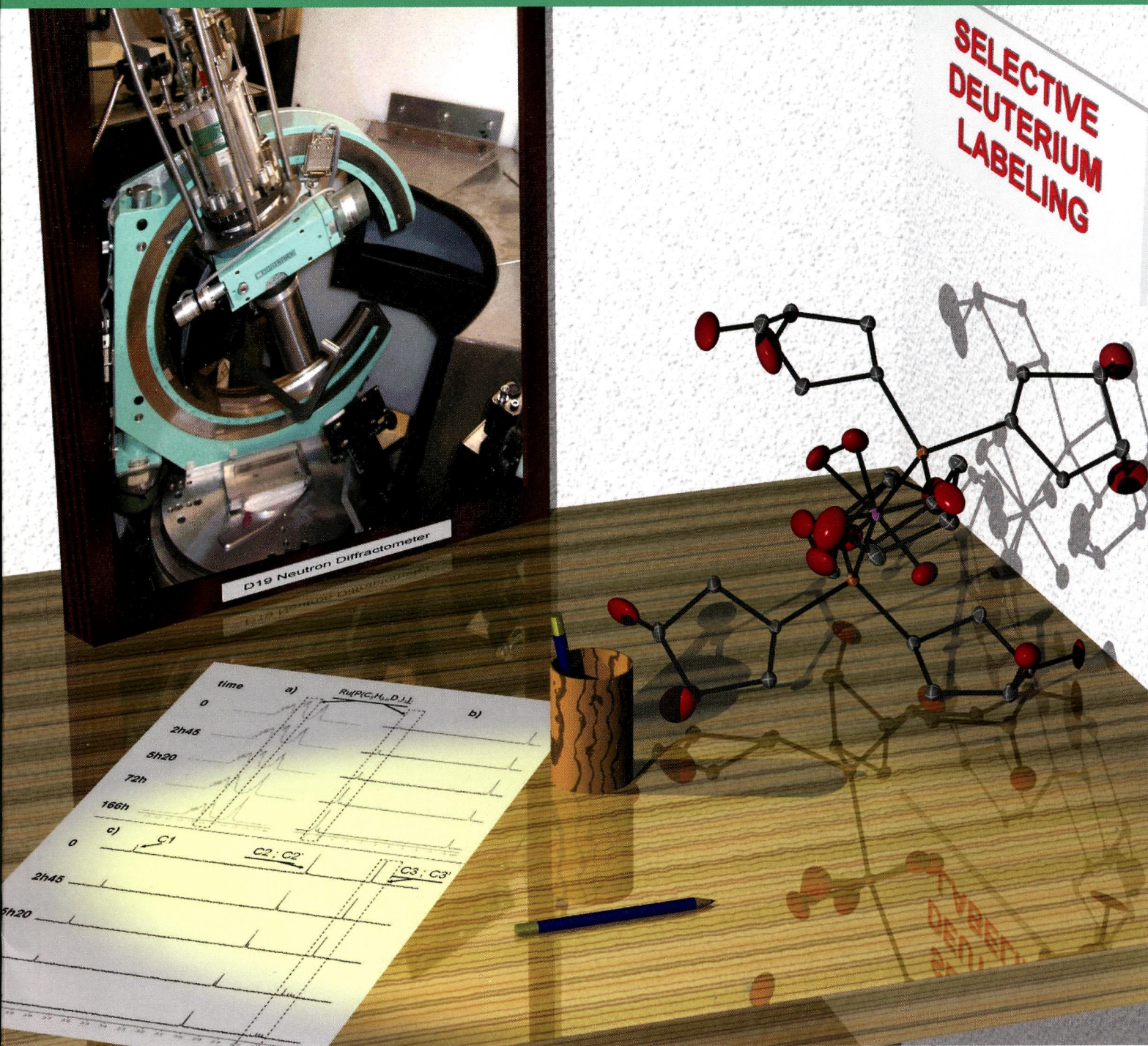


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ON THE COVER: Very selective high-deuterium contents can be achieved at room temperature in a non-classical polyhydride ruthenium phosphine complex. The selectivity of the H/D exchange process is demonstrated both in the solid state by neutron diffraction and in solution by multinuclear NMR data. See M. Grellier, S. A. Mason, A. Albinati, S. C. Capelli, S. Rizzato, C. Bijani, Y. Coppel, and S. Sabo-Etienne, p 7329.

Editorial

7307

dx.doi.org/10.1021/ic4013813
Editorial for the Virtual Issue on Models of Metalloenzymes

William B. Tolman

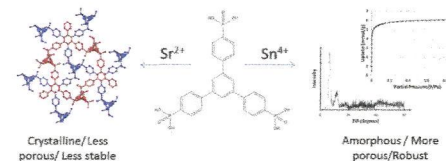
Communications

7311


dx.doi.org/10.1021/ic400274e
Enhancing Order and Porosity in a Highly Robust Tin(IV) Triphosphonate Framework

Roger K. Mah, Melanie W. Lui, and George K. H. Shimizu*

Using a doubly interpenetrated M^{2+} structure as a model, a robust and porous Sn^{4+} triphosphonate structure is obtained, albeit with low crystallinity. Powder X-ray diffraction and gas sorption are used to extract details of the open structure that, while not single crystalline, has a surface area $>500 \text{ m}^2/\text{g}$ and is water stable.

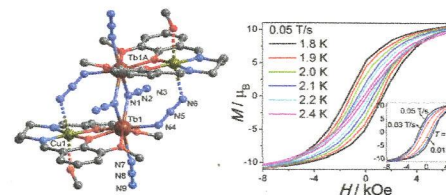


7314


dx.doi.org/10.1021/ic400986y
End-On Azido-Bridged 3d–4f Complexes Showing Single-Molecule-Magnet Property

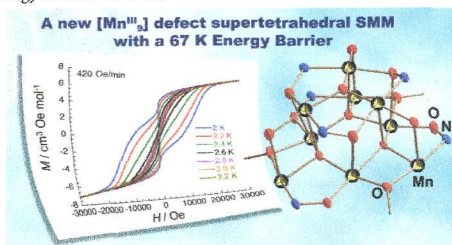
Xing-Cai Huang, Chun Zhou, Hai-Yan Wei,* and Xin-Yi Wang*

Tetranuclear $[MLn]_2$ clusters ($M^{2+} = \text{Cu, Zn}; Ln^{3+} = \text{Gd, Tb}$) with the Ln^{3+} centers bridged solely by double end-on azide bridges were successfully synthesized and magnetically characterized. The $[\text{CuTb}]_2$ compound is confirmed to be a single-molecule magnet (SMM). The temperature to observe the hysteresis loop is the highest among all of the reported Cu–Ln-based SMMs.

