deprotonated as a functionalized pyrazolate anion to coordinate with hard metal cations. However, the coordination chemistry of **L** with f-elements remains unexplored. We reacted **L** with lanthanides in aqueous solution at pH = 5 and synthesized four lanthanide complexes of general formula $[\text{Ln}(\text{L})_3(\text{H}_2\text{O})_2] \cdot n\text{H}_2\text{O}$.



Cd(II)-Coordination Framework: Synthesis, Anion-Induced Structural Transformation, Anion-Responsive Luminescence, and Anion Separation

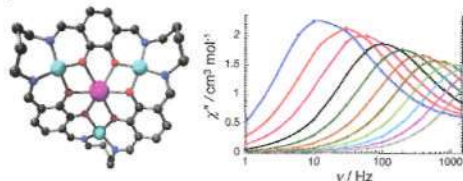
Shan Hou, Qi-Kui Liu, Jian-Ping Ma, and Yu-Bin Dong*

A series of Cd(II)-coordination frameworks with anion-induced structural transformation, anion-responsive luminescence, and anion separation were reported.



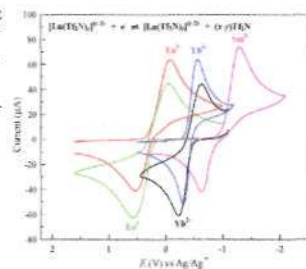
By Design: A Macrocyclic 3d–4f Single-Molecule Magnet with Quantifiable Zero-Field Slow Relaxation of Magnetization
Humphrey L. C. Feltham, Rodolphe Cl  rac, Liviu Ungur, Liviu F. Chibotaru, Annie K. Powell, and Sally Brooker*

$[\text{Cu}_3\text{Tb}(\text{L}^{\text{Bm}})]$ is the first example of a macrocyclic 3d–4f single-molecule magnet that exhibits quantifiable relaxation of magnetization in zero dc field. Rational modification of the equatorially bound macrocycle tuned the ligand field and resulted in apical binding of two nitrate ions to the oblate Tb(III) ion, giving enhanced uniaxial anisotropy and SMM properties despite the low symmetry of the Tb(III) site.



Electrochemical and Spectroscopic Investigation of Ln³⁺ (Ln = Sm, Eu, and Yb) Solvation in Bis(trifluoromethylsulfonyl)imide-Based Ionic Liquids and Coordination by N,N,N',N'-Tetraoctyl-3-oxa-pentane Diamide (TODGA) and Chloride
Yunfeng Pan and Charles L. Hussey*

Lanthanide ions can be introduced into bis(trifluoromethylsulfonyl)imide-based ionic liquids by anodic oxidation of the respective metals; Eu³⁺, Eu²⁺, Sm³⁺, Yb³⁺, and Yb²⁺ but not Sm²⁺ exhibit considerable stability. This article reports the electrochemistry and electronic absorption spectroscopy of these lanthanide ions in the neat ionic liquids and in these ionic solvents containing the neutral tridentate ligand N,N,N',N'-tetra(*n*-octyl)diglycolamide (TODGA) and the anionic hard ligand chloride.



(C₄N₂H₁₂)₃[Ln₃(OH)(SO₄)₇] (Ln = Sm, Eu, and Tb): A Series of Honeycomb-like Open-Framework Lanthanide Sulfates with Extra-Large Channels Containing 24-Membered Rings
Deng Zhang, Yun Lu, Dunru Zhu, and Yan Xu*

Three novel honeycomb-like lanthanide sulfates with extra-large channels containing 24MR have been synthesized by using chair form piperazine as the structure-directing agent under one-pot solvothermal reactions. They are isostructural, and the open framework is the first lanthanide sulfate with extra-large channels containing 24MR. It has an *acs* framework topology.

