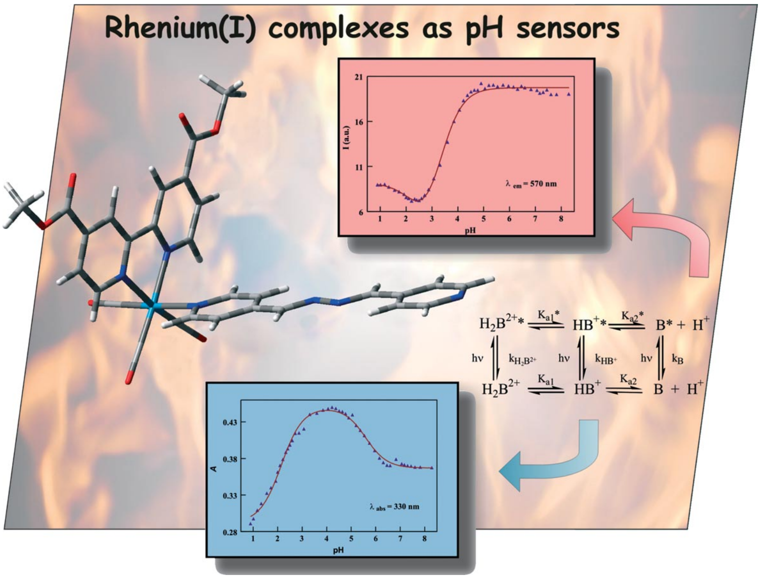
COVER PICTURE

The cover picture shows that consecutive protonation of the pyridine N and imine N atoms of 4-pyridinealdazine (PCA) in the complex [Re(4,4′-CO_2Me-bpy)$(CO)_3$(PCA)]$^+$ (bpy = 2,2′-bipiridine) lead to bell-shaped curves for both the absorbance and the emission intensity vs. pH; the latter property can be employed to devise novel luminescent pH sensors of the *on-off-on* type. Details are discussed in the article by N. E. Katz et al. on p. 5323ff.



CONTENTS

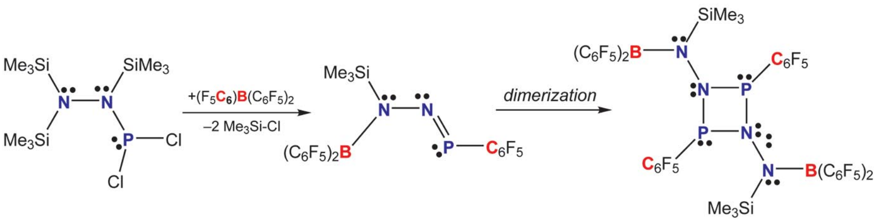
SHORT COMMUNICATION

B–C Bond Activation

M. Kowalewski, B. Krumm, P. Mayer, A. Schulz,* A. Villinger 5319–5322

Transition-Metal-Free Boron–Carbon Bond Activation: Insertion of an NNP Fragment into a Boron–Carbon Bond

Keywords: Azaphosphole / Diazadiphosphetidine / Insertion / Lewis acids / Boranes / X-ray elucidation



A formal NNP fragment insertion into a B–C bond was achieved by the reaction of $(Me_3Si)_2N-N(SiMe_3)-PCl_2$ with $B(C_6F_5)_3$. A novel diazadiphosphetidine with a phosphorus(III) atom attached to a pentafluorophenyl group was isolated and fully characterized.

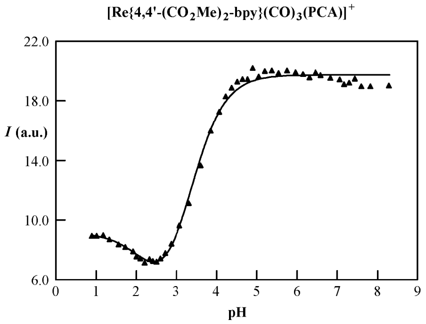
FULL PAPERS

Donor–Acceptor Systems

M. Cattaneo, F. Fagalde, N. E. Katz,* C. D. Borsarelli, T. Parella 5323–5332

pH-Induced Luminescence Changes of Chromophore-Quencher Tricarbonylpolypyridylrhenium(I) Complexes with 4-Pyridinealdazine