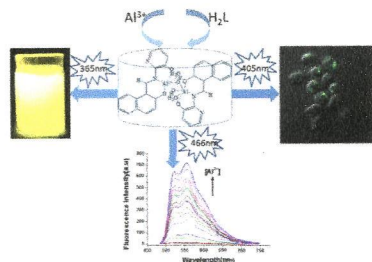


A Defect Supertetrahedron Naphthoxime-Based [Mn^{III}₉] Single-Molecule Magnet

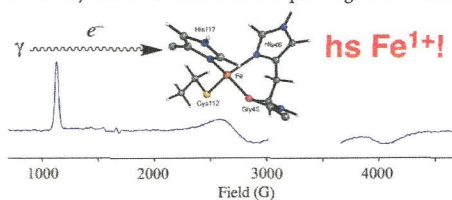
Małgorzata Holyńska,* Nicolas Frank, Céline Pichon, le-Rang Jeon, Rodolphe Clérac,* and Stefanie Dehnen

A new [Mn^{III}₉] complex with naphthoxime-based ligand was structurally and magnetically characterized, revealing promising SMM properties with a large energy barrier of 67 K.**A Highly Selective Fluorescent Chemosensor for Al^{III} Ion and Fluorescent Species Formed in the Solution**

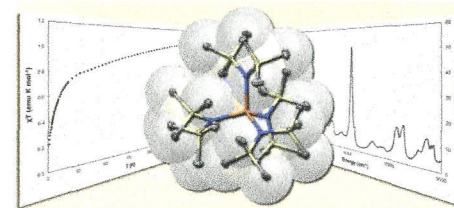
Wei-Hua Ding, Wei, Cao, Xiang-Jun Zheng,* De-Cai Fang,* Wing-Tak Wong, and Lin-Pei Jin

A chemosensor for the Al³⁺ ion, 1-[(3-hydroxypyridin-2-ylamino)methylene]naphthalen-2(1H)-one (H₂L), based on inhibited excited-state intramolecular proton transfer was synthesized. The experimental and theoretical calculations at B3LYP+PCM/6-31G(d) revealed that Al³⁺ and H₂L form a 1:1 complex, [AL(OH)(H₂O)]₂ in dimethyl sulfoxide that exhibits two remarkably enhanced fluorescent emissions at 523 and 553 nm. It is confirmed that H₂L could be used to detect Al³⁺ ions in cells by bioimaging.**Generation of High-Spin Iron(I) in a Protein Environment Using Cryoreduction**

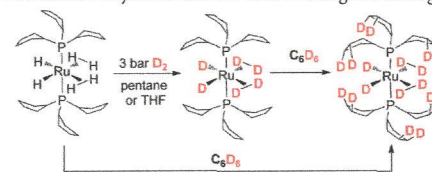
Roman M. Davydov, Matthew P. McLaughlin, Eckhard Bill, Brian M. Hoffman,* and Patrick L. Holland*

The Fe²⁺ complex of the azurin apoprotein can be reduced by γ rays at low temperature to give a pseudotetrahedral high-spin Fe^{I+} site in the metalloprotein, as shown by a combination of electron paramagnetic resonance and Mössbauer spectroscopies.**Tetrakis(bis(trimethylsilyl)amido)uranium(IV): Synthesis and Reactivity**

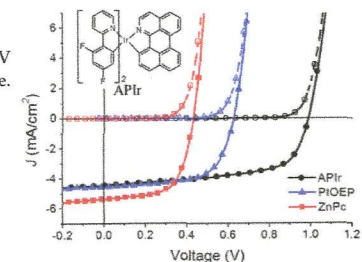
Andrew J. Lewis, Ursula J. Williams, Patrick J. Carroll, and Eric J. Schelter*

U[N(SiMe₃)₂]₄ (**1**), a compound previously believed to be unstable toward γ -deprotonation and cyclometalation, is shown to be isolable through a simple and direct synthetic route. Due to a high degree of steric saturation, **1** is more inert than expected, allowing for thorough characterization. The role of **1** in the oxidation chemistry of U[N(SiMe₃)₂]₃ is discussed.**Articles****Probing Highly Selective H/D Exchange Processes with a Ruthenium Complex through Neutron Diffraction and Multinuclear NMR Studies.**

Mary Grellier,* Sax A. Mason, Alberto Albinati,* Silvia C. Capelli, Silvia Rizzato, Christian Bijani, Yannick Coppel, and Sylviane Sabo-Etienne*

We show that very selective high-deuterium contents can be achieved for the polyhydride ruthenium phosphine complex [RuH₂(H₂)₂(PCyp₃)₂] (**1**) (PCyp₃ = P(C₅H₉)₃). The selectivity of the H/D exchange process is demonstrated by multinuclear NMR and neutron diffraction analyses. It has also been investigated through DFT calculations.**Exploring Cyclometalated Ir Complexes as Donor Materials for Organic Solar Cells**

Tyler B. Fleetham, Zixing Wang, and Jian Li*

We explored the use of iridium complexes as donor materials for organic photovoltaics. Planar heterojunctions of one cyclometalated iridium complex with C₆₀ had a power conversion efficiency as high as 2.8%. A high V_{OC} of 1 V was achieved and showed minimal temperature and light intensity dependence. This high V_{OC} at typical 1 sun operating conditions was achieved despite approximated exciton energy of only 1.55 eV.

7344

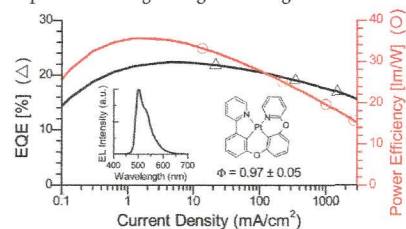
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dx.doi.org/10.1021/ic302490c

Cyclometalated Platinum Complexes with Luminescent Quantum Yields Approaching 100%

Eric Turner, Nathan Bakken, and Jian Li*

A series of highly efficient luminescent cyclometalated tetradentate platinum complexes was designed and synthesized. One such complex, PtOO3 achieved a quantum efficiency that approached 100% in thin film, as well as a nearly 100% electron-to-photon conversion efficiency when doped into an organic light emitting diode.



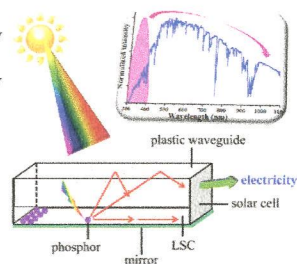
7352

dx.doi.org/10.1021/ic302561r

Near-Infrared Quantum Cutting Platform in Thermally Stable Phosphate Phosphors for Solar Cells

Tzu-Chen Liu, Gongguo Zhang, Xuebin Qiao, Jing Wang, Hyo Jin Seo, Din-Ping Tsai, and Ru-Shi Liu*

Under AM 1.5 G sunlight illumination on the front surface of a luminescent solar concentrator (LSC), quantum cutting phosphors can enhance the efficiency of LSC by cutting one high-energy photon to two lower-energy near infrared (NIR) photons, which match better with the band gap of crystalline silicon (c-Si) wafer and the energy of sunlight is thereby transformed to electricity.



7358

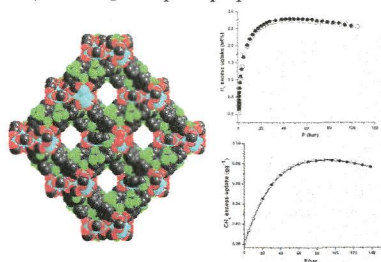
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dx.doi.org/10.1021/ic302645r

Gas Storage in a Partially Fluorinated Highly Stable Three-Dimensional Porous Metal–Organic Framework

Atanu Santra, Irena Senkowska, Stefan Kaskel,* and Parimal K. Bharadwaj*

A new partially fluorinated porous three-dimensional (3D) metal–organic framework has been synthesized by using linear rigid linker 2,2'-bis-trifluoromethyl-biphenyl-4,4'-dicarboxylic acid ($H_2bfbpdc$) in the presence of the colinker 4,4'-bipyridine (bpy) and $Zn(NO_3)_2 \cdot 6H_2O$ under solvothermal conditions. It possesses high thermal stability and exhibits permanent porosity with moderate surface area. N_2 , H_2 , CH_4 , and CO_2 adsorption properties of the framework are studied.



8A

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7367

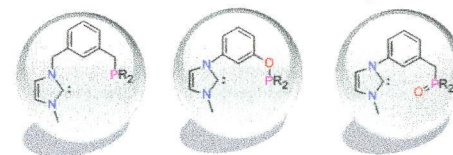
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dx.doi.org/10.1021/ic302854t

Complexes with Hybrid Phosphorus-NHC Ligands: Pincer-Type Ir Hydrides, Dinuclear Ag and Ir and Tetranuclear Cu and Ag Complexes

Xianghao Liu and Pierre Braunstein*

Mononuclear pincer-type Ir complexes, dinuclear Ag and Ir and tetranuclear Cu and Ag complexes have been prepared from hybrid ligands which associate a NHC donor with a phosphine, phosphinite, or phosphine-oxide donor group, respectively, which emphasizes the structural diversity provided by such heterofunctional ligands.



