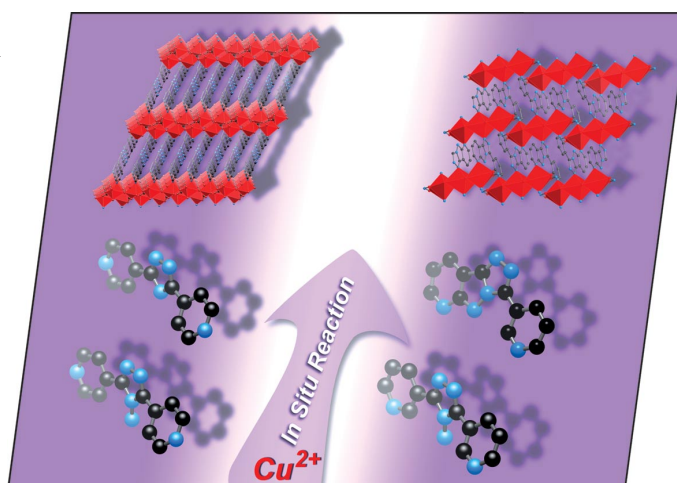


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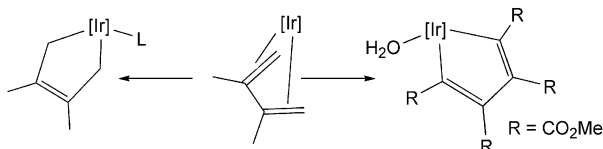
## COVER PICTURE

The cover picture shows that two coordination polymers exhibiting rare  $\text{NiP}_2$  topology and  $\text{kgd}$  topology are constructed on the basis of  $\text{Cu}^{2+}$  and ligands 3,5-bipyridyl-1,2,4-triazole and 5-(3-pyridyl)-1,2,4-triazolo[3,2-*c*](7-aza-1*H*-indazole) formed through in situ ligand deamination and in situ ligand intramolecular amination cyclization reactions. Details are discussed in the Short Communication by Z. Shi et al. on p. 35ff. Dedicated to Professors Ruren Xu and Wenqin Pang on the occasion of their 80th birthdays, with our warmest congratulations and best wishes.



## MICROREVIEW

### Iridacycles



Many kinds of iridacycles containing the  $\text{Tp}^{\text{Me}_2}\text{Ir}$  moiety (iridacyclopentene, -pentadiene, -heptadiene, -heptatriene and -benzenoid derivatives) have been obtained starting from the  $\text{Ir}^{\text{I}}$  precursors  $\text{Tp}^{\text{Me}_2}\text{Ir}(\text{C}_2\text{H}_4)_2$

and/or  $\text{Tp}^{\text{Me}_2}[\eta^4\text{-CH}_2=\text{C}(\text{R})\text{C}(\text{R})=\text{CH}_2]$  ( $\text{R} = \text{H}, \text{Me}$ ). The synthesis and reactivity of these species is the subject of the present review.

**M. Paneque,\* M. L. Poveda,  
N. Rendón** ..... 19–33

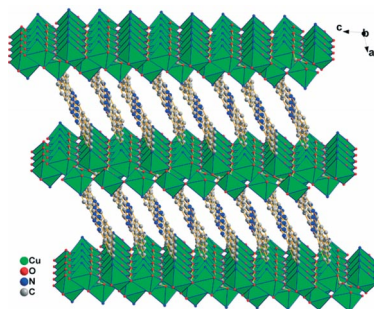
Synthesis and Reactivity of Iridacycles Containing the  $\text{Tp}^{\text{Me}_2}\text{Ir}$  Moiety

**Keywords:** Iridium / Metallacycles / Tris-(pyrazolyl)borate ligands

## SHORT COMMUNICATIONS

### In Situ Synthesis of MOFs

Two coordination polymers with rare  $\text{NiP}_2$  and  $\text{kgd}$  topologies have been synthesized by in situ deamination and intramolecular amination cyclization reactions. To the best of our knowledge, it is the first case in which an indazole cycle is formed through intramolecular amination cyclization. The magnetism of the polymers has also been studied.

