

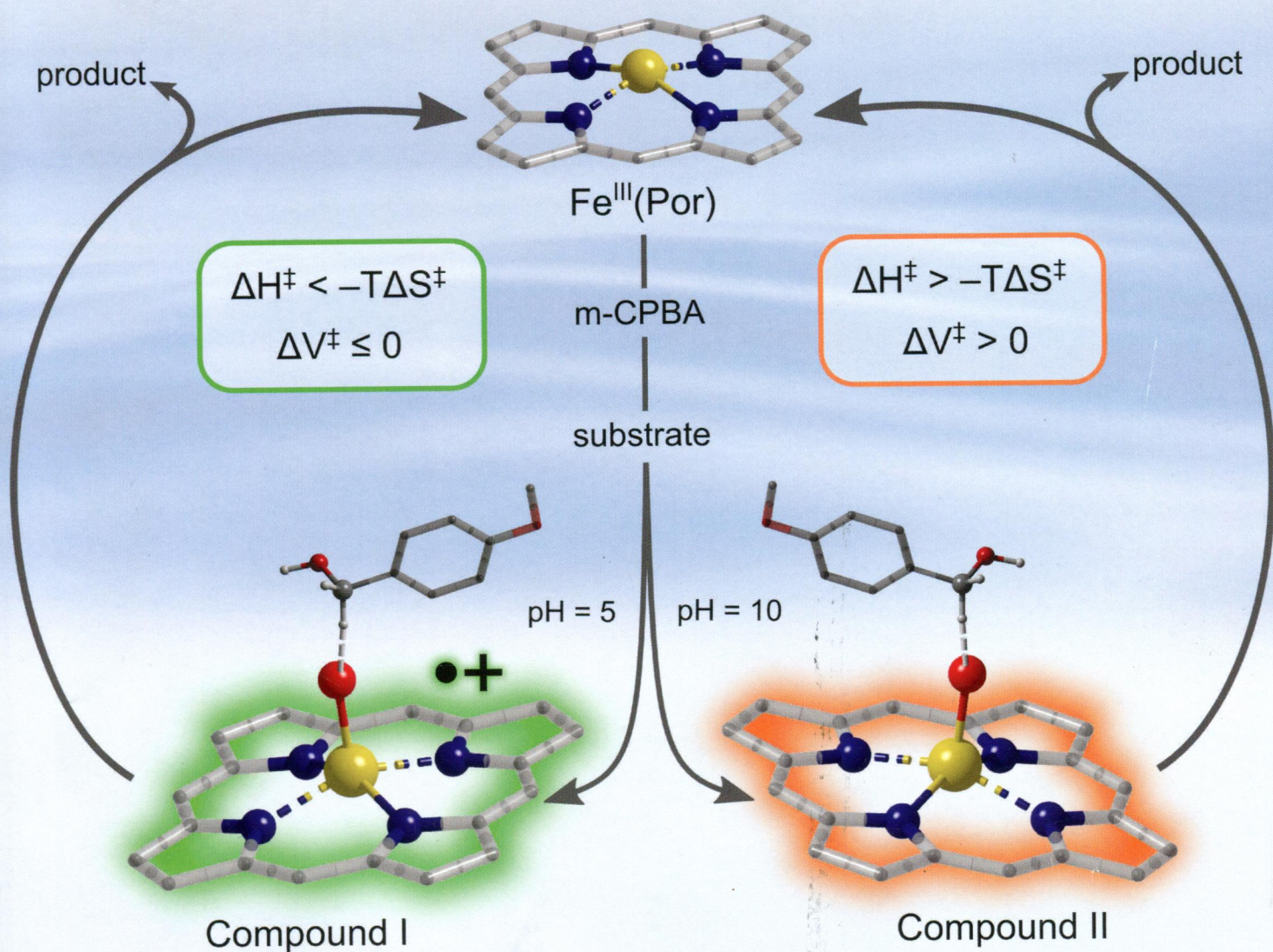
1171  
1-65

# Inorganic Chemistry

including bioinorganic chemistry

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## Mechanistic information from $\Delta H^\ddagger$ , $\Delta S^\ddagger$ and $\Delta V^\ddagger$



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**ON THE COVER:** Temperature and pressure effects on C–H abstraction reactions involving compound I and II mimics in aqueous solution revealed that in most cases the reaction catalyzed by compound I is entropy-controlled ( $\Delta H^\ddagger < -T\Delta S^\ddagger$ ) and mainly involves O–H bond formation ( $\Delta V^\ddagger \leq 0$ ), whereas the reaction catalyzed by compound II is enthalpy-controlled ( $\Delta H^\ddagger > -T\Delta S^\ddagger$ ) and mainly involves C–H bond homolysis ( $\Delta V^\ddagger > 0$ ). The cover art was designed by Marcin and Maria Oszajca from Jagiellonian University, Krakow, Poland. See M. Oszajca, A. Franke, A. Drzewiecka-Matuszek, M. Brindell, G. Stochel, and R. van Eldik, p 2848.

## Communications

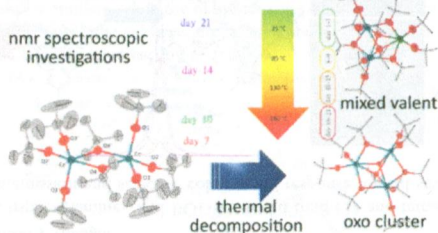
2751


[dx.doi.org/10.1021/ic4025876](https://doi.org/10.1021/ic4025876)

### Octakis(*tert*-butoxo)dicerium(IV) [Ce<sub>2</sub>(O<sup>t</sup>Bu)<sub>8</sub>]: Synthesis, Characterization, Decomposition, and Reactivity

Johannes Schläfer, Wieland Tyrra, and Sanjay Mathur\*

An advanced synthesis for the homoleptic complex [Ce<sub>2</sub>(O<sup>t</sup>Bu)<sub>8</sub>] is reported along with the first structural investigation of the dimeric alkoxide. Detailed NMR spectral studies provided new insight into its thermal and solution stability. Further the mixed-valent decomposition product [Ce<sub>2</sub>(O<sup>t</sup>Bu)<sub>11</sub>] and two new complexes of the general formula [Ce<sub>2</sub>(O<sup>t</sup>Bu)<sub>2</sub>L] (L = HO<sup>t</sup>Bu, OCPH<sub>2</sub>) were characterized by single-crystal X-ray diffraction.



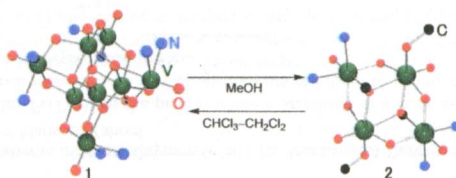
2754


[dx.doi.org/10.1021/ic4031393](https://doi.org/10.1021/ic4031393)

### A Novel Octanuclear Vanadium(V) Oxide Cluster Complex Having an Unprecedented Neutral V<sub>8</sub>O<sub>20</sub> Core Functionalized with 4,4'-Di-*tert*-butyl-2,2'-bipyridine

Shintaro Kodama,\* Nobuto Taya, and Youichi Ishii\*

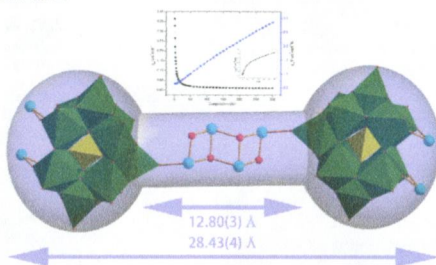
A novel octanuclear vanadium(V) oxide cluster complex, [V<sub>8</sub>O<sub>20</sub>(4,4'-*t*Bupy)<sub>4</sub>] (1), was synthesized and characterized by single-crystal X-ray structure analysis to reveal that 1 has an unprecedented neutral V<sub>8</sub>O<sub>20</sub> core. An unexpected interconversion between 1 and the methoxo(oxo)vanadium(V) cluster complex, [V<sub>4</sub>O<sub>8</sub>(OMe)<sub>4</sub>(4,4'-*t*Bupy)<sub>2</sub>] (2), was observed upon changes in the solvent systems.



### A Novel Dumbbell-like Polyoxometalate Assembled of Copper(II)-Disubstituted Monovacant Keggin Polyoxoanions with a Tetranuclear Copper Cluster

Hao Miao, Xiao Xu, Wei-Wei Ju, Hong-Xiang Wan, Yu Zhang, Dun-Ru Zhu, and Yan Xu\*

In compound **1**, two novel dicopper(II)-substituted monovacant Keggin polyoxoanions are bridged by a  $\text{Cu}_4$  cluster to construct a dumbbell-like dimeric polyoxometalate. Magnetic analysis indicates predominantly an antiferromagnetic interaction between copper(II) ions in **1**.