Phosphorus-NHC Hybrid ligands

7380

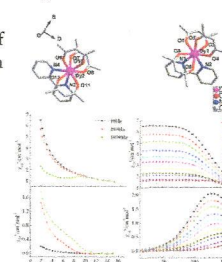
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dx.doi.org/10.1021/ic400006n

Syntheses, Structures, and Magnetic and Luminescence Properties of a New Dy^{III} -Based Single-Ion Magnet

Ya-Li Wang, Yue Ma,* Xi Yang, Jinkui Tang,* Peng Cheng, Qing-Lun Wang, Li-Cun Li, and Dai-Zheng Liao

The material $Dy(hfac)_3 \cdot 2H_2O$ has been confirmed to show practically no SMM behavior. Through a small change of the coordination sphere by adopting a nitrogen-containing ligand of 2,2'-bipyridine to the $Ln(hfac)_3 \cdot 2H_2O$ system, we obtain a new SIM of $[Dy(hfac)_3(bpy)]$ with an anisotropic barrier of 38.48 K.



7387

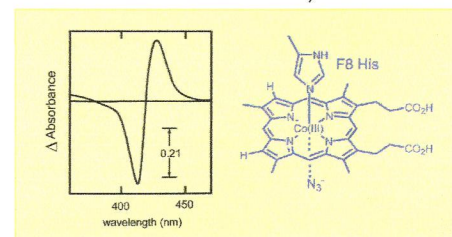
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dx.doi.org/10.1021/ic400078w

Relaxation Analysis of Ligand Binding to the Myoglobin Reconstituted with Cobaltic Heme

Saburo Neya,* Masaaki Suzuki, Tyuji Hoshino, and Akira T. Kawaguchi

Myoglobin reconstituted with Co(III) deuteroheme was found to exhibit relatively large affinities to CN^- , N_3^- , SCN^- , pyridine, and imidazole. The ligand-induced changes in electronic spectra, however, were less obvious owing to the absence of accompanied spin-state transition. The relaxation kinetic analysis revealed that the relatively large equilibrium ligand affinities arose from the compensation between small association rates and fairly smaller dissociation rates.



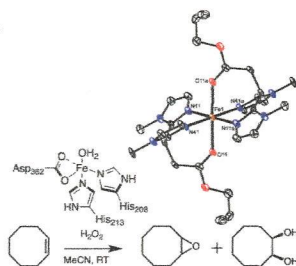
9A

Inorganic Chemistry, Volume 52, Issue 13

Bioinspired Nonheme Iron Complexes Derived from an Extended Series of N,N,O-Ligated BAIP Ligands

Marcel A. H. Moelands, Sjoerd Nijse, Emma Folkertsma, Bas de Bruin, Martin Lutz, Anthony L. Spek, and Robertus J. M. Klein Gebbink*

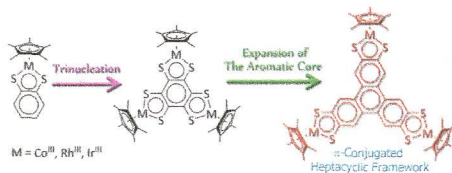
A series of mononuclear Fe(II) triflate complexes based on the 3,3-bis(1-alkylimidazole-2-yl)propionate ester (BAIP) ligand scaffold are reported. Variation of the steric and electronic properties of the BAIP ligand, a mimic of the 2-His-1-carboxylate facial triad found in mononuclear-nonheme iron enzymes, provided insight into its coordination flexibility and structural demands as a facial ligand. The Fe(II) complexes were investigated as catalysts in the epoxidation/dihydroxylation of olefins.



π -Conjugated Trinuclear Group-9 Metalladithiolenes with a Triphenylene Backbone

Ryota Sakamoto,* Tetsuya Kambe, Satoru Tsukada, Kenji Takada, Ken Hoshiko, Yasutaka Kitagawa, Mitsutaka Okumura, and Hiroshi Nishihara*

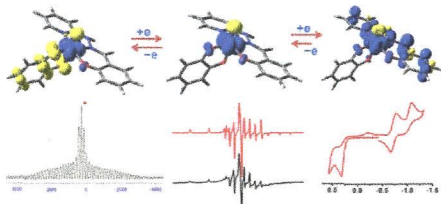
We report π -conjugated trinuclear metalladithiolenes complexes with a triphenylene backbone and group-9 metals. Their planar heptacyclic structure is determined using single crystal X-ray diffraction analysis. The trinucleation affords red-shifted ligand-to-metal charge transfer bands. Electrochemical measurements and UV-vis-NIR spectroscopy disclose the existence of electronic communication among the three metal nuclei in the reduced mixed-valent states. These observations prove that the triphenylene backbone transmits π -conjugation among the three metalladithiolenes units.



Oxidovanadium Catechol Complexes: Radical versus Non-Radical States and Redox Series

Suman Kundu, Suwendu Maity, Thomas Weyhermüller, and Prasanta Ghosh*

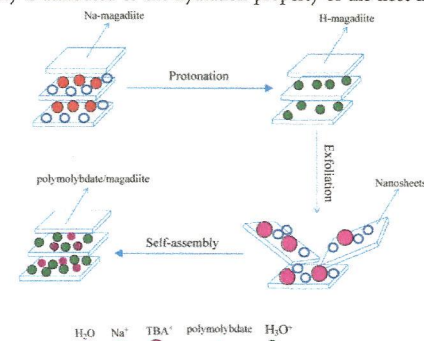
The molecular and electronic structures of the oxidovanadium complexes, $[(L^R)(VO)(L^{R'})]$ ($R = H, -CMe_3$; $R' = H, -CMe_3$) incorporating tridentate $L_1^R H$ ligands ($L_1^R H = 2,4$ -di-*R*-6- $\{(2$ -pyridin-2-yl)hydrazono)methyl)phenol) and substituted catechols ($L^{R'} H_2$) explaining the downfield NMR shifts of the ^{51}V nuclei are disclosed.



Synthesis and Visible-Light Photochromism of a New Composite Based on Polymolybdate Enclosed in Magadiite

Yufeng Chen,* Gensheng Yu, Fei Li, and Michael Severance

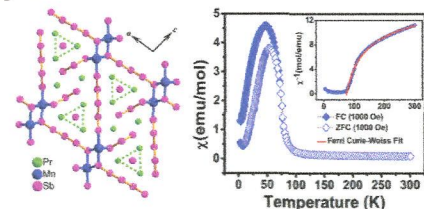
A new composite based on polymolybdate incorporated in layered magadiite has been synthesized by exfoliation/self-assembly process. Upon the irradiation of visible light (420–630 nm), the composite changes color from yellow to dark blue; moreover, the color can be bleached upon exposure to 15% H_2O_2 solution. The coloration–decoloration can be repeated many times, and the photochromic reversibility is attributed to the hydration property of the host magadiite.



A Ferrimagnetic Zintl Phase Pr_4MnSb_9 : Synthesis, Structure, and Physical Properties

Xiong Chen, Jin-Ni Shen, Li-Ming Wu, and Ling Chen*

A new valence precise Zintl phase, Pr_4MnSb_9 , featuring its own structure type of the anionic covalent 3D network constructed by Sb_3^{7-} and Sb_3^{5-} ribbons jointed by Mn^{3+} nodes, has been discovered. The Pr^{3+} and Mn^{3+} interact ferrimagnetically and show isothermal hysteresis loops at low temperature. The semimetal feature has been revealed by the electrical conductivity, Seebeck coefficient, and the spin-polarized LMTO calculations.