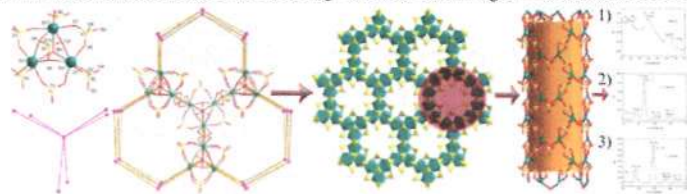
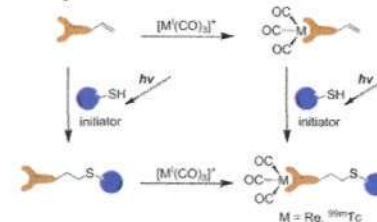


Photo-initiated Thiol-ene Click Reactions as a Potential Strategy for Incorporation of $[\text{M}(\text{CO})_3]^+$ (M = Re, ^{99m}Tc) Complexes
Thomas R. Hayes, Patrice A. Lyon, Elsa Silva-Lopez, Brendan Twamley, and Paul D. Benny*

The radical initiated thiol-ene click reaction between a thiol and an alkene was investigated for potential in Re/^{99m}Tc(CO)₃ radiopharmaceuticals applications by functionalizing a 2,2'-dipicolylamine chelate with an allyl group. Two strategies, *chelate then click* and *click then chelate*, were examined to determine the versatility of this click reaction in the presence of the metal, where both approaches were found to be capable of the thiol-ene click reaction at the macroscopic and tracer concentrations.



¹H and ¹⁷O NMR Relaxometric and Computational Study on Macrocyclic Mn(II) Complexes
Gabriele A. Rolla, Carlos Platas-Iglesias, Mauro Botta,* Lorenzo Tei, and Lothar Helm

The solution structure of Mn(II) complexes with a homogeneous series of chelators based on cyclen with one, two, and three acetic pendant arms was investigated by ¹H and ¹⁷O NMR relaxometry and DFT calculations. Particular attention was devoted to the detailed study of the dynamics of the metal coordinated water molecule. Remarkably, $[\text{Mn}(1,4\text{-DO2A})]$ and $[\text{Mn}(1,7\text{-DO2A})]$ were found to be in equilibrium between the mono- and the nonhydrated species.



Antimonato Polyoxovanadate Based Three-Dimensional Framework Exhibiting Ferromagnetic Exchange Interactions: Synthesis, Structural Characterization, and Magnetic Investigation of $[\text{Fe}(\text{C}_6\text{H}_{14}\text{N}_2)_2]_3[\text{V}_{15}\text{Sb}_6\text{O}_{42}(\text{H}_2\text{O})] \cdot 8\text{H}_2\text{O}$
Adam Wutkowski, Christian N  ther, Paul K  gerler, and W. Bensch*

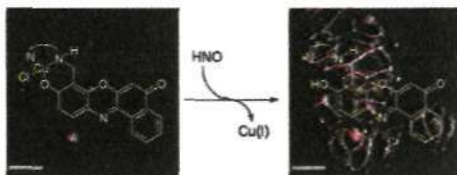
The spherical $[\text{V}_{15}\text{Sb}_6\text{O}_{42}]^{6-}$ cluster shell is bound to six Fe³⁺-centered complexes, which join the clusters to form a three-dimensional network. Ferromagnetic exchange interactions are observed upon cooling.



Detection of Nitric Oxide and Nitroxyl with Benzoresorufin-Based Fluorescent Sensors

Ulf-Peter Apfel, Daniela Buccella, Justin J. Wilson, and Stephen J. Lippard*

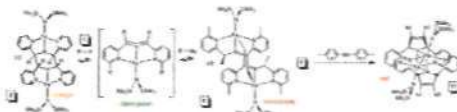
A new family of benzoresorufin-based copper complexes for fluorescence detection of NO and HNO is reported. The copper complexes, CuBRNO1–3, elicit 1.5–4.8-fold emission enhancement in response to NO and HNO. The three sensors differ in the nature of the metal-binding site. The photophysical properties of these sensors are investigated with assistance from density functional theory calculations. The fluorescence turn-on observed upon reaction with HNO is an unexpected result that is discussed in detail. The utility of the new sensors for detecting HNO and NO in HeLa cells and RAW 264.7 macrophages is demonstrated.



C–C Bond Formation and Related Reactions at the CNC Backbone in (smif)FeX (smif = 1,3-Di-(2-pyridyl)-2-azaallyl): Dimerizations, 3 + 2 Cyclization, and Nucleophilic Attack; Transfer Hydrogenations and Alkyne Trimerization (X = N(TMS)₂, dpma = (Di-(2-pyridyl)-methyl)-amide)

Brenda A. Frazier, Valerie A. Williams, Peter T. Wolczanski,* Suzanne C. Bart, Karsten Meyer, Thomas R. Cundari, and Emil B. Lobkovsky

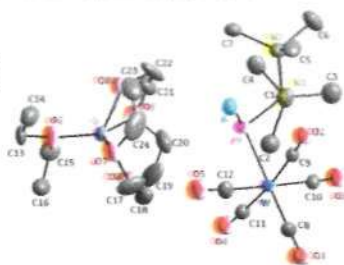
The smif (smif = 1,3-di-(2-pyridyl)-2-azaallyl) backbone in (smif)FeX complexes exhibits C–C bond-forming and related reactions that can be rationalized by viewing the CNC^{nb} backbone-localized orbital as having covalent diradical and/or ionic character.