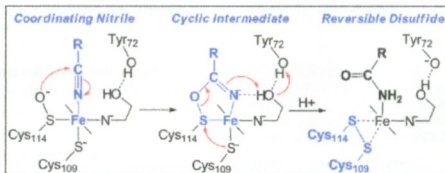


### Full Reaction Mechanism of Nitrile Hydratase: A Cyclic Intermediate and an Unexpected Disulfide Switch

Kathrin H. Hopmann\*

A full reaction mechanism for nitrile hydratase is presented, involving a cyclic intermediate and a reversible disulfide. Sulfenic acid acts as a nucleophile, attacking the metal-coordinated nitrile. The formed intermediate is cleaved through disulfide formation with the axial thiol. Subsequently, active-site regeneration occurs through the attack of water on the disulfide. The computed barriers identify this pathway as the most feasible mechanism hitherto.

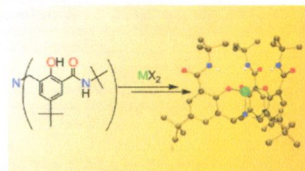
#### NHase REACTION MECHANISM



### Synthesis and Characterization of Iron Trisphenolate Complexes with Hydrogen-Bonding Cavities

Mario Adelhardt, Matthew J. Chalkley, Frank W. Heinemann, Jörg Sutter, Andreas Scheurer, and Karsten Meyer\*

A new series of tripodal N-anchored tris(phenolate) ligands featuring amides in the secondary coordination sphere were synthesized. Coordination to iron leads to the formation of complexes containing a cavity that supports a hydrogen-bonding network and may serve to stabilize reactive intermediates of biological interest. The synthesis and characterization of a new family of ligands, as well as iron(II), iron(III), and zinc(II) complexes, are presented.



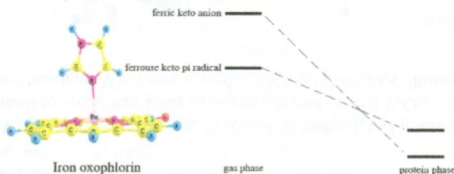
2766 **S**

dx.doi.org/10.1021/ic402754y

### Chameleonic Nature of Hydroxyheme in Heme Oxygenase and Its Reactivity: A Density Functional Theory Study

Mahin Gheidi, Nasser Safari,\* and Mansour Zahedi

The oxophlorin intermediate  $[(\text{Im})\text{Fe}(\text{PO})]$  in the protein phase is stabilized to a ferric keto anion form, while in the gas phase and in the presence of small molecules such as  $\text{O}_2$ , it becomes stabilized to a keto  $\pi$ -neutral radical resonance form, which is highly reactive in the heme degradation process.

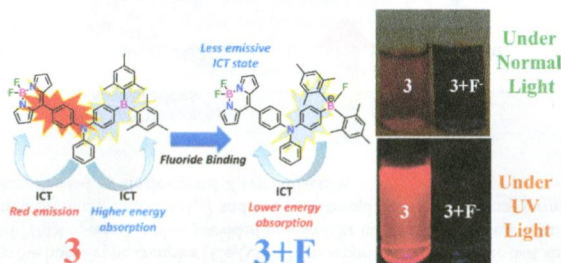
2776 **S**

dx.doi.org/10.1021/ic402898n

### Triarylborane-Appended New Triad and Tetrad: Chromogenic and Fluorogenic Anion Recognition

Chinna Ayya Swamy P and Pakkirisamy Thilagar\*

Facile syntheses of triarylborane-, triphenylamine-, and BODIPY-based triad (**3**) and tetrad (**4**) are reported. The new compounds show intriguing triple emission and selective colorimetric response toward small anions such as fluoride and cyanide.

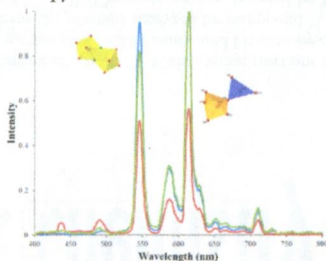
2787 **S**

dx.doi.org/10.1021/ic401897n

### Three New Silver Uranyl Diphosphonates: Structures and Properties

Anna-Gay D. Nelson,\* Zsolt Rak, Thomas E. Albrecht-Schmitt, Udo Becker, and Rodney C. Ewing

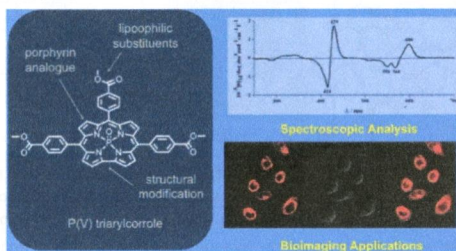
Three uranyl complexes were synthesized with methylenediphosphonic acid under hydrothermal conditions in the presence of silver cations, HF, and a molar solution of LiOH. Their structures illustrate the different roles played by the silver cation and pH. The experimental results are elucidated by electronic calculations that reveal that P–O and Ag–O bonds are responsible for the assembly of the uranyl pentagonal bipyramids.



### Phosphorus(V)-Corrole: Synthesis, Spectroscopic Properties, Theoretical Calculations, and Potential Utility for *in Vivo* Applications in Living Cells

Xu Liang, John Mack, Li-Min Zheng, Zhen Shen, and Nagao Kobayashi\*

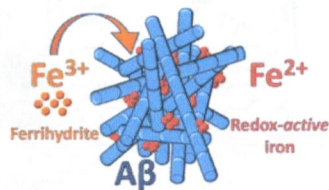
A novel lipophilic P(V) corrole complex was prepared by reacting 5,10,15-tris(4-methoxycarbonylphenyl)corrole with  $\text{PCl}_3$ , and its electronic structure and optical properties were analyzed by comparing optical spectral data to TD-DFT calculations. There is an intensification of the Q band relative to those of P(V) tetraphenylporphyrins, and significant emission intensity is observed in the red/NIR region. The potential utility of the dye for bioimaging applications was assessed by carrying out staining experiments in living HeLa cells.



### Evidence of Redox-Active Iron Formation Following Aggregation of Ferrihydrite and the Alzheimer's Disease Peptide $\beta$ -Amyloid

James Everett, Eva Céspedes, Leigh R. Shelford, Chris Exley, Joanna F. Collingwood, Jon Dobson, Gerrit van der Laan, Catherine A. Jenkins, Elke Arenholz, and Neil D. Telling\*

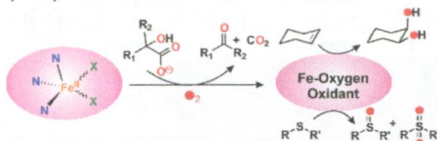
Here, we demonstrate that the peptide  $\beta$ -amyloid, which forms the senile plaques characteristic of the Alzheimer's disease (AD) brain, has a remarkable efficiency to chemically change the benign natural iron mineral ferrihydrite to a redox-active and potentially neurotoxic form. These findings indicate that both amyloid and iron could contribute to AD pathology, and they also suggest an origin for the reactive iron minerals magnetite and wüstite, which have been found previously in Alzheimer's tissue.



### Reactivity of an Iron–Oxygen Oxidant Generated upon Oxidative Decarboxylation of Biomimetic Iron(II) $\alpha$ -Hydroxy Acid Complexes

Sayantan Paria, Sayanti Chatterjee, and Tapan Kanti Paine\*

Dioxygen is reduced by iron(II)  $\alpha$ -hydroxy acid complexes to generate a nucleophilic iron–oxygen intermediate. The sacrificial reductants,  $\alpha$ -hydroxy acids, undergo two-electron oxidative decarboxylation to the corresponding carbonyl compounds. The novel iron–oxygen oxidant exhibits versatile reactivity like oxygen-atom transfer to sulfides, aliphatic C–H bond activation, and olefin cis-dihydroxylation.

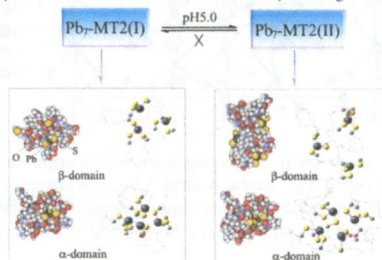




### pH-Dependent Coordination of Pb<sup>2+</sup> to Metallothionein2: Structures and Insight into Lead Detoxification

Yonghui He, Mengmeng Liu, Narek Darabedian, Yizeng Liang, Deyin Wu, Juan Xiang,\* and Feimeng Zhou\*

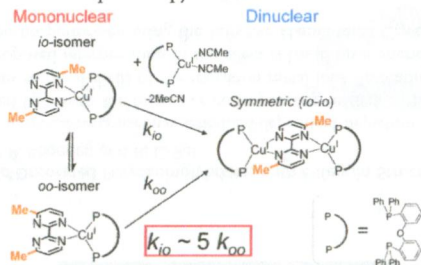
The pH-dependent structures of two different Pb<sub>7</sub>-MT2 complexes were revealed. The chemical stabilities and structural flexibility of these two complexes in proteolytic processing were investigated to gain insight into the lead detoxification process involving MTs. The similar structural, chemical, and biological properties between rabbit liver Pb<sub>7</sub>-MT2(II) and human Pb<sub>7</sub>-MT2(II) suggest a commonality in the Pb<sup>2+</sup> coordination chemistry among mammalian MT2s.