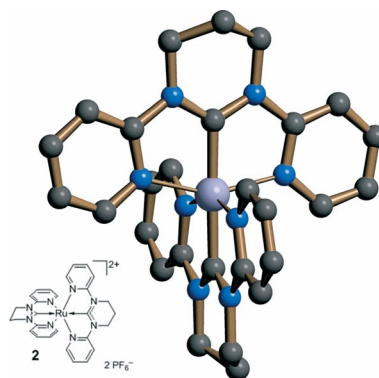


**B. Li, D. Jin, B. Ma, D. Liu, G. Li,  
Z. Shi,\* S. Feng** ..... 35–38

Two Coordination Polymers with Rare Topologies Based on Copper(II) and Ligands Generated by In Situ Reactions

**Keywords:** Copper / Coordination polymers / Magnetic properties / Topology / Structure elucidation

A six-membered NHC forms the  $\sigma$ -donating core of a tridentate ligand incorporating two pyridine moieties. The enlarged NHC angles allow the formation of fully tridentate complexes, confirmed by X-ray crystallography. The electrochemistry and spectroscopy results of its  $\text{Ru}^{\text{II}}$  complexes confirm its electron-rich character. Powder samples of the complexes display red phosphorescence in the 735–750 nm region.



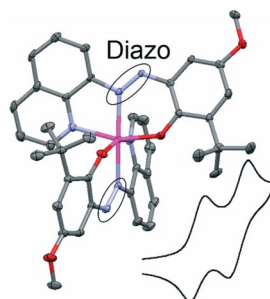
**V. Friese, S. Nag, J. Wang, M.-P. Santoni,  
A. Rodrigue-Witchel, G. S. Hanan,\*  
F. Schaper\*** ..... 39–44

Red Phosphorescence in  $\text{Ru}^{\text{II}}$  Complexes of a Tridentate N-Heterocyclic Carbene Ligand Incorporating Tetrahydropyrimidine

**Keywords:** Carbene ligands / Ruthenium / Ligand design / Electrochemistry / Phosphorescence

### Azophenol Radicals

The hydrazone iminoquinone HL is a precursor for hydrogen-bonded phenoxyl (oxidation) and delocalized iminosemiquinonate/hydrazyl radical (reduction) species. Oxidation of the zinc complex  $[\text{Zn}(\text{L})_2]$  affords persistent mono- and bis(phenoxyl) radicals. The electronic effect of the azo group has been evaluated by measuring the zero-field splitting (ZFS) parameters in the diradical complex.



**A. Kochem, M. Orio, C. Philouze,  
H. Jamet, A. du Moulinet d'Hardemare,\*  
F. Thomas\*** ..... 45–48

Radicals of Free and Zinc(II)-Coordinated  $\alpha$ -Azophenols

**Keywords:** N ligands / Zinc / Radicals / Hydrazones / Redox chemistry

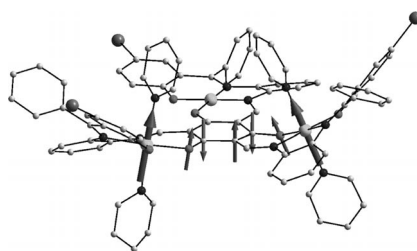
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## Spin-Polarization

C.-G. Freiherr von Richthofen,  
A. Stämmler, H. Bögge,  
T. Glaser\* ..... 49–52



From Triplesalen to Triplesalophen: Ferromagnetic Interactions through Spin-Polarization in a Trinuclear Ni<sup>II</sup> Triplesalophen Complex



The tripesalophen ligand system is introduced and allowed the synthesis of the first phloroglucinol-bridged trinuclear Ni<sup>II</sup> complex with paramagnetic Ni<sup>II</sup> ions, which exhibit ferromagnetic interactions in accordance to the spin-polarization mechanism.