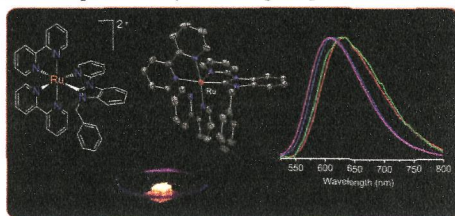


7448  [dx.doi.org/10.1021/ic400263r](https://doi.org/10.1021/ic400263r)

Electrochemiluminescent Ruthenium(II) *N*-Heterocyclic Carbene Complexes: a Combined Experimental and Theoretical Study

Gregory J. Barbante, Paul S. Francis, Conor F. Hogan,* Peyman R. Kheradmand, David J. D. Wilson, and Peter J. Barnard*

A series of four Ru(II) complexes of pyridine-functionalized imidazolylidene- or benzimidazolylidene-based *N*-heterocyclic carbene (NHC) ligands and 2,2'-bipyridine have been synthesized. The complexes display photoluminescence within the range 611–629 nm, with the emission wavelength of the benzimidazolylidene containing structures blue-shifted relative to the imidazolylidene containing complexes. All complexes exhibited a reversible, one-electron oxidation and electrochemiluminescence (ECL) with the obtained ECL spectra closely resembling the photoluminescence spectra.

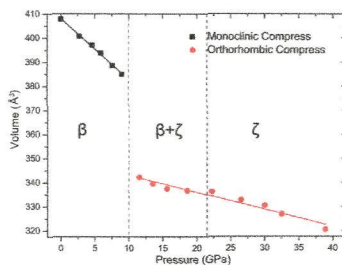


7460  [dx.doi.org/10.1021/ic400268p](https://doi.org/10.1021/ic400268p)

Observation of the Sixth Polymorph of BiB₃O₆: In Situ High-Pressure Raman Spectroscopy and Synchrotron X-ray Diffraction Studies on the β -Polymorph

Rihong Cong, Tao Yang,* Junliang Sun, Yingxia Wang, and Jianhua Lin*

A pressure-induced phase transition from β -BiB₃O₆ to ζ -BiB₃O₆ has been identified by careful analyses of in situ high-pressure Raman spectroscopy and angle-dispersive synchrotron X-ray diffraction at room temperature.

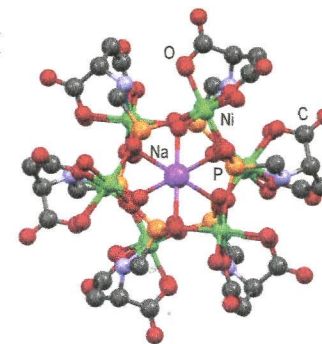


7477  [dx.doi.org/10.1021/ic400355u](https://doi.org/10.1021/ic400355u)

Sodium-Centered Dodecanuclear Co(II) and Ni(II) Complexes with 2-(Phosphonomethyl)aminosuccinic Acid: Studies of Spectroscopic, Structural, and Magnetic Properties

Andriy O. Gudima,* Ganna V. Shovkova, Olena K. Trunova, Fernande Grandjean, Gary J. Long,* and Nikolay Gerasimchuk*

A new 2-(phosphonomethyl)aminosuccinic acid, H₂O₃PCH₂NCH(CO₂H)-CH₂CO₂H (H₄PMAS), which represents an asymmetric, structural isomer of *N*-(phosphonomethyl)iminodiacetic acid, was obtained for the first time. Two new isostructural metal complexes of the new ligand that have NaM₁₂(PMAS)₆(H₂O)₁₇(OH) composition (M = Co(II), 1, or Ni(II), 2) have been synthesized and characterized by single crystal X-ray diffraction, IR, UV-visible spectroscopy, thermal analysis, and magnetic susceptibility measurements between 5 and 300 K.

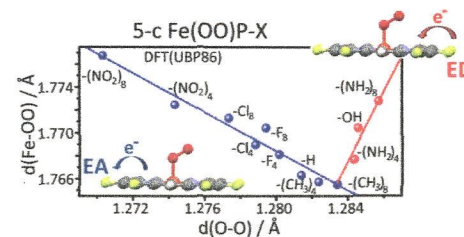


7478  [dx.doi.org/10.1021/ic400364x](https://doi.org/10.1021/ic400364x)

Electronic Structure and Ligand Vibrations in FeNO, CoNO, and FeOO Porphyrin Adducts

Alexandra V. Soldatova, Mohammed Ibrahim, and Thomas G. Spiro*

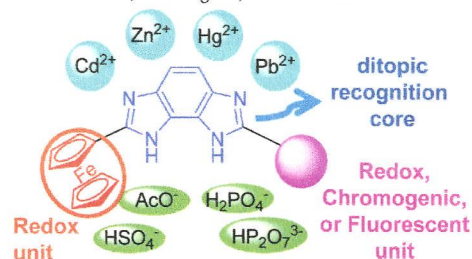
Resonance Raman data for 5-coordinate Co^{II}(NO) porphyrin adducts, and the results of DFT modeling for 5-coordinate Fe^{II}(NO), Co^{II}(NO), and Fe^{II}(OO) adducts, M^{II}(XO), are reported. Negative backbonding M-XO/X-O distance and frequency correlations are obtained for all the adducts, except for Fe^{II}(OO) models with electron-donating porphyrin substituents, for which the correlation becomes positive. This reversal is attributed to the dominance of superoxide-Fe(III) σ -bonding when electron-donating substituents raise the porphyrin-Fe orbital energies, making the backbonding π overlap ineffective.



Ferrocenylbenzobisimidazoles for Recognition of Anions and Cations

María Alfonso, Alberto Tárraga,* and Pedro Molina*

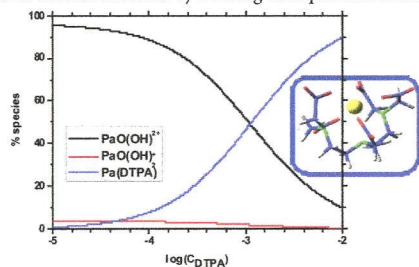
7-Substituted 2-ferrocenylbenzobisimidazoles behave as ditopic multichannel receptors for sensing anionic and cationic species through different electrooptical channels: redox, chromogenic, and fluorescent.



Thermodynamic Study of the Complexation of Protactinium(V) with Diethylenetriaminepentaacetic Acid

Mickaël Mendes, Sébastien Leguay, Claire Le Naour,* Séna Hamadi, Jérôme Roques, Philippe Moisy, Dominique Guillaumont, Sylvain Topin, Jean Aupiais, Christophe Den Auwer, and Christoph Hennig

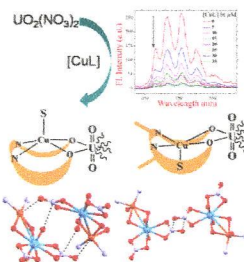
The complex formation of protactinium(V) with DTPA was studied at different temperatures (25–50°C) and ionic strengths (0.1–1 M). Only one complex was identified, most probably Pa(DTPA) as deduced from Density Functional Theory calculations. The formation constants were determined and extrapolated to zero ionic strength by SIT methodology. The standard thermodynamic data determined with these extrapolated constants revealed a stable complex formed energetically by an endothermic contribution which is counter balanced by a strong entropic contribution.