### Regulation of the Rate of Dinucleation of a Monocopper(I) Complex Containing Bipyrimidine Rotary Units by Restricted Double Pyrimidine Rotation

Yohei Hattori, Michihiro Nishikawa, Tetsuro Kusamoto, Shoko Kume,\* and Hiroshi Nishihara\*

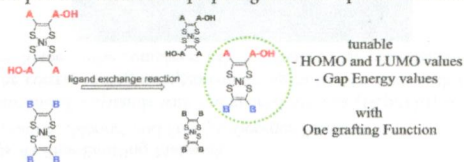
Mono- and dinuclear copper(I) complexes ligated by bis[2-(diphenylphosphino)phenyl] ether (DPEPhos) and 4,4'-dimethyl-2,2'-bipyrimidine were synthesized, and the isomerism of their pyrimidine ring linkage and their kinetics was investigated. The mononuclear complex showed *io* and *oo* isomers, while the dinuclear complex was only found as a symmetric (*io-io*) isomer. By the addition of [Cu(MeCN)<sub>2</sub>(DPEPhos)], the *io* isomer dinucleated about 5 times more quickly than the *oo* isomer, which was analyzed using time-dependent UV-vis spectroscopy at 193 K.



### Heteroleptic Bis(*cis*-1,2-disubstituted ethylene-1,2-dithiolato)nickel Complexes Obtained by Ligand-Exchange Reaction: Synthesis and Properties

Thi Minh Ha Vuong, Thanh-Tuan Bui, Alix Sournia-Saquet, Alain Moreau, and Kathleen I. Moineau-Chane Ching\*

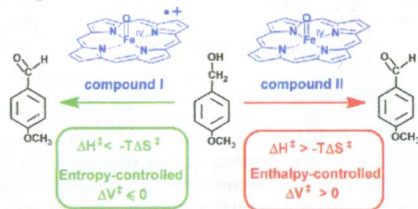
The ligand-exchange reaction has been investigated to synthesize heteroleptic nickel bis(dithiolene) complexes with the ethylene-1,2-dithiolato core substituted by either alkyl or aryl moieties and bearing one hydroxyl functional group. We demonstrate that this reaction is a powerful method for preparing nickel complexes with tailor-made frontier orbital energies.



### Temperature and Pressure Effects on C–H Abstraction Reactions Involving Compound I and II Mimics in Aqueous Solution

Maria Oszajca, Alicja Franke, Agnieszka Drzewiecka-Matuszek, Małgorzata Brindell, Grazyna Stochel,\* and Rudi van Eldik\*

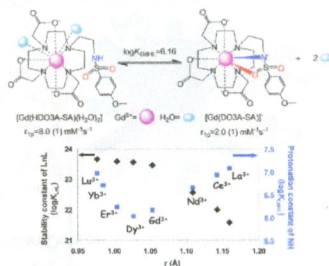
Activation parameters were determined for the oxidation of selected organic substrates by mimics for Cpd I and II in aqueous solution. The temperature dependence of the oxidation reactions suggests that they are either enthalpy- or entropy-controlled processes. The pressure dependence data allow differentiation between the stepwise and concerted nature of the rate-determining step. These results are important to understand the mechanistic characteristics of the Cpd I and II mimics.



### Solution Structures, Stabilities, Kinetics, and Dynamics of DO3A and DO3A–Sulphonamide Complexes

Anett Takács, Roberta Napolitano, Mihály Purgel, Attila Csaba Bényei, László Zékány, Ernő Brücher, Imre Tóth, Zsolt Baranyai,\* and Silvio Aime\*

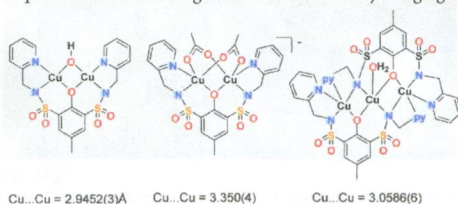
$[\text{Gd}(\text{DO3A}-\text{SA})]^-$  is a novel pH-sensitive Gd(III) complex showing optimal relaxometric properties and acceptable thermodynamic stability and kinetic inertness, which make it suitable for MRI preclinical studies. The deprotonation and coordination of the sulphonamide group improves the stability and kinetic inertness of the Ln(DO3A–SA) complexes due to the strong interaction between the Ln<sup>3+</sup> ion and the deprotonated sulphonamide group. This structural change decreases the hydration number of the Gd(III) complex, and the relaxivity drops by 6.0 mM<sup>-1</sup> s<sup>-1</sup> unit.



### A Versatile Dinuclear Ligand Containing Sulphonamide Groups

Jonas Sundberg, Hannes Witt, Lisa Cameron, Mikael Häkansson, Jesper Bendix, and Christine J. McKenzie\*

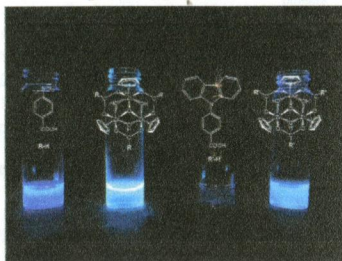
In its complexes, a new bis-sulfonamido ligand is capable of varying degrees of deprotonation. The series of copper complexes of the ligand in its fully deprotonated trianionic form shows a range of topologically contrasting structures, metal geometries, and considerable flexibility with respect to accommodating the bite of the ancillary bridging ligands in the dicopper complexes.



**Zirconium(IV) Metallocavitands As Blue-Emitting Materials**

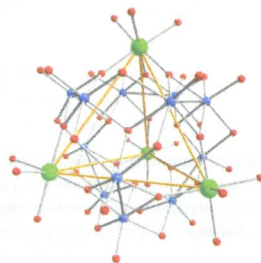
Hassan Iden, Wenhua Bi, Jean-François Morin,\* and Frédéric-Georges Fontaine\*

A series of zirconium-carboxylate metallocavitands with the general formula  $[(\text{CpZr})_3(\mu\text{-}\kappa_2\text{O}'\text{O}'\text{CR})_3(\mu_3\text{-O})(\mu_2\text{-OH})_3]\text{Cl}$  were synthesized by reacting the corresponding nitrogen-containing carboxylic acids with  $\text{Cp}_2\text{ZrCl}_2$  in a self-assembly procedure at room temperature. Some of the complexes exhibit efficient blue photoluminescence properties in solution.

**Magneto-optical Response of 3d-Decorated Polyoxomolybdates with  $\epsilon$ -Keggin Structure**

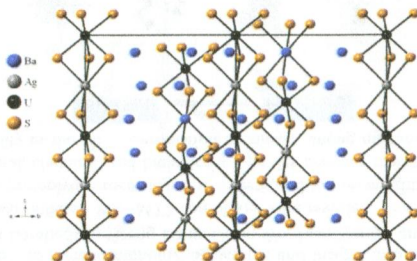
I. V. Andreev, A. L. Tchougréeff,\* P. Kögerler, and R. C. Rai

We report a new type of magneto-optical-response:magnetic-field-dependent depletion of intensity of reflected nonpolarized light with the frequency corresponding to that of the formally spin-forbidden transitions in the  $d$ -shells of the transition metal ions decorating polyoxomolybdate cages. The proposed interpretation of the effect is based on numerical analysis of the  $d-d$  excitation spectra performed using the Effective Hamiltonian Crystal Field Method.

**Syntheses, Structures, and Electronic Properties of  $\text{Ba}_3\text{FeUS}_6$  and  $\text{Ba}_3\text{AgUS}_6$** 

Adel Mesbah, Christos D. Malliakas, Sébastien Lebègue, Amy A. Sarjeant, Wojciech Stojko, Lukasz A. Koscielski, and James A. Ibers\*

$\text{Ba}_3\text{FeUS}_6$  and  $\text{Ba}_3\text{AgUS}_6$  crystallize in the  $\text{K}_4\text{CdCl}_6$  structure type and feature infinite  $^1_0[\text{M-US}_6^{6-}]$  chains. The  $^1_0[\text{FeUS}_6^{6-}]$  chains are formed by the face-sharing of  $\text{US}_6$  trigonal prisms with  $\text{FeS}_6$  octahedra; in contrast, the  $^1_0[\text{AgUS}_6^{6-}]$  chains are formed by the face-sharing of  $\text{US}_6$  octahedra with  $\text{AgS}_6$  trigonal prisms. The  $\text{Ba}_3\text{FeUS}_6$  compound contains  $\text{U}^{5+}$ , whereas  $\text{Ba}_3\text{AgUS}_6$  contains  $\text{U}^{5+}$ . This structure offers a remarkable flexibility in terms of the oxidation state of the incorporated uranium.