Li/X Phosphinidenoid Pentacarbonylmetal Complexes: A Combined Experimental and Theoretical Study on Structures and Spectroscopic Properties

Rainer Streubel,* Aysel Özbolat-Schön, Gerd von Frantzius, Holly Lee, Gregor Schnakenburg, and Dietrich Gudat

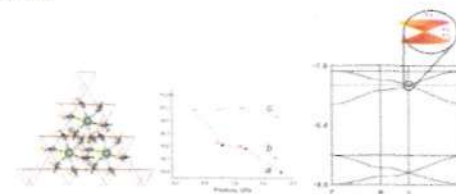
The first comprehensive study on Li/X phosphinidenoid metal(0) complexes (M = Cr, Mo, W) is presented including DOSY NMR experiments, DFT calculations of structures, energies, NMR, and compliance constants, as well as the first single-crystal X-ray diffraction study that reveals an ion pair structure.



Robust Dirac-Cone Band Structure in the Molecular Kagome Compound (EDT-TTF-CONH₂)₆[Re₆Se₆(CN)₆]

Sandra Carlsson, Leokadiya Zorina, David R. Allan, J. Paul Attfield,* Eric Canadell,* and Patrick Batail*

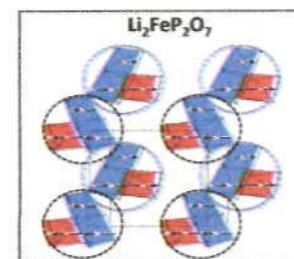
The molecular solid (EDT-TTF-CONH₂)₆[Re₆Se₆(CN)₆] has hybrid donor layers with a kagome topology that maintain rhombohedral symmetry on cooling down to 220 K or up to 0.7 GPa pressure, beyond which a metal to insulator transition and lattice distortion occur. Band structure calculations reveal a Dirac-cone at the Fermi level, like that of graphene, which may result in exotic electronic properties.



Neutron Diffraction Study of the Li-Ion Battery Cathode Li₂FeP₂O₇

Prabeer Barpanda,* Gwenaëlle Rouse, Tian Ye, Chris D. Ling, Zakiah Mohamed, Yannick Klein, and Atsuo Yamada

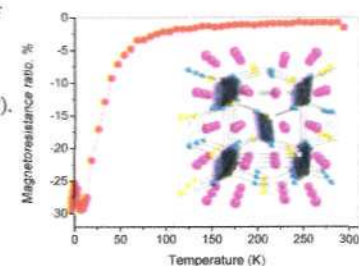
Li₂FeP₂O₇ forms a 3.5 V polyanionic cathode for Li-ion batteries. Its magnetic structure has been illustrated with the help of magnetic susceptibility and neutron powder diffraction. It involves an overall antiferromagnetic arrangement with the presence of local ferromagnetic clusters.



Flux Growth and Magnetoresistance Behavior of Rare Earth Zintl Phase EuMgSn

Xiaowei Ma, Jun Lu, Jeffrey B. Whalen, and Susan E. Lattner*

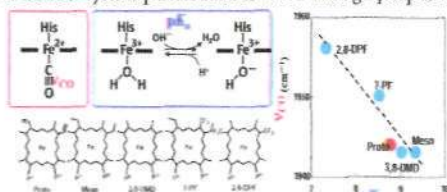
Large crystals of EuMgSn can be grown in Mg/Al flux, enabling the study of magnetic anisotropy and transport properties. Despite its well-known TiNiSi structure type, the title compound exhibits competing magnetic coupling interactions between Eu²⁺ ions which result in metamagnetic transitions and large negative magnetoresistance (−29.5% at 12 K and an applied field of 2.5 T).