Use of Metalloligands [CuL] (H₂L = Salen Type Di-Schiff Bases) in the Formation of Heterobimetallic Copper(II)-Uranyl Complexes: Photophysical Investigations, Structural Variations, and Theoretical Calculations

Soumavo Ghosh, Saptarshi Biswas, Antonio Bauzá, Miquel Barceló-Oliver, Antonio Frontera,* and Ashutosh Ghosh*

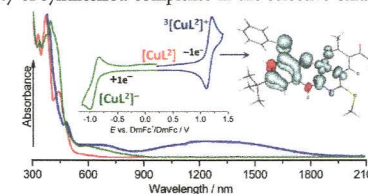
The steady state and time-resolved fluorescence quenching experiments of uranyl nitrate with the Cu(II)-chelate of salen type di-Schiff base ligands indicate the formation of 1:1 copper(II)-uranium(VI) complexes in solution. Crystal structures reveal that each complex contains diphenoxido bridged Cu(II)-U(VI) dinuclear core with two chelated nitrate coligands. The complexes are solvated in the axial position of the Cu(II) in different manner or desolvated. The significance of various solvation modes and the uncommon noncovalent interactions, for example, NO₃⁻...NO₃⁻ and U=O...NO₃⁻ interactions has been analyzed using theoretical calculations.



Marked Stabilization of Redox States and Enhanced Catalytic Activity in Galactose Oxidase Models Based on Transition Metal S-Methylisothiosemicarbazones with -SR Group in Ortho Position to the Phenolic Oxygen

Vladimir B. Arion,* Sonja Platzer, Peter Rapta,* Peter Machata, Martin Breza, Daniel Vegh, Lothar Dunsch, Joshua Telser, Sergiu Shova, Tatiana C. O. MacLeod, and Armando J. L. Pombeiro*

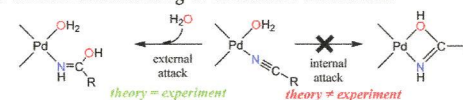
Reactions of *S*-*tert*-butyl-2-hydroxy-3-methylsulfanylbenzaldehyde *S*-methylisothiosemicarbazone and *S*-*tert*-butyl-2-hydroxy-3-phenylsulfanylbenzaldehyde *S*-methylisothiosemicarbazone with pentane-2,4-dione (Hacac) and triethyl orthoformate in the presence of M(acac)₂ as template source at 107 °C afforded metal complexes of the type M^{II}L¹ and M^{II}L², where M = Ni and Cu. The effect of -SR groups and metal ion identity on stabilization of phenoxyl radicals generated electrochemically was studied in detail. The catalytic activity of synthesized complexes in the selective oxidations of alcohols was also been studied.



Unraveling the Reaction Mechanism on Nitrile Hydration Catalyzed by [Pd(OH₂)₄]²⁺: Insights from Theory

Elkin Tílvez, María I. Menéndez, and Ramón López*

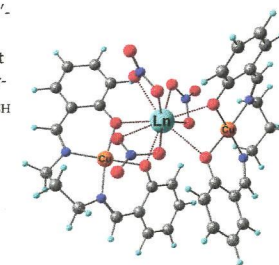
The inclusion of explicit water molecules in the density functional computations on the [Pd(OH₂)₄]²⁺-catalyzed nitrile hydration is crucial to provide a better understanding of its reaction mechanism.



Fascinating Role of the Number of *f* Electrons in Dipolar and Octupolar Contributions to Quadratic Hyperpolarizability of Trinuclear Lanthanides-Biscopper Schiff Base Complexes

Antonino Gulino,* Ignazio L. Fragalà, Fabio Lupo, Graziella Malandrino, Alessandro Motta, Alessia Colombo, Claudia Dragonetti,* Stefania Righetto, Dominique Roberto, Renato Ugo, Francesco Demartin, Isabelle Ledoux-Rak, and Anu Singh

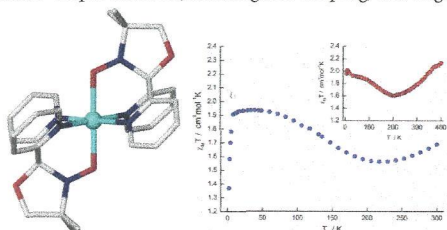
The trinuclear [Ln(NO₃)₃(CuL)₂] complexes (Ln = La, Ce, Sm, Eu, and Er, L = N,N'-1,3-propylen-bis(salicylideneiminato)) have been investigated by HLS and EFISH techniques to evaluate both the dipolar and octupolar contributions to their significant quadratic hyperpolarizability. The major contribution to the total quadratic hyperpolarizability is largely controlled by the octupolar contribution, but the values of both β_{EFISH} and ||β²||, the dipolar part, are significantly influenced by the number of *f* electrons.



7557 **S** dx.doi.org/10.1021/ic400565h
Observation of Ferromagnetic Exchange, Spin Crossover, Reductively Induced Oxidation, and Field-Induced Slow Magnetic Relaxation in Monomeric Cobalt Nitroxides

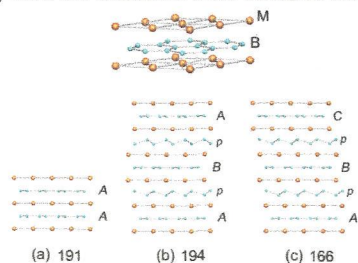
Ian A. Gass, Subrata Tewary, Ayman Nafady, Nicholas F. Chilton, Christopher J. Gartshore, Mousa Asadi, David W. Lupton, Boujemaa Moubaraki, Alan M. Bond, John F. Boas, Si-Xuan Guo, Gopalan Rajaraman, and Keith S. Murray*

The complex $[\text{Co}^{\text{II}}(\text{L}^{\bullet})_2](\text{NO}_3)_2$ (**1**), where L^{\bullet} = the radical 4-dimethyl-2,2-di(2-pyridyl) oxazolidine-N-oxide, has been investigated using temperature-dependent magnetic susceptibility, electron paramagnetic resonance (EPR) spectroscopy, electrochemistry, density functional theory (DFT) calculations, and variable-temperature X-ray structure analysis. The complex $[\text{Co}^{\text{III}}(\text{L}^-)_2](\text{BPh}_4)$ (**2**) is formed by a rare, reductively induced oxidation of the Co center in **1**. The multifunctional complex **1** shows a rare combination of spin crossover, ferromagnetic coupling, and single molecule magnetism.



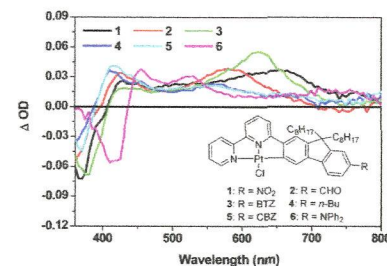
7573 dx.doi.org/10.1021/ic400587j
Effect of Defects in the Formation of AlB_2 -Type WB_2 and MoB_2
 Wataru Hayami,* Ai Momozawa, and Shigeki Otani

Tungsten diboride usually has a hexagonal structure with the space group $P6_3/mmc$ (number 194), and molybdenum diboride has a trigonal structure with $R\bar{3}m$ (number 166). Both diborides have another phase with an AlB_2 -type structure ($P6/mmm$, number 191). AlB_2 -type MoB_2 is easy to synthesize and has been extensively studied, whereas AlB_2 -type WB_2 is difficult to synthesize and has been reported only once. The influence of boron defects on their synthesizability has been investigated.