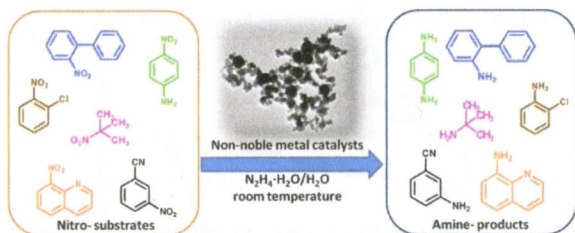




### Room-Temperature Chemoselective Reduction of Nitro Groups Using Non-noble Metal Nanocatalysts in Water

Rohit K. Rai, Arup Mahata, Sushobhan Mukhopadhyay, Sampa Gupta, Pei-Zhou Li, Kim T. Nguyen, Yanli Zhao, Biswarup Pathak, and Sanjay K. Singh\*

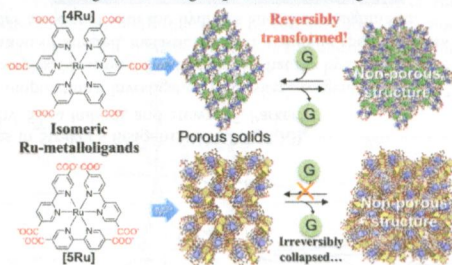
Purely aqueous-phase chemoselective reduction of a wide range of aromatic and aliphatic nitro substrates to the respective amines has been achieved in the presence of inexpensive Ni and Co metal nanocatalysts, with a high tolerance to other highly reducible groups present in close proximity to the targeted nitro groups, using hydrous hydrazine as a reducing agent at room temperature.



### Flexible Coordination Polymers Composed of Luminescent Ruthenium(II) Metalloligands: Importance of the Position of the Coordination Site in Metalloligands

Atsushi Kobayashi,\* Tadashi Ohba, Erika Saitoh, Yui Suzuki, Shin-ichiro Noro, Ho-Chol Chang, and Masako Kato\*

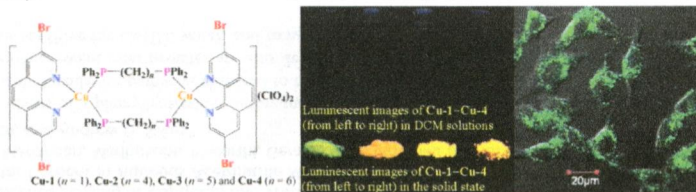
We have successfully synthesized five novel luminescent and porous coordination compounds fabricated from two different isomeric ruthenium(II) metalloligands  $[\text{Ru}(n,n'\text{-dcbpy})_3]^{2+}$  ( $n = 4$  or  $5$ ;  $n,n'\text{-dcbpy} = n,n'\text{-dicarboxy-2,2'-bipyridine}$ ) with divalent metal ions ( $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Cd}^{2+}$ ) and found that the guest-induced structural phase transition behavior strongly depends on the position of the coordinating functional group in the metalloligand.



### Aggregation-Induced Emissive Copper(I) Complexes for Living Cell Imaging

Xue-Lian Xin, Min Chen, Yu-bo Ai, Feng-lei Yang, Xiu-Ling Li,\* and Fuyou Li\*

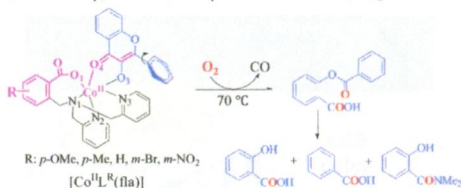
Dynamically stable phosphorescent binuclear copper(I) mixed-ligand complexes  $[\text{Cu}_2(\text{Brphen})_2(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)_2] \cdot (\text{ClO}_4)_2$  are very stable to air and moisture in the solid state. They exhibit good AIPE behavior and are used for living cell imaging successfully.



### Series of Structural and Functional Models for the ES (Enzyme–Substrate) Complex of the Co(II)-Containing Quercetin 2,3-Dioxygenase

Ying-Ji Sun,\* Qian-Qian Huang, and Jian-Jun Zhang

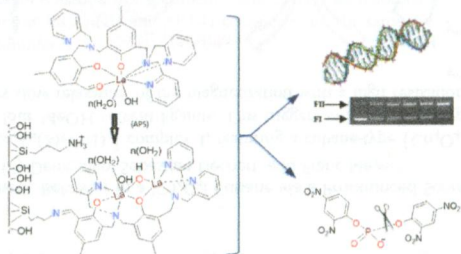
A series of Co<sup>II</sup>-flavonolate complexes [Co<sup>II</sup>L<sup>R</sup>(fla)] are reported as structural and functional ES models of the Co<sup>II</sup>-containing quercetin 2,3-dioxygenase (Co-2,3-QD). They exhibit high enzyme-type dioxygenation reactivity due to the carboxylate group of L<sup>R</sup>. Their structures, properties, and reactivity show some dependence on the substituent group of L<sup>R</sup> via the “electron conduit”, providing important insights into the structure–property–reactivity relationship, the carboxylate and electronic effects on the enzymatic reactivity, and the catalytic role of Co-2,3-QD.



### New La(III) Complex Immobilized on 3-Aminopropyl-Functionalized Silica as an Efficient and Reusable Catalyst for Hydrolysis of Phosphate Ester Bonds

Alfredo A. Muxel, Ademir Neves,\* Maryene A. Camargo, Adailton J. Bortoluzzi, Bruno Szpoganicz, Eduardo E. Castellano, Nathalia Castilho, Tiago Bortolotto, and Hernán Terenzi

Herein, we report the synthesis, characterization, and hydrolase-like activity of a new mononuclear La<sup>III</sup> complex **I** containing a La<sup>III</sup>-bound phenolate with a carbonyl functional group. When linked to 3-aminopropyl-functionalized silica (APS), the mononuclear complex undergoes disproportionation to form a dinuclear species APS-[(OH)La<sup>III</sup>(μ-OH)La<sup>III</sup>(OH<sub>2</sub>)], whose catalytic efficiency is increased when compared to the homogeneous reaction, and the anchored catalyst APS-1 can be recovered and reused for subsequent hydrolysis reactions.

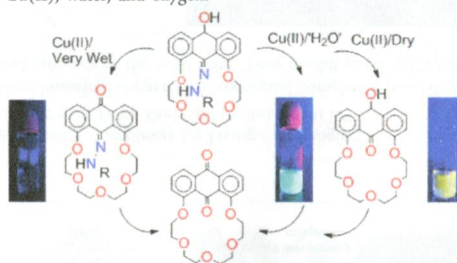




### Selective Fluorescence Sensing of Copper(II) and Water via Competing Imine Hydrolysis and Alcohol Oxidation Pathways Sensitive to Water Content in Aqueous Acetonitrile Mixtures

Kadarkaraisamy Mariappan, Madhubabu Alaparthy, Gerald Caple, Vinothini Balasubramanian, Mariah M. Hoffman, Mikaela Hudspeth, and Andrew G. Sykes\*

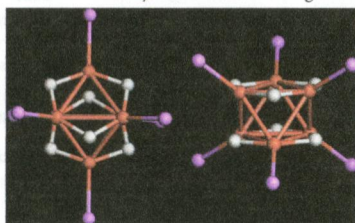
The selective synthesis of a phenylhydrazine–anthraquinone macrocycle results in different copper(II)-catalyzed imine hydrolysis and alcohol oxidation pathways that lead to the same product and are dependent on the water concentration. The yellow- and green-fluorescent intermediates are also dependent on the water and oxygen concentrations, producing a fluorescent sensor sensitive for Cu(II), water, and oxygen.



### Characterization of the Hydrides in Stryker's Reagent: $[\text{HCu}(\text{P}(\text{C}_6\text{H}_5)_3)]_6$

Elliott L. Bennett, Patrick J. Murphy, Silvia Imberti, and Stewart F. Parker\*

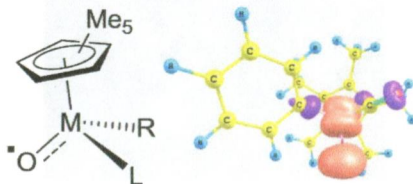
A structural, spectroscopic, and computational investigation of Stryker's reagent,  $[\text{HCu}(\text{P}(\text{C}_6\text{H}_5)_3)]_6$ , and its isotopomers has provided new insights into the complex. Neutron diffraction shows that the hydrides are best described as edge bridging rather than face bridging. The combination of infrared, inelastic neutron scattering spectroscopies and *ab initio* studies has allowed the location of most of the modes associated with the hydrides and their assignments.



### Density Functional Theory Study of Oxygen-Atom Insertion into Metal–Methyl Bonds of Iron(II), Ruthenium(II), and Osmium(II) Complexes: Study of Metal-Mediated C–O Bond Formation

Daniel B. Pardue,\* Jiajun Mei, Thomas R. Cundari, and T. Brent Gunnoe

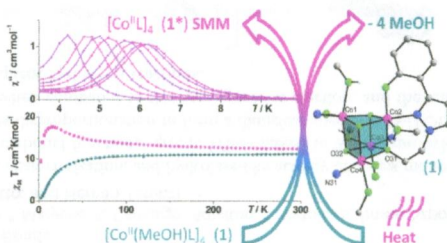
Guidance is provided on experimentally feasible research directions in the catalytic functionalization of strong C–H bonds at low temperatures and pressures. Computational results employing density functional theory reveal that the functionalization M–R to M–OR (R = Me, Ph) is plausible through the use of Earth-abundant iron(II) complexes. This reaction is predicted to proceed through a two-step pathway with a metal–oxo intermediate. The energetics of possible side reactions are also evaluated.