Relationship between the Electron Density of the Heme Fe Atom and the Vibrational Frequencies of the Fe-Bound Carbon Monoxide in Myoglobin

Ryu Nishimura, Tomokazu Shibata, Hulin Tai, Izumi Ishigami, Takashi Ogura,* Satoshi Nagao, Takashi Matsuo, Shun Hirota, Kiyohiro Imai, Saburo Neya, Akihiro Suzuki, and Yasuhiko Yamamoto*

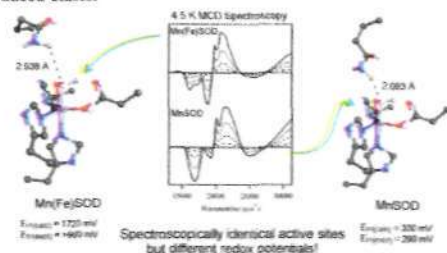
We analyzed the vibrational frequencies of the Fe-bound carbon monoxide (CO) of myoglobin reconstituted with a series of chemically modified heme cofactors possessing a heme Fe atom with a variety of electron densities. The stretching frequency of Fe-bound CO (ν_{CO}) was found to increase with decreasing electron density of the heme Fe atom (ρ_{Fe}). This finding demonstrated that the ν_{CO} value can be used as a sensitive measure of the ρ_{Fe} value and that the π back-donation of the heme Fe atom to CO is affected by the heme π -system perturbation induced through peripheral side chain modifications.



Geometric and Electronic Structures of Manganese-Substituted Iron Superoxide Dismutase

Timothy A. Jackson, Craig T. Gutman, James Maliekal, Anne-Frances Miller, and Thomas C. Brunold*

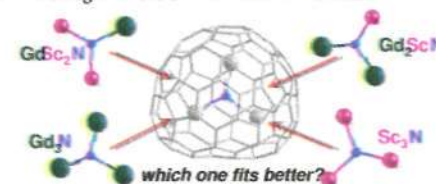
The active-site structures of the oxidized and reduced forms of manganese-substituted iron superoxide dismutase (Mn(Fe)SOD) have been examined by employing a combination of spectroscopic and computational methods. Our spectroscopic data reveal that in its oxidized state, the active site of this species is virtually identical to that of wild-type manganese SOD (MnSOD), both featuring a trigonal bipyramidal ligand environment. This proposal is corroborated by quantum and molecular mechanical computations performed on complete protein models of Mn(Fe)SOD and MnSOD in both their oxidized and their reduced states.



Gd–Sc-Based Mixed-Metal Nitride Cluster Fullerenes: Mutual Influence of the Cage and Cluster Size and the Role of Scandium in the Electronic Structure

Anna L. Svitova, Alexey A. Popov,* and Lothar Dunsch*

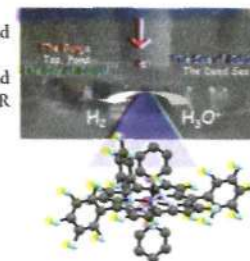
The synthesis of mixed-metal nitride cluster fullerenes $\text{Gd}_x\text{Sc}_{3-x}\text{N}@C_{2n}$ ($2n = 78-88$) with melamine as the source of nitrogen is systematically studied, and the optimum cluster size for each carbon cage ranging from C_{78} to C_{88} is revealed. Spectroscopic, electrochemical, and density functional theory computational studies reveal the special role of scandium in $\text{Gd}_x\text{Sc}_{3-x}\text{N}@C_{2n}$ molecules that affects the nature and energies of the frontier molecular orbitals.



Cobalt Corrole Catalyst for Efficient Hydrogen Evolution Reaction from H₂O under Ambient Conditions: Reactivity, Spectroscopy, and Density Functional Theory Calculations

Biswajit Mondal, Kushal Sengupta, Atanu Rana, Atif Mohammed, Mark Botoshansky, Somdatta Ghosh Dey,* Zeev Gross,* and Abhishek Dey*

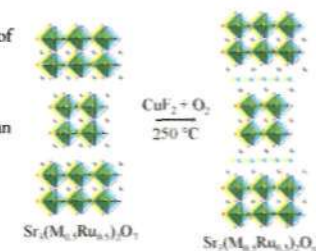
We report here an electronically tuned Co(III) corrole that can catalyze the HER from aqueous sulfuric acid at as low as -0.3 V vs NHE, with a turnover frequency of 600 s^{-1} and $\gg 10^7$ catalytic turnovers. Under aerobic conditions, using H_2O from naturally available sources without any pretreatment, the same complex catalyzes the reduction of both O_2 and H^+ , utilizing the Co(II) and Co(I) oxidation states, respectively. The mechanism of the HER has been investigated with in situ spectroscopy and DFT.