Keywords: Donor-acceptor systems / Rhenium / Photochemistry / Molecular devices / Mixed-valent compounds



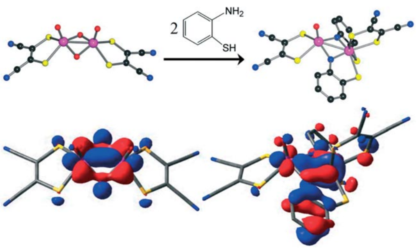
New emissive mono- and dinuclear chromophore-quencher tricarbonylpolypyridylrhenium(I) complexes containing 4-pyridinealdazine (PCA) are prepared and characterized by spectroscopic, electrochemical, and photophysical techniques. Consecutive protonation of the pyridinyl nitrogen atom and the imine nitrogen atom of PCA leads to bell-shaped curves for both the absorbance and emission intensities vs. pH for some of these complexes; this latter property can be employed to devise novel luminescent pH sensors of the on-off-on type.

Asymmetric Dimolybdenum Complex

K. Pal, S. Sarkar* 5333–5344

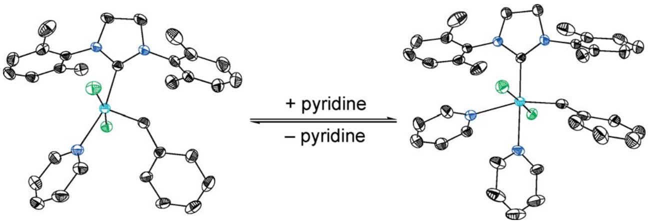
Synthesis, Structure and a DFT/TDDFT Study of a Diimido-Bridged Asymmetric Dimolybdenum Complex

Keywords: Mixed-valence compounds / Molybdenum / Cyclic voltammetry / Electronic structure / Density functional calculations



The two Mo centers in an asymmetric dimeric mixed-valence molybdenum complex containing oxidomolybdenum and desoxomolybdenum entities have formal oxidation states that result from a combination of Mo^{VI} and Mo^{IV}, as confirmed by IR, EPR, and CV investigations and the results of DFT-TDDFT calculations.

Metathesis Catalysts



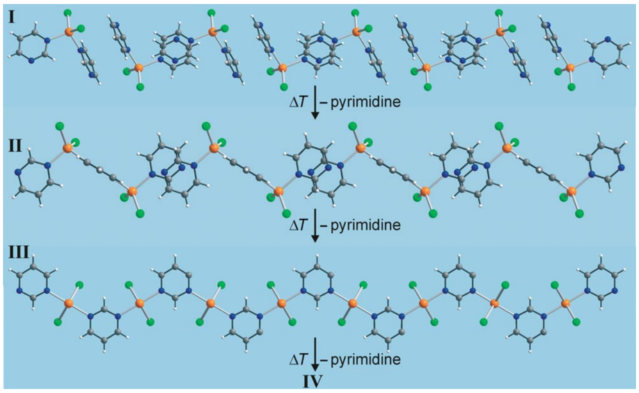
Benzylideneruthenium complexes bearing one or two pyridine-based ligands are synthesized and the influence of these ligands on the formation and interconversion of these complexes is discussed based on X-ray crystallographic and mass spectrometric evidence. Color code: black = C, blue = N, green = Cl, cyan = Ru.

**W.-Z. Zhang, R. He,*
R. Zhang** .... **5345−5352**

Benzylideneruthenium Complexes Bearing Pyridine-Based Ligands and Their Influence on the Formation of Mono- or Bis(pyridine) Complexes

Keywords: Metathesis / Ruthenium / N ligands / Ligand effects / Homogeneous catalysis

ZnBr$_2$(pyrimidine) Compounds



Four new ZnBr$_2$(pyrimidine) coordination polymers were prepared, either in solution or by thermal decomposition reactions, and the thermal reactivity and thermodynamic stability of these compounds were investigated.