### Inducing Single Molecule Magnetic Behavior in a $[\text{Co}_4\text{O}_4]$ Cubane via a Pronounced Solvatomagnetic Effect

Felix J. Klinke, Animesh Das, Serhiy Demeshko, Sebastian Dechert, and Franc Meyer\*

Thermal treatment of a new  $[\text{Co}_4\text{L}_4(\text{MeOH})_4]$  complex **1**, featuring a cubane-type  $\{\text{Co}_4\text{O}_4\}$  core with  $S_T = 0$  spin ground state, leads to the release of all four MeOH solvent ligands. This triggers switching to a high-spin ground state, and the resulting “naked”  $[\text{Co}_4\text{L}_4]$  shows slow relaxation of the magnetization with a high relaxation barrier of 64.4 K; magnetic hysteresis is observed at 2 K.

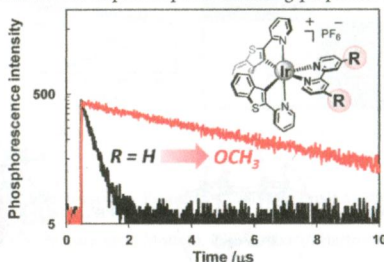




### Controlling the Excited State and Photosensitizing Property of a 2-(2-Pyridyl)benzo[b]thiophene-Based Cationic Iridium Complex through Simple Chemical Modification

Shin-ya Takizawa,\* Kengo Shimada, Yoichi Sato, and Shigeru Murata

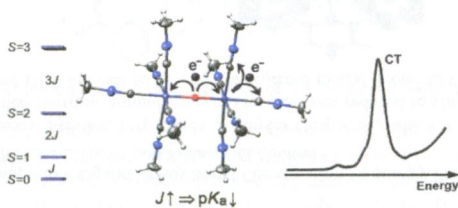
Cationic iridium complexes comprising two 2-(2-pyridyl)benzo[b]thiophene (btp) ligands and one 2,2'-bipyridyl (bpy) ancillary ligand with different substituents as visible light-absorbing sensitizers were synthesized and examined for their photophysical and photosensitizing properties. Systematic investigation of these complexes revealed that such a simple chemical modification controls the excited-state lifetime due to a strong influence of the substituents on the ligand field strength. The resulting long-lived excited states improved photosensitizing properties of the btp-based Ir complexes.



### Oxo-Bridged Dinuclear Chromium(III) Complexes: Correlation between the Optical and Magnetic Properties and the Basicity of the Oxo Bridge

Thorbjørn J. Morsing, Jesper Bendix, Høgni Weihe, and Anders Døssing\*

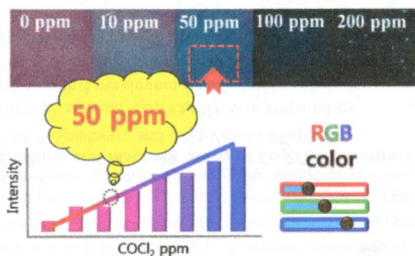
We present a model that explains the >10-orders-of-magnitude variation of the acid dissociation constant of the hydroxo bridge in dinuclear chromium(III) complexes, in terms of differences of the lowering of energies and Landé splitting of the ground-state manifold. The lowering in energy of all spin states by configuration interaction between the ground state and ligand-to-metal charge transfer (LMCT) states dominates the influence of electronic structure on the bridge basicity in these oxo-bridged complexes.



### Geometric Change of a Thiacalix[4]arene Supramolecular Gel with Volatile Gases and Its Chromogenic Detection for Rapid Analysis

Ka Young Kim, Sunhong Park, Sung Ho Jung, Shim Sung Lee, Ki-Min Park, Seiji Shinkai, and Jong Hwa Jung\*

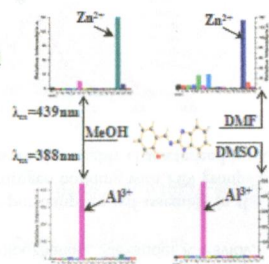
We prepared a coordination polymer gel that is self-assembled to form a network structure between a thiacalix[4]arene derivative and  $\text{Co}^{2+}$ . This gel is capable of selectively changing color in the presence of phosgene. We found that this rapid and dramatic color change under ambient conditions originated from a change from an octahedral to a tetrahedral structure. Furthermore, the quantitative concentration of phosgene can be easily calculated by employing the RGB histogram available in a smartphone application.



### A Highly Selective Chemosensor for Al(III) and Zn(II) and Its Coordination with Metal Ions

Wei Cao, Xiang-Jun Zheng,\* Ji-Ping Sun, Wing-Tak Wong, De-Cai Fang,\* Jia-Xin Zhang, and Lin-Pei Jin

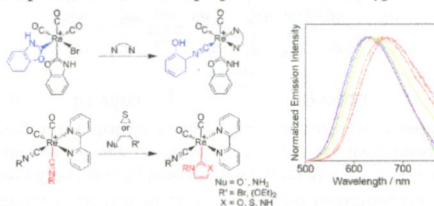
A fluorescence chemosensor for both Zn(II) and Al(III) ions, based on inhibition of excited-state intramolecular proton transfer, has low toxicity for HeLa cells and could detect Zn(II) and Al(III) ions in living cells by bioimaging. The fluorescent species formed in solution were established by a combination of experimental and theoretical methods. The coordination modes in solutions for Zn(II) and Al(III) complexes are the same as those in  $[\text{M}(\text{HL})_2(\text{CH}_3\text{OH})_2]$  complexes.



### Synthesis, Characterization, and Photophysical Study of Luminescent Rhenium(I) Diimine Complexes with Various Types of N-Heterocyclic Carbene Ligands

Chi-On Ng, Shek-Man Yiu, and Chi-Chiu Ko\*

A series of luminescent Re(I) diimine complexes with various types of NHC ligands has been synthesized from the isocyano Re(I) complexes. All these complexes showed  $^3\text{MLCT}$  [ $d\pi(\text{Re}) \rightarrow \pi^*(\text{N}-\text{N})$ ] phosphorescence. The photophysics and electrochemistry of these complexes have been investigated. Through the study of the photophysical and electrochemical properties of these Re(I) NHC complexes, the electronic properties of different types of NHC ligands were investigated.

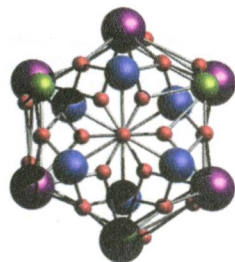




**Iron Lanthanide Phosphonate Clusters:  $\{\text{Fe}_6\text{Ln}_6\text{P}_6\}$  Wells—Dawson-like Structures with  $D_{3d}$  Symmetry**

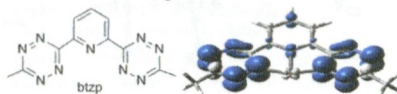
Eufemio Moreno Pineda, Floriana Tuna, Yan-Zhen Zheng, Simon J. Teat, Richard E. P. Winpenny,\* Jürgen Schnack, and Eric J. L. McInnes\*

A family of  $\{\text{Fe}^{\text{III}}_6\text{Ln}^{\text{III}}_6\text{P}_6\}$  cages of general formula  $[\text{Fe}_6\text{Ln}_6(\text{O})_2(\text{CO}_3)(\text{O}_3\text{PR})_6(\text{O}_2\text{C}^i\text{Bu})_{18}]$  has been prepared with a range of phosphonic acids ( $\text{R} = \text{Me}, \text{Ph}, n\text{-hexyl}$ ). The structures are related to the previously reported  $\{\text{Ni}^{\text{II}}_6\text{Ln}_6\text{P}_6\}$  Wells—Dawson analogues, but the difference in charge of the 3d ion leads to much higher symmetry ( $D_{3d}$ ) structures. Consequences for the magnetic and magnetocaloric properties are discussed.

**Chemical Implications of Incompatible Ligand versus Metal Coordination Geometry Preferences**

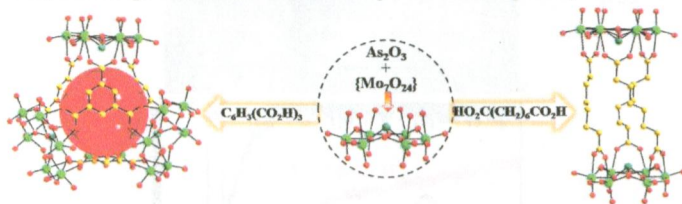
Alice K. Hui, Yaroslav Losovj, Richard L. Lord,\* and Kenneth G. Caulton\*

The pincer ligand 2,2'-bis-tetrazinyl pyridine, btzp, forms a complex  $(\text{btzp})\text{CuCl}$  which is a chloride-bridged polymer in the solid state, hence with 20 valence electrons around copper. This has been reduced to  $(\text{btzp})\text{Cu}$ , which EPR, X-ray photoelectron spectroscopy, and DFT indicate to be a ligand-centered radical bound to  $\text{Cu}(\text{I})$ .