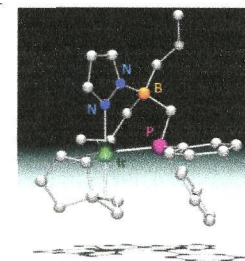


7578 **S** dx.doi.org/10.1021/ic400683u
Platinum Chloride Complexes Containing 6-[9,9-Di(2-ethylhexyl)-7-R-9H-fluoren-2-yl]-2,2'-bipyridine Ligand (R = NO_2 , CHO, Benzothiazol-2-yl, *n*-Bu, Carbazol-9-yl, NPh_2): Tunable Photophysics and Reverse Saturable Absorption
 Zhongjing Li, Ekaterina Badaeva, Angel Ugrinov, Svetlana Kilina, and Wenfang Sun*

Six platinum(II) chloride complexes (**1–6**) containing a 6-[9,9-di(2-ethylhexyl)-7-R-9H-fluoren-2-yl]-2,2'-bipyridine (R = NO_2 , CHO, benzothiazol-2-yl, *n*-Bu, carbazol-9-yl, NPh_2) ligand were synthesized and their photophysics were systematically investigated via spectroscopic methods and simulated by time-dependent density functional theory. Reverse saturable absorption of **1–6** was studied at 532 nm for nanosecond laser pulses. The electron-donating or -withdrawing substituents at the 7-position of the fluorenyl component influence the excited-state properties and reverse saturable absorption characteristics significantly.

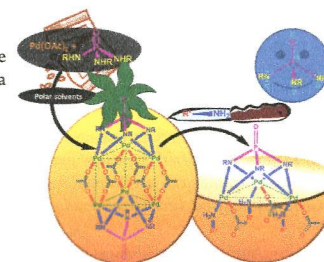


7593 **S** dx.doi.org/10.1021/ic400684s
Rhodium and Iridium Complexes with a New Scorpionate Phosphate Ligand
 Angel L. Serrano, Miguel A. Casado,* José A. López, and Cristina Tejel*
 A straightforward synthesis of a new hybrid scorpionate ligand $[(\text{allyl})_2\text{B}(\text{CH}_2\text{PPh}_2)(\text{Pz})^-]$ ($[\text{A}_2\text{BPN}]^-$) and some complexes of rhodium and iridium are reported.



7608 **S** dx.doi.org/10.1021/ic400686e
Facile Formation of Stable Tris(imido)phosphate Trianions as Their Tri- and Hexanuclear Pd(II) Complexes in Protic Solvents
 Arvind K. Gupta, S. Arun Dixith Reddy, and Ramamoorthy Boomishankar*

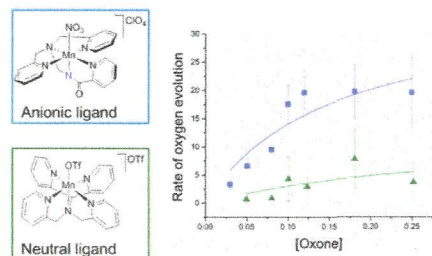
Using $\text{Pd}(\text{OAc})_2$, a simple deprotonation route to access the highly basic tris(alkylimido)phosphate trianions, $[(\text{RN})_3\text{PO}]^{3-}$, analogous to the orthophosphate (PO_4^{3-}) ion in polar and in protic solvents has been developed. These were isolated exclusively as their trinuclear and prismatic Pd(II) clusters of the formula $\{\text{Pd}_3[(\text{NR})_3\text{PO}](\text{OAc})_3\}_n$ ($n = 1$ or 2) in which the trianionic species acts as a robust chelating ligand for a triangular Pd_3 unit.



An Anionic N-Donor Ligand Promotes Manganese-Catalyzed Water Oxidation

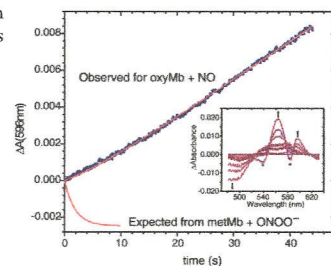
Karin J. Young, Michael K. Takase, and Gary W. Brudvig*

Incorporating an anionic carboxamido donor atom in the coordination sphere of a manganese complex promotes oxygen evolution using Oxone as a sacrificial oxidant. Manganese complexes with similar neutral pentadentate ligands are observed to form high-valent species that are less reactive toward oxygen evolution. The position of the carboxamide nitrogen *trans* to the catalyst open site is proposed to favor the formation of a high-valent manganese species that is reactive toward O–O bond formation.

**Does the Oxidation of Nitric Oxide by oxyMyoglobin Share an Intermediate with the metMyoglobin-Catalyzed Isomerization of Peroxynitrite?**

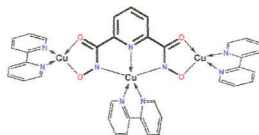
Karl J. Koebeke, Daniel J. Pauly, Leonid Lerner, Xien Liu, and A. Andrew Pacheco*

When oxy-myoglobin reacts with nitric oxide, the product distribution differs from that obtained during ferri-myoglobin-catalyzed isomerization of peroxynitrite. This suggests that the two reactions follow discrete pathways, contrary to a common assumption.

**Coordination Diversity in Mono- and Oligonuclear Copper(II) Complexes of Pyridine-2-Hydroxamic and Pyridine-2,6-Dihydroxamic Acids**

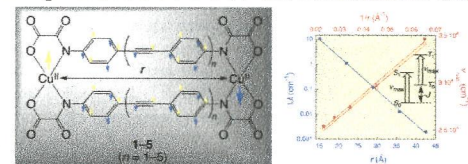
Elzbieta Gumienka-Kontecka,* Irina A. Golenya, Agnieszka Szebesczyk, Matti Haukka, Roland Krämer, and Igor O. Fritsky*

Solution and solid state studies on Cu(II) complexes of pyridine-2-hydroxamic acid (HPicHA) and pyridine-2,6-dihydroxamic acid (H₂PyDHA) were carried out in an effort to obtain structural evidence of mono- and oligonuclear complexes' formation.

**Dicopper(II) Metallacyclophanes with Oligo(*p*-phenylene-ethynylene) Spacers: Experimental Foundations and Theoretical Predictions on Potential Molecular Magnetic Wires**

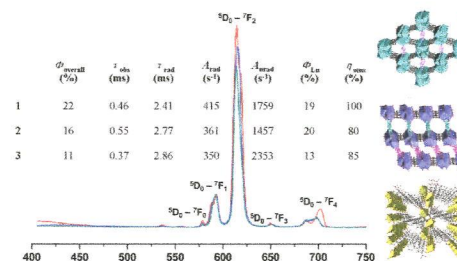
María Castellano, Francisco R. Fortea-Pérez, Abdeslem Bentama, Salah-Eddine Stiriba, Miguel Julve, Francesc Lloret,* Giovanni De Munno, Donatella Armentano,* Yangling Li, Rafael Ruiz-García, and Joan Cano*

On the road to “molecular magnetic wires”: based on a combined experimental and computational study on the optical and magnetic properties of a novel family of oxamato-based dinuclear copper(II) metallacyclophanes, we evaluate the ability of extended π -conjugated oligo(*p*-phenylene-ethynylene) spacers to act as effective molecular wires for the propagation of the exchange interaction between the unpaired electrons of two Cu^{II} ions with intermetallic distances in the range of 1.5–4.3 nm.

**Photophysical Studies of Europium Coordination Polymers Based on a Tetracarboxylate Ligand**

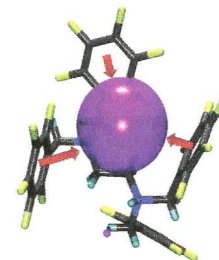
Yan-Li Gai, Fei-Long Jiang, Lian Chen, Yang Bu, Kong-Zhao Su, Shaeel A. Al-Thabaiti, and Mao-Chun Hong*

Three novel europium metal–organic coordination polymers, formulated as $\{[\text{Eu}(\text{ptptc})_{0.75}(\text{H}_2\text{O})_2] \cdot 0.5\text{DMF} \cdot 1.5\text{H}_2\text{O}\}_n$ (1), $\{[\text{Me}_2\text{H}_2\text{N}]_2[\text{Eu}_2(\text{ptptc})_2(\text{H}_2\text{O})(\text{DMF})] \cdot 1.5\text{DMF} \cdot 7\text{H}_2\text{O}\}_n$ (2), and $\{[\text{Eu}(\text{Hptptc})(\text{H}_2\text{O})_4] \cdot 0.5\text{DMF} \cdot \text{H}_2\text{O}\}_n$ (3), have been successfully synthesized with structurally characterized and optically studied. The energy level of the triplet state of the ligand determined from the phosphorescence at 77 K of the Gd(III) complex is higher than the emitting level of the Eu(III) ion, demonstrating the potential of H₄ptptc as an efficient UV-light sensitizer for europium-based red emission. The luminescence properties of these complexes are further studied in terms of their emission quantum yields, emission lifetimes, and the radiative/nonradiative rates.