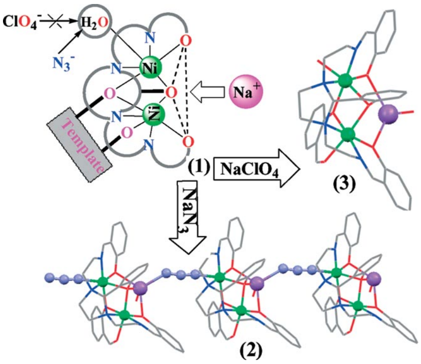
C. Näther,* G. Bhosekar, I. Jeß ....
.... **5353−5359**

Synthesis, Crystal Structures and Thermal Properties of New ZnBr$_2$(pyrimidine) Coordination Compounds

Keywords: Coordination compounds / Synthesis / Crystal structure / Thermal reactivity

Mixed-Metal Aggregates

The reaction between the Ni$_2$ assembly on a formylphenolate template with a coordinated terminal water molecule and a capping imidazolidine ligand and N$_3^-$ or ClO$_4^-$ anions leads to two different types of products. The metallacrown-type coordination of the Na$^+$ cations results in new NaNi$_2$ complexes engaged in ferromagnetic interactions.



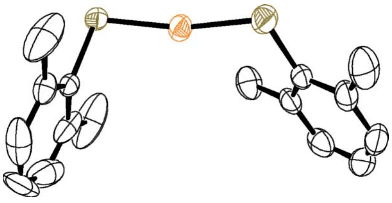
**A. R. Paital, M. Mikuriya,
D. Ray*** .... **5360−5368**

New Mixed-Metal Aggregates Derived From Dinickel Complexes on a 2-Formylphenolate Template: Counteranion Dependent Formation of 1D Chain and Discrete NaNi$_2$ Complexes

Keywords: Mixed-metal complexes / Imidazolidine / Dinuclear Ni^{II} complexes / Crystal structure / Magnetic properties

Thiolatocopper(I) Complexes

A series of mono- and polynuclear thiolatocopper(I) complexes exhibiting various coordination spheres is structurally characterized. The steric demands of the thiolato ligand have a clear effect on the coordination features with little influence of the reaction conditions. As low as the two-coordinate Cu centers were obtained, which represent structural models of the active site of copper metallochaperones.



S. Zeevi, E. Y. Tshuva* .... **5369−5376**

Synthesis and X-ray Characterization of Mono- and Polynuclear Thiolatocopper(I) Complexes: The Effect of Steric Bulk on Coordination Number and Nuclearity

Keywords: Copper / S ligands / Cluster compounds / Coordination modes / Metallochaperones

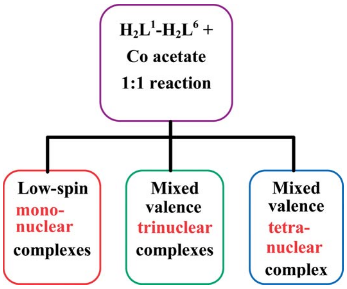
CONTENTS

Chiral Cobalt Complexes

C. P. Pradeep, P. S. Zacharias,
S. K. Das* 5377–5389

Enantiopure Mono- and Mixed-Valence Multinuclear Cobalt Complexes from Amino Alcohol Based Ligands

Keywords: Chiral complexes / Cobalt / Chiral amino alcohols / Supramolecular chemistry / Ligand-controlled nuclearity



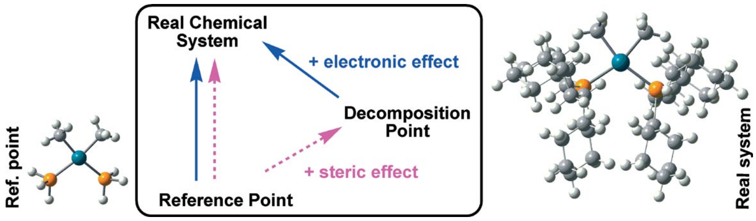
Chiral amino alcohol based tridentate Schiff bases, derived from 5-OMe-, 5-H-, and 5-NO_2-substituted salicylaldehydes and (*S*)-(+)-2-phenylglycinol and (*S*)-(−)-2-amino-3-phenyl-1-propanol, were found to act as versatile ligands in their coordination behavior towards cobalt ions and gave a range of optically active complexes like mononuclear low-spin Co^{III} complexes, mixed-valence trinuclear $Co^{III}-Co^{II}-Co^{III}$ complexes, and a mixed-valence tetranuclear $(Co^{III})_3Co^{II}$ complex.