**Ligand-Directed Conformation of Inorganic–Organic Molecular Capsule and Cage**

Donghui Yang, Yanfen Liang, Pengtao Ma, Suzhi Li, Jingping Wang,\* and Jingyang Niu\*

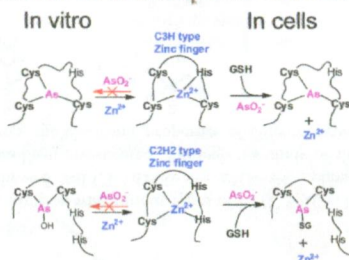
The different carboxylate ligands were covalently attached to the  $[\text{AsMo}_6\text{O}_{21}]^{2-}$  clusters to generate four inorganic–organic hybrids with monomer, dimer (capsule), trimer, and tetramer (cage) structures, respectively.



### The Reaction of Arsenite with Proteins Relies on Solution Conditions

Linhong Zhao, Zhen Wang, Zhaoyong Xi, Dechen Xu, Siming Chen, and Yangzhong Liu\*

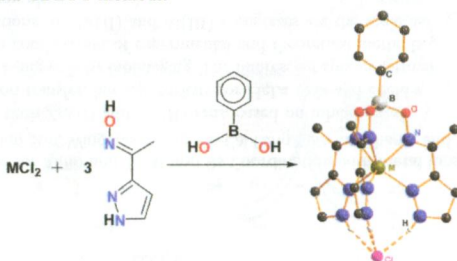
Arsenite targets zinc finger proteins (ZFPs) in cells; however, it is not reactive to ZFPs in vitro. In this work, we found that the reaction of arsenite with ZFPs relies on solution conditions such as pH and the presence of some small biomolecules, for instance, glutathione. These findings reveal that the cellular conditions could be crucial for the function of arsenite.



### Chloride Ion-Aided Self-Assembly of Pseudocathrochelate Metal Tris-pyrazoloximates

Oleg A. Varzatskii, Larysa V. Penkova, Svitlana V. Kats, Alexander V. Dolganov, Anna V. Vologzhanina, Alexander A. Pavlov, Valentin V. Novikov, Artem S. Bogomyakov, Victor N. Nemykin, and Yan Z. Voloshin\*

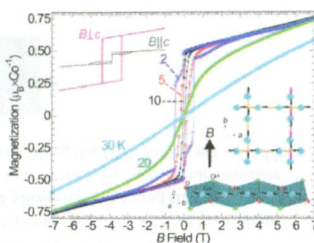
The first pseudocathrochelate metal tris-pyrazoloximates were obtained by efficient one-pot template self-assembly in the presence of chloride anions capping their pseudomacrobicyclic frameworks via strong hydrogen bonding with HN groups of three pyrazoloximate chelate fragments. These high-spin 3d transition metal complexes were thoroughly characterized by X-ray diffraction, spectral, DFT, and TDDFT methods.



### Ionothermal Synthesis, Crystal Structure, and Magnetic Study of $\text{Co}_2\text{PO}_4\text{OH}$ Isostructural with Caminite

Guangmei Wang, Martin Valldor, Eike T. Spielberg, and Anja-Verena Mudring\*

A new framework cobalt(II) hydroxyl phosphate,  $\text{Co}_2\text{PO}_4\text{OH}$ , was prepared by ionothermal synthesis using 1-butyl-4-methyl-pyridinium hexafluorophosphate as the reaction medium and mineralizer.  $\text{Co}_2\text{PO}_4\text{OH}$  undergoes a magnetic transition at low temperatures to a canted antiferromagnet.

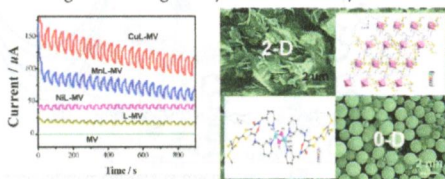




### Role of the Coordination Center in Photocurrent Behavior of a Tetrathiafulvalene and Metal Complex Dyad

Yong-Gang Sun, Shu-Fang Ji, Peng Huo, Jing-Xue Yin, Yu-De Huang, Qin-Yu Zhu,\* and Jie Dai\*

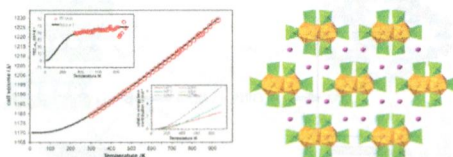
The role of metal coordination centers in photocurrent response is first studied based on three electrochemically active coordination dyads with TTF and divalent transition metal. This discovery is significant in helping to design and explore new photoelectrode active materials with inorganic and organic hybrid molecular systems.



### High-Temperature Phase Transitions, Spectroscopic Properties, and Dimensionality Reduction in Rubidium Thorium Molybdate Family

Bin Xiao, Thorsten M. Gesing, Philip Kegler, Giuseppe Modolo, Dirk Bosbach, Hartmut Schlenz, Evgeny V. Suleimanov, and Evgeny V. Alekseev\*

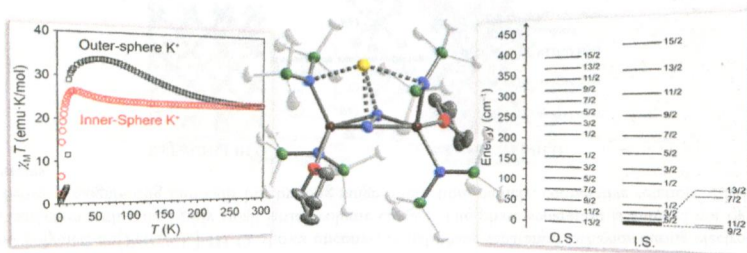
Four new rubidium thorium molybdates have been synthesized using high temperature route. Structures, thermal behavior, and detailed Raman and IR spectroscopic properties of these compounds were investigated. Temperature-dependent phase transition effects in  $\text{Rb}_2\text{Th}(\text{MoO}_4)_3$  and  $\text{Rb}_4\text{Th}(\text{MoO}_4)_4$  were observed and characterized using DSC and high-temperature powder diffraction methods.



### Influence of an Inner-Sphere $\text{K}^+$ Ion on the Magnetic Behavior of $\text{N}_2^{3-}$ Radical-Bridged Dilanthanide Complexes Isolated Using an External Magnetic Field

Katie R. Meihaus, Jordan F. Corbey, Ming Fang, Joseph W. Ziller, Jeffrey R. Long,\* and William J. Evans\*

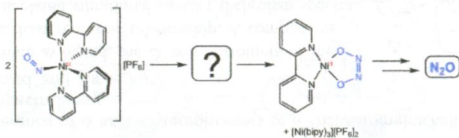
A new series of  $\text{N}_2^{3-}$  radical-bridged complexes  $\{[(\text{R}_2\text{N})_2(\text{THF})\text{Ln}]_2(\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\text{N}_2)\text{K}\}$  ( $\text{Ln} = \text{Gd}, \text{Tb}, \text{Dy}$ ) with an inner-sphere  $\text{K}^+$  cation is presented. Magnetic characterization reveals strong antiferromagnetic coupling between lanthanide centers and the  $\text{N}_2^{3-}$ , as observed previously for  $[\text{K}(18\text{-crown-6})(\text{THF})_2]\{[(\text{R}_2\text{N})_2(\text{THF})\text{Ln}]_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-}\text{N}_2)\}$ , with additional antiferromagnetic  $\text{Ln}\cdots\text{Ln}$  exchange at low temperatures. This competing interaction leads to lower blocking temperatures for the Tb and Dy species, highlighting the importance of a planar  $\text{Ln}\text{-N}_2^{3-}\text{-Ln}$  unit in promoting concerted exchange and slow magnetic relaxation.



### Mechanistic Insights into the Formation of $N_2O$ by a Nickel Nitrosyl Complex

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

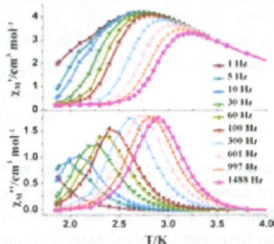
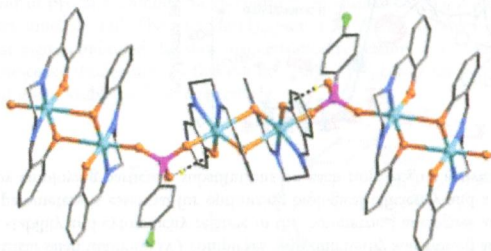
A mechanistic investigation of *trans*-hyponitrite ( $N_2O_2^{2-}$ ) formation mediated by a nickel nitrosyl complex suggests that the  $N_2O_2^{2-}$  ligand is not formed by coupling of an  $NO^-$  ligand with exogenous NO, or by coupling of an  $NO^-$  ligand with an  $NO^+$  ligand. Instead, formation of  $N_2O_2^{2-}$  via coupling of two  $NO^-$  ligands is the pathway that is most consistent with the experimental observations.