**Di-, Tri-, and Tetra(pentafluorophenyl) Derivatives for Oligotopic Anion– π Interactions**

Michael Giese, Markus Albrecht,* Simon Steike, Anton Ackermann, Arto Valkonen, and Kari Rissanen

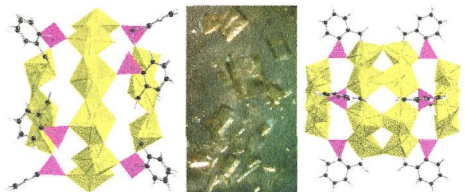
Oligo pentafluorophenyl ammonium salts show anion– π interactions in the solid state. In optimized systems, multiple such weak interactions are observed.



Hybrid Uranyl-Carboxyphosphonate Cage Clusters

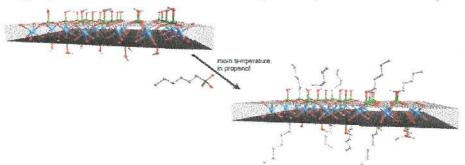
Pius O. Adelani, Michael Oga, Christine M. Wallace, Jie Qiu, Jennifer E. S. Szymanski, Ginger E. Sigmon, and Peter C. Burns*

Two new hybrid uranyl-carboxyphosphonate cage clusters built from uranyl peroxide units were crystallized from aqueous solution under ambient conditions in approximately 2 months. Cluster **A** crystallizes over a wide pH range of 4.6–6.8, while cluster **B** was isolated under the narrower pH range of 6.9–7.8. Studies of their fate in aqueous solution upon dissolution of crystals by ESI-MS and SAXS provide evidence for their persistence in solution.

**Looking for New Hybrid Polymer Fillers: Synthesis of Nanosized α -Type Zr(IV) Organophosphonates through an Unconventional Topotactic Anion Exchange Reaction**

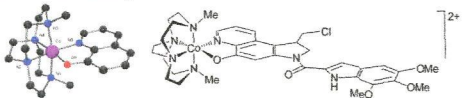
Monica Pica,* Anna Donnadio, Elisabetta Troni, Donatella Capitani, and Mario Casciola

Up to now, α -zirconium phosphate (α -ZrP) was believed not able to give topotactic exchange reactions in mild conditions. The present paper reports, for the first time, an easy route to prepare α -zirconium phosphonates by exchanging phosphate with phosphonate groups in α -ZrP nanoparticles. The random distribution of the phosphonate groups on the layers could promote the solid exfoliation by a polymer because of accessible pathways in the interlayer region.

**Cross-Bridged Cyclen or Cyclam Co(III) Complexes Containing Cytotoxic Ligands as Hypoxia-Activated Prodrugs**

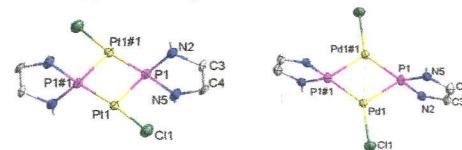
John Yu-Chih Chang, Guo-Liang Lu, Ralph J. Stevenson, Penelope J. Brothers, George R. Clark, K. Jane Botting, Dianne M. Ferry, Moana Tercel, William R. Wilson, William A. Denny,* and David C. Ware*

Cobalt(III) complexes of the potent DNA minor groove alkylator *seco*-CPyI-TMI, with ethylene cross-bridged cyclen or cyclen auxiliary ligands, were prepared, and the structures of the simple 8-quinolinato analogues of these were characterized by X-ray crystallography. The *seco*-CPyI-TMI Co(III) complexes functioned as bioreductive prodrugs, being 80–200-fold more potent toward human tumor cell lines in culture under hypoxic conditions than under 20% oxygen, but a representative complex did not show activity in a mouse xenograft model.

**Donor-Free Phosphenium–Metal(0)–Halides with Unsymmetrically Bridging Phosphenium Ligands**

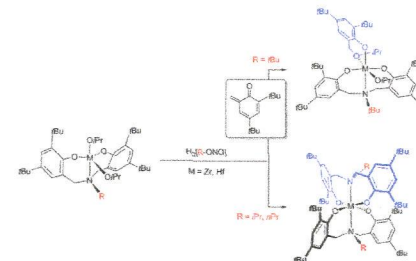
Daniela Förster, Jan Nickolaus, Martin Nieger, Zoltán Benkő, Andreas W. Ehlers, and Dietrich Gudat*

Dinuclear complexes [(NHP)MCl]₂ (NHP = *N*-heterocyclic phosphenium, M = Pd, Pt) were prepared by different routes. Computational and spectroscopic studies suggest description of these species as metal(0)–halides with bridging phosphenium ligands that show an unequal distribution of σ -donor/ π -acceptor contributions in the two M–P bonds. The complexes provide a viable source of ligand-stabilized metal(0)–halide fragments.

**Zirconium and Hafnium Complexes Containing *N*-Alkyl-Substituted Amine Biphenolate Ligands: Unexpected Ligand Degradation and Divergent Complex Constitutions Governed by *N*-Alkyls**

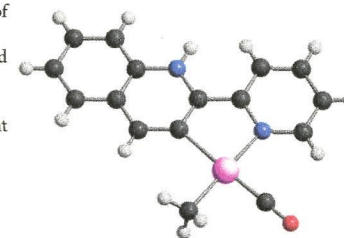
Lan-Chang Liang,* Chia-Cheng Chien, Ming-Tsz Chen, and Sheng-Ta Lin

Depending on the identity of the *N*-alkyls, the *ONO* ligands may thermally degrade to unexpectedly produce an *ortho*-quinone methide derivative that is susceptible to reactions with metal alkoxides to afford complexes containing a novel etheral phenolate ligand.

**Rollover Cyclometalation with 2-(2'-Pyridyl)quinoline**

Antonio Zucca,* Diletta Cordeschi, Luca Maidich, Maria Itria Pilo, Elisabetta Masolo, Sergio Stoccoro, Maria Agostina Cinellu, and Simona Galli

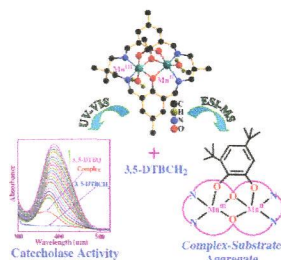
Rollover cyclometalation of 2-(2'-pyridyl)quinoline, **L**, allowed the synthesis of the family of complexes [Pt(L-H)(X)(L')] and [Pt(L*)(X)(L')][BF₄] (X = Me, Cl; L' = neutral ligand), the first rollover complexes derived from the ligand **L**. The ligand **L*** is a cyclometalated, *N*-protonated isomer of **L**. The new species were investigated through NMR and UV–vis spectroscopy, cyclic voltammetry, X-ray powder diffraction, and DFT methods, correlating different chemico-physical properties to the nature of the cyclometalated and neutral ligands.