Topochemical Fluorination of $\text{Sr}_3(\text{M}_{0.5}\text{Ru}_{0.5})_2\text{O}_7$ (M = Ti, Mn, Fe), $n = 2$, Ruddlesden–Popper Phases

Fabio Denis Romero, Paul A. Bingham, Susan D. Forder, and Michael A. Hayward*

Reaction of the appropriate $\text{Sr}_3(\text{M}_{0.5}\text{Ru}_{0.5})_2\text{O}_7$ (M = Ti, Mn, Fe), $n = 2$, Ruddlesden–Popper oxide with CuF_2 under flowing oxygen results in formation of the oxide–fluoride phases $\text{Sr}_3(\text{Ti}_{0.5}\text{Ru}_{0.5})_2\text{O}_7\text{F}_2$, $\text{Sr}_3(\text{Mn}_{0.5}\text{Ru}_{0.5})_2\text{O}_7\text{F}_2$, and $\text{Sr}_3(\text{Fe}_{0.5}\text{Ru}_{0.5})_2\text{O}_7\text{F}_{3.5}$ via a topochemical anion insertion/substitution process. Analysis indicates the titanium and manganese phases have Ti^{4+} , Ru^{6+} and Mn^{4+} , Ru^{6+} oxidation state combinations respectively, while Mössbauer spectra indicate an Fe^{3+} , $\text{Ru}^{5.5+}$ combination for the iron phase.



Additions and Corrections

3399

[dx.doi.org/10.1021/ic400131c](https://doi.org/10.1021/ic400131c)

Correction to Changes in Electronic Properties of Polymeric One-Dimensional $[M(CN)]_n$ ($M = Au, Ag$) Chains Due to Neighboring Closed-Shell Zn(II) or Open-Shell Cu(II) Ions

François Baril-Robert, Xiaobo Li, Michael J. Katz, Andrew R. Geisheimer, Daniel B. Leznoff, and Howard Patterson*

3400

[dx.doi.org/10.1021/ic4001335](https://doi.org/10.1021/ic4001335)

Correction to Photophysical Properties of $[Au(CN)_2]^-_2$ Dimers Trapped in a Supramolecular Electron-Acceptor Organic Framework

Ahmed S. Abouelwafa, Christopher E. Anson, Andreas Hauser, Howard H. Patterson, François Baril-Robert, Xiaobo Li, and Annie K. Powell*

3401

[dx.doi.org/10.1021/ic4001347](https://doi.org/10.1021/ic4001347)

Correction to Copper(I) Thiocyanate-Amine Networks: Synthesis, Structure, and Luminescence Behavior

Kayla M. Miller, Shannon M. McCullough, Elena A. Lepekhina, Isabelle J. Thibau, Robert D. Pike,* Xiaobo Li, James P. Killarney, and Howard H. Patterson

3402

[dx.doi.org/10.1021/ic400135a](https://doi.org/10.1021/ic400135a)

Correction to Optical Memory and Multistep Luminescence Thermochromism in Single Crystals of $K_2Na[Ag(CN)_2]_3$

Mohammad A. Omary,* Julie Clarissa F. Colls, C. L. Larochele, and Howard H. Patterson*

3403

[dx.doi.org/10.1021/ic4001363](https://doi.org/10.1021/ic4001363)

Correction to Copper(I) Cyanide Networks: Synthesis, Structure, and Luminescence Behavior. Part 2. Piperazine Ligands and Hexamethylenetetramine

Mi Jung Lim, Courtney A. Murray, Tristan A. Tronic, Kathryn E. deKrafft, Amanda N. Ley, Jordan C. deButts, Robert D. Pike,* Haiyan Lu, and Howard H. Patterson*

3404

[dx.doi.org/10.1021/ic400137g](https://doi.org/10.1021/ic400137g)

Correction to Observation of a Mixed-Metal Transition in Heterobimetallic Au/Ag Dicyanide Systems

Samanthika R. Hettiarachchi, Brian K. Schaefer, Renante L. Yson, Richard J. Staples, Regine Herbst-Imer, and Howard H. Patterson*