### Effect of Structural Isomerism on Magnetic Dynamics: from Single-Molecule Magnet to Single-Chain Magnet

Ting-Ting Wang, Min Ren, Song-Song Bao, Bin Liu, Li Pi, Zhong-Sheng Cai, Ze-Hua Zheng, Zhong-Li Xu, and Li-Min Zheng\*

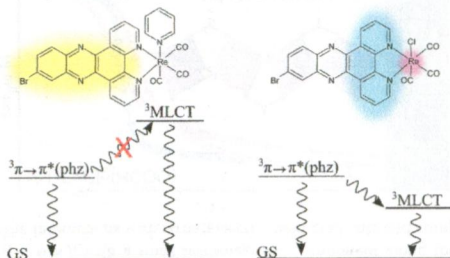
This Paper reports the first examples of O–P–O bridged  $Mn_2(salen)_2$  ( $salen = N,N'$ -bis(salicylidene)ethylenediamine) chain compounds, the magnetic dynamics of which is modulated by positional isomerism of the bridging ligands.



### Re(I) Complexes of Substituted dppz: A Computational and Spectroscopic Study

Holly van der Salm, Michael G. Fraser, Raphael Horvath, Scott A. Cameron, Jonathan E. Bamsley, Xue-Zhong Sun, Michael W. George,\* and Keith C. Gordon\*

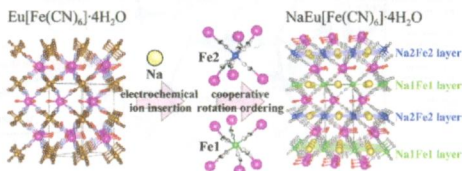
A series of brominated dppz-type complexes have been synthesized. These show phenazine-based  $\pi, \pi^*$  and MLCT excited states which may be tuned by the ancillary ligand (pyridine or  $Cl^-$ ). These excited states have been fully characterized using DFT calculations, resonance Raman spectroscopy, transient absorption, and time-resolved infrared spectroscopy.



### Phase Separation of a Hexacyanoferrate-Bridged Coordination Framework under Electrochemical Na-ion Insertion

Satoshi Kajiyama, Yoshifumi Mizuno, Masashi Okubo,\* Ryosuke Kurono, Shin-ichi Nishimura, and Atsuo Yamada

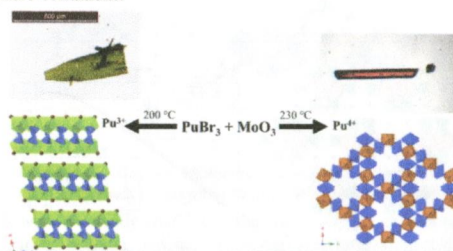
A coordination polymer,  $\text{Eu}[\text{Fe}(\text{CN})_6] \cdot 4\text{H}_2\text{O}$ , shows unconventional phase separation behavior during electrochemical Na-ion insertion/extraction with a negligibly small lattice volume change. The phase separation is induced not by conventional elastic strain between neighboring unit cells but by long-range interaction, namely, cooperative rotation ordering of hexacyanoferrates.



### Synthesis and Spectroscopy of New Plutonium(III) and -(IV) Molybdates: Comparisons of Electronic Characteristics

Justin N. Cross, Samantha K. Cary, Jared T. Stritzinger, Matthew J. Polinski, and Thomas E. Albrecht Schmitt\*

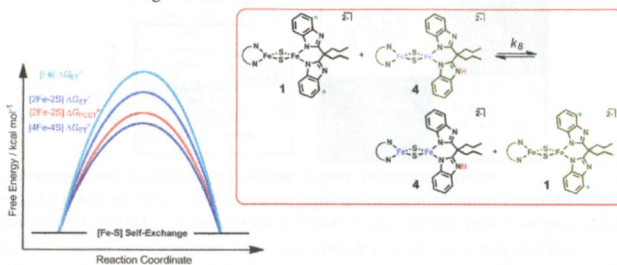
The hydrothermal reaction of  $\text{PuBr}_3$  and  $\text{MoO}_3$  produces a bright-green plutonium(III) complex that is strikingly different from the complex isolated from the analogous neodymium(III) reaction. The unusual color is attributed to a broad charge-transfer band, indicating redox instability. This is confirmed by increasing reaction temperature, forming a plutonium(IV) molybdate despite inert-atmosphere conditions.



### Electron Transfer and Proton-Coupled Electron Transfer Reactivity and Self-Exchange of Synthetic [2Fe–2S] Complexes: Models for Rieske and mitoNEET Clusters

Caroline T. Saouma, Margaux M. Pinney, and James M. Mayer\*

$[\text{Fe}_2\text{S}_2(\text{P}^{\text{bbim}})(\text{P}^{\text{bbimH}_2})]^{\pm}$  clusters have been generated in multiple redox and protonation states. Their PCET and ET thermochemistry and reactivity are described. The PCET self-exchange reaction occurs by concerted  $e^-/\text{H}^+$  exchange, and the ET self-exchange barriers for different clusters are shown to scale with  $[\text{Fe}–\text{S}]$  cluster size. The implications of these results for the reactivity of biochemical imidazole-ligated clusters is discussed.

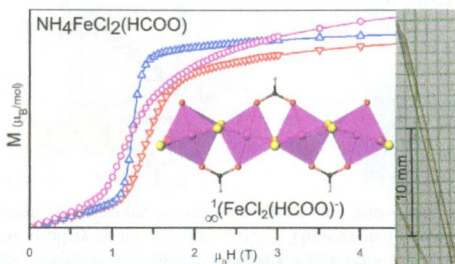




### NH<sub>4</sub>FeCl<sub>2</sub>(HCOO): Synthesis, Structure, and Magnetism of a Novel Low-Dimensional Magnetic Material

Joshua T. Greenfield, Saeed Kamali, Nezhueyoti Izquierdo, Michael Chen, and Kirill Kovnir\*

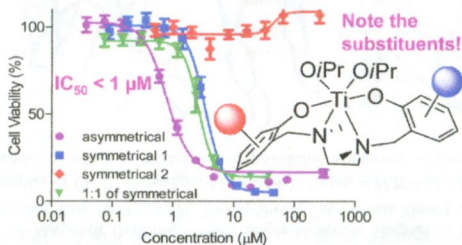
Solvothermal synthesis was used to create a low-dimensional iron(II) chloride formate compound, NH<sub>4</sub>FeCl<sub>2</sub>(HCOO). The crystal structure consists of infinite zigzag chains of distorted Fe<sup>2+</sup>-centered octahedra linked by μ<sub>2</sub>-Cl and syn-syn formate bridges. Magnetic measurements show anisotropic metamagnetic transitions and magnetic coupling dominated by antiferromagnetic interactions ( $T_N = 6$  K), with a small ferromagnetic component along the chains. <sup>57</sup>Fe Mössbauer spectroscopy reveals mixed hyperfine interactions with strong electric field gradients and complex noncollinear arrangement of the magnetic moments.



### C<sub>1</sub>-Symmetrical Titanium(IV) Complexes of Salan Ligands with Differently Substituted Aromatic Rings: Enhanced Cytotoxic Activity

Hagai Glasner and Edit Y. Tshuva\*

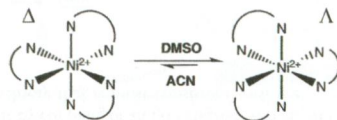
C<sub>1</sub>-symmetrical salan titanium(IV) complexes with differently substituted aromatic rings were prepared and analyzed for their hydrolytic stability and cytotoxicity relative to the symmetrical analogues and their equimolar mixtures. Fine tuning of ligand structural parameters is essential for optimizing biological efficiency and a marked enhancement of cytotoxicity may be obtained by employing particular substitutions on each ring. Highly active (IC<sub>50</sub> as low as <1 μM) and stable complexes are reported.



### Strong Solvent-Dependent Preference of Δ and Λ Stereoisomers of a Tris(diamine)nickel(II) Complex Revealed by Vibrational Circular Dichroism Spectroscopy

Christian Merten,\* Robert McDonald, and Yunjie Xu\*

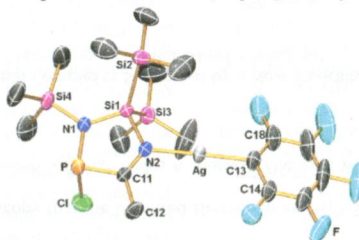
With chiral diphenylethylenediamine as ligand, the Δ and Λ isomers of the investigated tris-complex are in a diastereomeric relationship. A comparison between the experimental and calculated vibrational circular dichroism spectra proves the existence of both isomers in an acetonitrile solution. However, a significant shift of the equilibrium toward the Λ diastereomer is found for the complex in dimethyl sulfoxide.