C–C Coupling

V. P. Ananikov,* D. G. Musaev,
K. Morokuma 5390–5399

Critical Effect of Phosphane Ligands on the Mechanism of Carbon–Carbon Bond Formation Involving Palladium(II) Complexes: A Theoretical Investigation of Reductive Elimination from Square-Planar and T-Shaped Species

Keywords: C–C coupling / Palladium / Catalysis / Steric effect / Electronic effect / Phosphane ligands



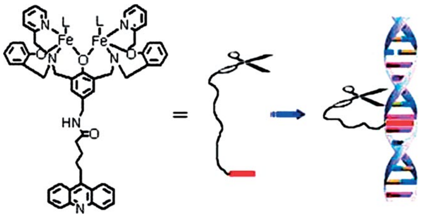
Relative reactivity in carbon–carbon bond formation involving a four-coordinated pathway follows the order: L = PPh_3 > PH_3 > PCy_3 > PMe_3. However, for reductive elimination involving T-shaped complexes by the ligand predissociation pathway, relative reactivity changes in the order: L = PCy_3 > PPh_3 > PH_3 > PMe_3.

Artificial Nucleases

X.-Q. Chen, X.-J. Peng,* J.-Y. Wang, Y. Wang, S. Wu, L.-Z. Zhang, T. Wu, Y.-K. Wu 5400–5407

Efficient Increase of DNA Cleavage Activity of a Diiron(III) Complex by a Conjugating Acridine Group

Keywords: DNA cleavage / Iron complex / Diiron(III) complex / Intercalator / Acridine



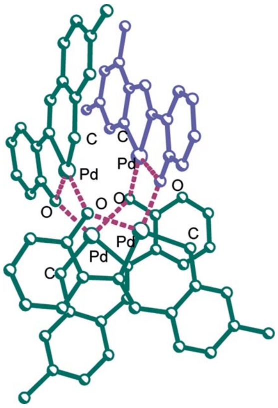
As a result of the binding interaction between DNA and an acridine moiety, a 14-fold promotion in the cleavage activity of a diiron(III) complex can be brought about.

Tetranuclear Palladium Complexes

J. J. Fernández,* A. Fernández,
D. Vázquez-García, M. López-Torres,
A. Suárez, N. Gómez-Blanco,
J. M. Vila* 5408–5418

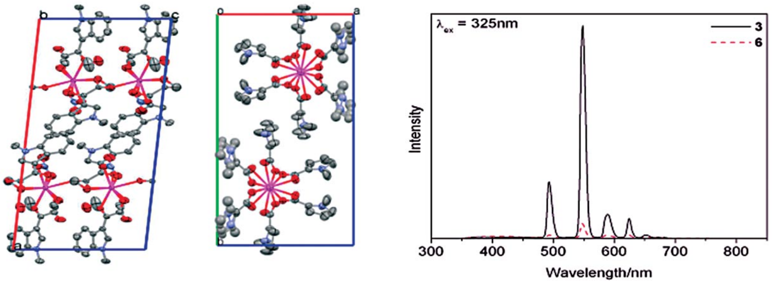
Tetranuclear Complexes of Pd^{II} with Tridentate [*C*,*N*,*O*] and [*O*,*N*,*O*] Ligands: Synthesis, Reactivity and Structural Isomerism

Keywords: Palladium / Cyclometallation / Metallacycles / Tridentate [*C*,*N*,*O*] ligands / C–H activation



Palladium(II) compounds with tridentate [*C*,*N*,*O*] ligands display tetranuclear structures regardless of whether they are cyclometallated. A new type of tetranuclear palladacycle bearing two different metallated moieties was found.

Luminescent Lanthanide Complexes



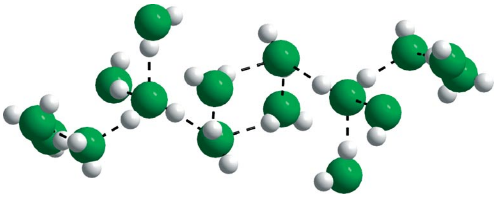
Luminescence studies on six lanthanide complexes with two pyrrole-derivatized carboxylic acid ligands show that modification of the ligands can tune the triplet energy levels of the ligands to match the $^5D_0$ energy level of Eu^{3+} and the $^5D_4$ energy level of Tb^{3+}, which improves the energy transfer efficiency from the antenna to the Eu/Tb^{3+} ions.