Structures, Magnetochemistry, Spectroscopy, Theoretical Study, and Catechol Oxidase Activity of Dinuclear and Dimer-of-Dinuclear Mixed-Valence $Mn^{III}Mn^{II}$ Complexes Derived from a Macrocyclic Ligand

Arpita Jana, Núria Aliaga-Alcalde, Eliseo Ruiz,* and Sasankasekhar Mohanta*

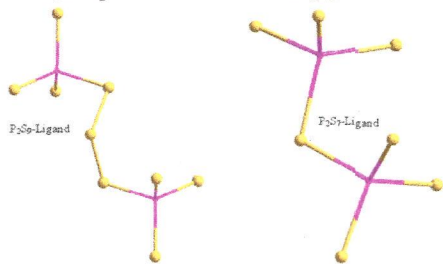
Syntheses, structures, catecholase activity, experimental and density functional theoretical magnetic properties, and ESI-MS (positive) spectra of two mixed-valence dinuclear $Mn^{III}Mn^{II}$ complexes and one tetranuclear $Mn^{III}Mn^{II}Mn^{II}Mn^{III}$ complex derived from a tetraaminodiphenolate macrocyclic ligand, obtained as [2 + 2] condensation product of 2,6-diformyl-4-methylphenol and 2,2-dimethyl-1,3-diaminopropane, have been described.



Synthesis, Structure, and Spectroscopy of Two Ternary Uranium(IV) Thiophosphates: UP_2S_9 and UP_2S_7 Containing $P_2S_9^{2-}$ and $P_2S_7^{2-}$ Ligands

Jean-Marie Babo, Laurent Jouffret, Jian Lin, Eric M. Villa, and Thomas E. Albrecht-Schmitt*

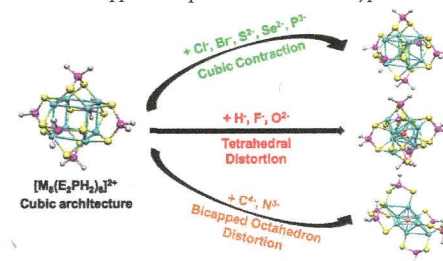
The two ternary uranium thiophosphate compounds, UP_2S_9 and UP_2S_7 were isolated from polychalcogenide flux reactions. The structures of the two compounds are formed from $[US_6]^{8-}$ chains connected to each other by either the tridentate-chelating $P_2S_9^{4-}$ in UP_2S_9 or the $P_2S_7^{4-}$ in UP_2S_7 , resulting in 3D frameworks. These two ligands have different geometries, but they exhibit similar coordination modes, comparable to the ethane-like $P_2S_6^{4-}$.



Shape Modulation of Octanuclear Cu(I) or Ag(I) Dichalcogeno Template Clusters with Respect to the Nature of their Encapsulated Anions: A Combined Theoretical and Experimental Investigation

Camille Latouche, Samia Kahlal, Eric Furet, Ping-Kuei Liao, Yan-Ru Lin, Ching-Shiang Fang, Jérôme Cuny, C. W. Liu,* and Jean-Yves Saillard*

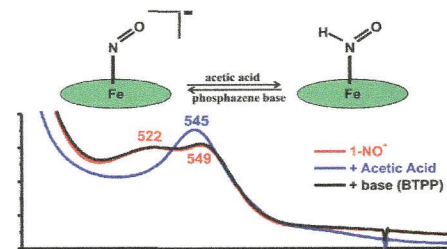
Calculations indicate that octanuclear Cu(I) and Ag(I) dichalcogeno cubic clusters of the type $[M_8(E_2PR_2)_6]^{2+}$ ($E = S, Se$) can encapsulate hydride and main-group anions, adapting their size and shape to the size and electronic demand of their host. Experimental X-ray structures of previously published clusters and of new characterized oxygen- and fluorine-containing species confirm the theoretical results and support the prediction for so far hypothetical compounds.



Electronic Structure and Biologically Relevant Reactivity of Low-Spin $\{FeNO\}^8$ Porphyrin Model Complexes: New Insight from a Bis-Picket Fence Porphyrin

Lauren E. Goodrich, Saikat Roy, E. Ercan Alp, Jiyong Zhao, Michael Y. Hu, and Nicolai Lehnert*

The bis-picket fence porphyrin complex $[Fe(3,5-Me-BAFP)(NO)]$ is utilized for the preparation of new ferrous heme-nitroxyl, $\{FeN(H)O\}^8$, complexes. The bulky pickets of this porphyrin stabilize the bound nitroxyl ligand and allow for the preparation of an HNO complex. In addition, new insight into the biologically relevant reactivity of $\{FeN(H)O\}^8$ complexes with NO is obtained.



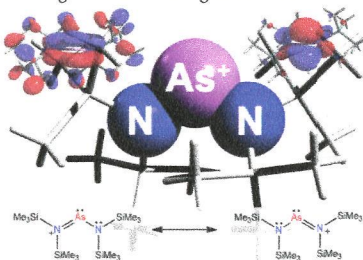
7781 5

dx.doi.org/10.1021/ic4010104

Structure and Bonding of Novel Acyclic Bisaminoarsenium Cations

Christian Hering, Julia Rothe, Axel Schulz,* and Alexander Villinger

The synthesis and structural characterization of salts bearing a labile bisaminoarsenium cation of the type $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{As}^+[\text{GaCl}_4]^-$ is presented. Furthermore, the reactivity is compared with the analogous antimony systems, along with computational studies that shed light on the bonding in these elusive cations.



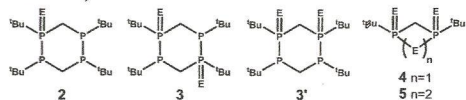
7791 5

dx.doi.org/10.1021/ic401002b

Chalcogenation of the 1,4-C₂P₄ Ring: Oxidation, Isomerization, Insertion, and Ring Contraction

Philip J. W. Elder and Tristram Chivers*

Oxidation of the six-membered ring 1,4-(CH₂)₂(P^tBu)₄ with controlled amounts of sulfur or selenium in toluene produces monochalcogenides **2** initially and then the 2,5-dichalcogenated isomer **3**, which undergoes thermal isomerization to the 2,6-isomer **3'**. At elevated temperatures with an excess of chalcogen with an excess of chalcogen the four- and five-membered rings **4** and **5**, respectively, are the major products (E = S or Se for 2–5).



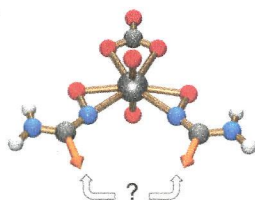
7805 5

dx.doi.org/10.1021/ic401089u

De Novo Structure-Based Design of Bis-amidoxime Uranophiles

Sinisa Vukovic and Benjamin P. Hay*

This paper demonstrates the use of de novo structure-based design methods in coordination chemistry by describing how they were used to identify chelate architectures for bis-amidoximes that are structurally organized for binding the uranyl cation.



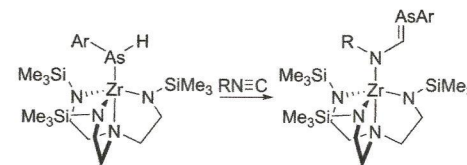
7811 5

dx.doi.org/10.1021/ic4012058

Zirconium-Mediated Synthesis of Arsaalkene Compounds from Arsines and Isocyanides

Annalese F. Maddox, Jillian J. Davidson, Tamila Shalumova, Joseph M. Tanski, and Rory Waterman*

Triamidoamine-supported zirconium complexes featuring primary arsenido ligands react with isocyanides to afford arsaalkene-containing products. This atom-economical synthesis appears to proceed via initial 1,1-insertion of the isocyanide prior to rearrangement.

**Additions and Corrections**

7817

dx.doi.org/10.1021/ic401267u

Correction to An Unprecedented Fe₃₆ Phosphonate Cage

Christine M. Beavers, Andrey V. Prosvirin, John D. Cashion, Kim R. Dunbar,* and Anne F. Richards*