**The Reactivity of Silylated Amino(dichloro)phosphanes in the Presence of Silver Salts**

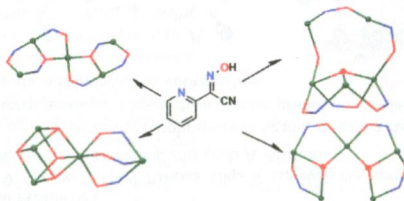
Axel Schulz,\* Alexander Villinger, and Andrea Westenkirchner

Cyclic and acyclic phosphorus–nitrogen compounds have been synthesized in reactions of Hyp–N(SiMe<sub>3</sub>)PCl<sub>2</sub> (hypersilyl = Hyp = (Me<sub>3</sub>Si)<sub>3</sub>Si) with silver salts of the perfluorinated anions [CF<sub>3</sub>CO<sub>2</sub>]<sup>−</sup>, [CF<sub>3</sub>SO<sub>3</sub>]<sup>−</sup>, and [C<sub>6</sub>F<sub>5</sub>]<sup>−</sup>.

**New Topologies in Pentanuclear Nickel/Oximate Clusters: Structural and Magnetic Characterization**

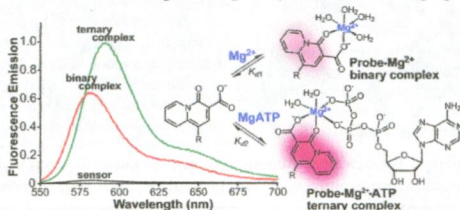
Jordi Esteban,\* Mercè Font-Bardia, José Sánchez Costa, Simon J. Teat, and Albert Escuer\*

Reaction of 2-pyridylcyanoxime with a variety of Ni<sup>II</sup> salts results in five new pentanuclear clusters and three unprecedented cores have been characterized. Analysis of their magnetic properties shows ground states between *S* = 3 and 0 as function of the topology and competitive interactions inside the clusters.

**Formation of Ternary Complexes with MgATP: Effects on the Detection of Mg<sup>2+</sup> in Biological Samples by Bidentate Fluorescent Sensors**

Sarina C. Schwartz, Brismar Pinto-Pacheco, Jean-Philippe Pitteloud, and Daniela Buccella\*

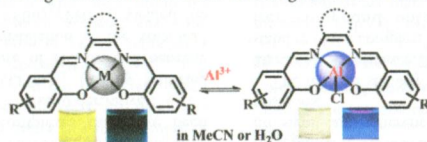
The formation of ternary complexes between low-denticity β-keto-acid fluorescent chelators and MgATP leads to optical responses similar to or greater than those elicited by the formation of their binary counterparts, thus posing challenges in the study of ionized magnesium in nucleotide-rich biological samples by fluorescence imaging.



### Optical Chemosensors Based on Transmetalation of Salen-Based Schiff Base Complexes

Jinghui Cheng, Xiaofeng Ma, Yuhui Zhang, Jiaoyan Liu, Xiangge Zhou, and Haifeng Xiang\*

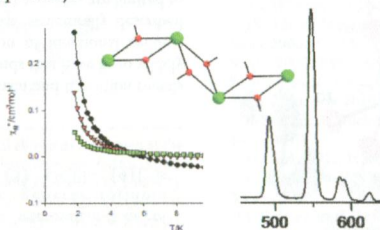
Optical (both colorimetric and fluorescent) chemosensors for detecting  $Al^{3+}$  based on transmetalation reactions (metal displacement or exchange reactions) of a series of  $K(I)$ ,  $Ca(II)$ ,  $Zn(II)$ ,  $Cu(II)$ , and  $Pt(II)$  complexes containing different ligands of salen-based Schiff bases are demonstrated. The selectivities of these complex-based chemosensors are much better than those of the corresponding free ligands as a result of the shielding function of the filled-in metal ion in the complex.



### Tetranuclear Lanthanide(III) Complexes with a Zigzag Topology from the Use of Pyridine-2,6-dimethanol: Synthetic, Structural, Spectroscopic, Magnetic and Photoluminescence Studies

Dimitris I. Alexandropoulos, Luis Cunha-Silva, Linh Pham, Vlasoula Bekiari, George Christou, and Theocharis C. Stamatatos\*

Employment of pyridine-2,6-dimethanol ( $pdmH_2$ ) in lanthanide(III), noncarboxylate chemistry has provided access to a family of tetranuclear  $[Ln^{III}_4(NO_3)_2(pdmH)_6(pdmH_2)_2](NO_3)_4$  complexes with a rare zigzag topology. The appearance of out-of-phase signals indicated the slow magnetization relaxation of an SMM for the  $Dy^{III}_4$  analogue, while solid-state photoluminescence studies showed that the  $Eu^{III}_4$  and  $Tb^{III}_4$  compounds exhibit intense, sharp, and narrow emission bands in the red and green visible regions, respectively.

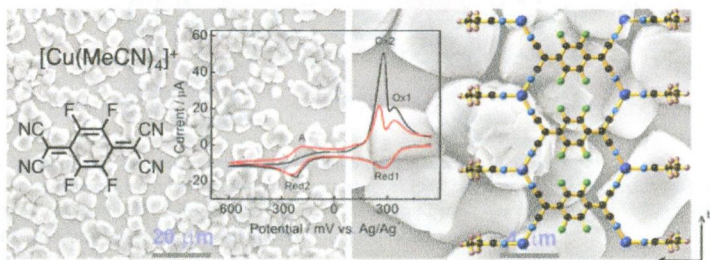




**Electrochemically Directed Synthesis of  $\text{Cu}_2(\text{TCNQF}_4^{II-})(\text{MeCN})_2$  ( $\text{TCNQF}_4 = 2,3,5,6\text{-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane}$ ): Voltammetry, Simulations, Bulk Electrolysis, Spectroscopy, Photoactivity, and X-ray Crystal Structure of the  $\text{Cu}_2(\text{TCNQF}_4^{II-})(\text{EtCN})_2$  Analogue**

Thanh H. Le, Ayman Nafady, Nguyen T. Vo, Robert W. Elliott, Timothy A. Hudson, Richard Robson, Brendan F. Abrahams, Lisandra L. Martin,\* and Alan M. Bond\*

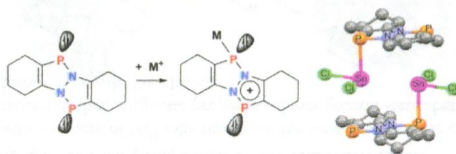
The new compound  $\text{Cu}_2(\text{TCNQF}_4^{II-})(\text{MeCN})_2$  ( $\text{TCNQF}_4^{2-}$  = dianion of 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane) has been synthesized by electrochemically directed synthesis involving reduction of  $\text{TCNQF}_4$  to  $\text{TCNQF}_4^{2-}$  in  $[\text{Cu}(\text{MeCN})_4]^+(\text{MeCN})$ . Thermogravimetric and elemental analysis data confirm the presence of  $\text{CH}_3\text{CN}$ , and single-crystal X-ray diffraction of  $\text{Cu}_2(\text{TCNQF}_4)(\text{EtCN})_2$  shows that this compound is structurally related to  $\text{Cu}_2^I(\text{TCNQF}_4^{II-})(\text{MeCN})_2$ .



**$N,N'$ -Fused Bisphosphole: Heteroaromatic Molecule with Two-Coordinate and Formally Divalent Phosphorus. Synthesis, Electronic Structure, and Chemical Properties**

Alexander N. Kornev,\* Vyacheslav V. Sushev, Yulia S. Panova, Olga V. Lukoyanova, Sergey Yu. Ketkov, Evgenii V. Baranov, Georgy K. Fukin, Mikhail A. Lopatin, Yulia G. Budnikova, and Gleb A. Abakumov

$N,N'$ -Fused bisphosphole, being a novel type of organophosphorus ligand, reveals a high coordination activity compared to that of the usual azaphospholes. Heteroaromatic 10 $\pi$ -electron system provides two electrons for  $\text{P} \rightarrow \text{M}$  bond formation, whereas the phosphorus lone pairs are not involved in coordination.



## Additions and Corrections

**Correction to Proof by EPR Spectroscopy that the Unpaired Electron in an  $\text{Os}_2^{7+}$  Species Is in a  $\delta^*$  Metal-based Molecular Orbital**

F. Albert Cotton, Gina M. Chiarella, Naresh S. Dalal,\* Carlos A. Murillo,\* Zhenxing Wang, and Mark D. Young

**Correction to 3d Early Transition Metal Complexes Supported by a New Sterically Demanding Aryloxide Ligand**

Keith Searles, Ba L. Tran, Maren Pink, Chun-Hsing Chen, and Daniel J. Mindiola\*