G.-L. Law, K.-L. Wong, K.-K. Lau, H.-L. Tam, K.-W. Cheah, W.-T. Wong* **5419–5425**

Synthesis, Crystal Structures, and Photophysical Properties of Lanthanide Complexes Containing Pyrrole-Derivatized Carboxylate Ligands

Keywords: Lanthanide / Luminescence / Terbium / Europium / Pyrrole

Water Clusters



Porous metal–organic framework structures are built from a podand ligand and transition metal ions under ambient conditions to form infinite chains of metallacycles. Discrete high-nuclearity water clusters have been identified inside the voids in these structures.

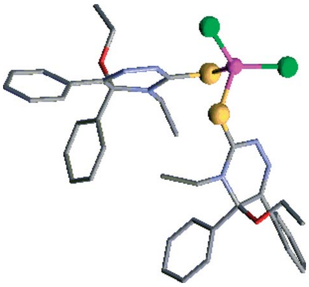
S. Neogi, E. C. Sañudo, P. K. Bharadwaj* **5426–5432**

Transition-Metal Porous Coordination Polymers with a Podand Ligand: Structure of Discrete Water Clusters and Variable-Temperature Magnetism

Keywords: Water clusters / Coordination polymers / Metal–organic frameworks / Podand ligands / Magnetism

Versatility of Thiosemicarbazones

The [α-diphenylethanedione bis(4-ethylthiosemicarbazonato)]palladium(II) complex and the dichloridobis(5-ethoxy-4-ethyl-5,6-diphenyl-4,5-dihydro-2*H*-[1,2,4]-triazine-3-thione)zinc(II) complex, obtained by metal-induced cyclization, have been prepared and characterized by X-ray analysis.



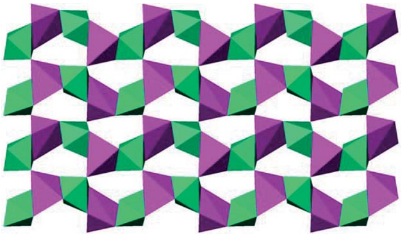
A. I. Matesanz, C. Pastor, P. Souza* **5433–5438**

Synthesis, Characterization and X-ray Structures of [α-Diphenylethanedione bis(4-ethylthiosemicarbazonato]palladium(II) and 1,2,4-Triazine-3-thione–Zinc(II) Complexes Obtained by Metal-Induced Cyclization

Keywords: Thiosemicarbazones / Cocrystals / Palladium(II) / Zinc(II) / X-ray diffraction

Metal Phosphonates

Four heterometal phosphonates, $NaM[O_3PCH(OH)CO_2]$ (M = Mn, Fe, Co, Zn), with a 3D framework were synthesized hydrothermally, and their structures were determined by single-crystal X-ray diffraction. Their thermal stabilities and their magnetic and luminescent properties are also described.



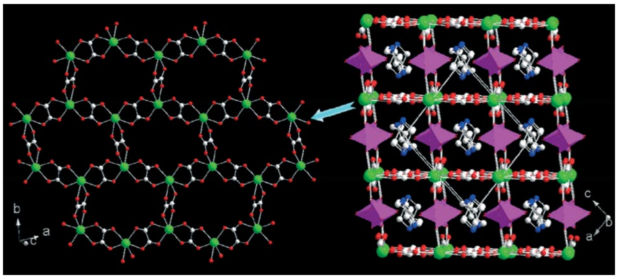
Z. Lai, R. Fu, S. Hu, X. Wu* **5439–5446**

Syntheses, Crystal Structures, Thermal Stabilities, and Magnetic and Luminescent Properties of 3D Heterometal Phosphonates: $NaM[O_3PCH(OH)CO_2]$ (M = Mn, Fe, Co, Zn)

Keywords: Crystal structure / Phosphorus / Luminescence / Magnetism / Thermal stability

Oxalate−Selenate Hybrids

Keywords: Hydrothermal syntheses / Lanthanides / Selenium / Crystal structures / Luminescent properties



Two series of novel organically templated lanthanide(III) oxalate−selenate hybrids were prepared and structurally characterized. Their structures range from 2D layers to 3D networks. They exhibit strong luminescent emission bands in the visible or near IR region.