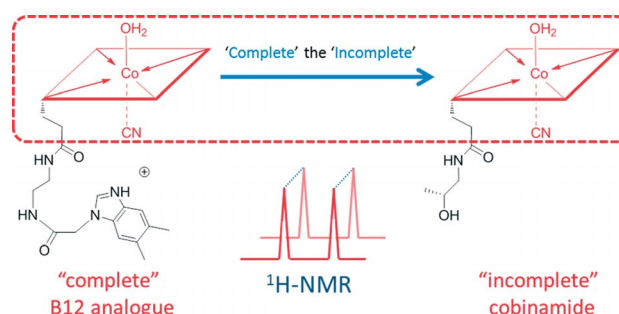
**Keywords:** Magnetic properties / Nickel / Schiff bases

## Modified B12 Derivatives

K. Zhou, F. Zelder\* ..... 53–57



Identification of Diastereomeric Cyano–Aqua Cobinamides with a Backbone-Modified Vitamin B12 Derivative and with <sup>1</sup>H NMR Spectroscopy



**Keywords:** Vitamin B12 / NMR spectroscopy / Cobalt / Diastereomers / Bio-inorganic chemistry/ Corrinoids

A new backbone-modified vitamin B12 derivative with an unusual configuration at the cobalt center has been used for the

identification of the two axial diastereomers of cyano–aqua cobinamides (Cbi) by using <sup>1</sup>H-NMR spectroscopy.

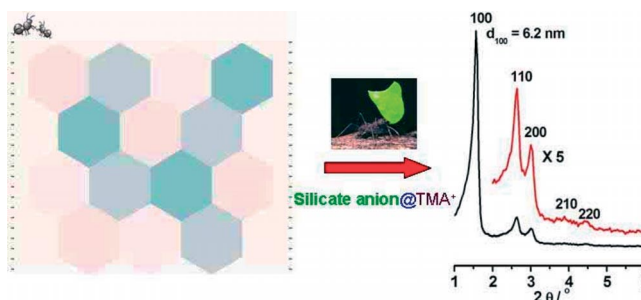
# FULL PAPERS

## Mesoporous Materials with Thick Walls

K. Zhang,\* H.-L. Chen, B. Albela,  
J.-G. Jiang, Y.-M. Wang,\* M.-Y. He,  
L. Bonneviot ..... 59–67



High-Temperature Synthesis and Formation Mechanism of Stable, Ordered MCM-41 Silicas by Using Surfactant Cetyltrimethylammonium Tosylate as Template



**Keywords:** Silicas / Mesoporous materials / Cetyltrimethylammonium tosylate / Hydrothermal synthesis / Template synthesis

Well-ordered MCM-41 silicas with thick pore walls were directly synthesized by using the new surfactant cetyltrimethylammonium tosylate as template. A new

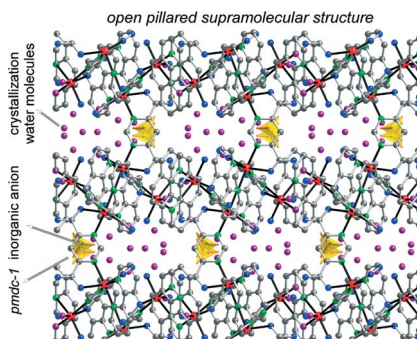
mechanism was proposed to understand the unit-lattice expansion and pore-wall thickening.

## Crystal Engineering

G. Beobide, O. Castillo,\* J. Cepeda,  
A. Luque,\* S. Pérez-Yáñez, P. Román,  
D. Vallejo-Sánchez ..... 68–77



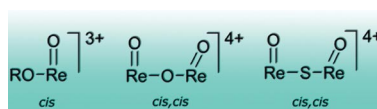
Low-Nuclearity Mn<sup>II</sup> Complexes Based on Pyrimidine-4,6-dicarboxylato Bridging Ligand: Crystal Structure, Ion Exchange and Magnetic Properties




Crystal structures, chemical characterization, ion exchange processes and magnetic properties of the first examples of low-nuclearity complexes based on the pyrimidine-4,6-dicarboxylato bridging dianion are reported.

**Keywords:** Crystal engineering / Manganese / Ion exchange / Magnetic properties

Complexes with the unusual oxidorhenium(V) cores,  $cis\text{-}\{\text{ReO}(\text{OR})\}^{3+}$ ,  $cis,cis\text{-}\{\text{ORe-O-ReO}\}^{4+}$ , and  $cis,cis\text{-}\{\text{ORe-S-ReO}\}^{4+}$ , are formed from the reaction of  $[\text{ReOCl}_4]^-$  and  $N\text{-}(N',N'\text{-dialkylaminothiocarbonyl})\text{-}N'\text{-}(2\text{-hydroxyphenyl})\text{benzamidine}$  ligands depending on the conditions applied.



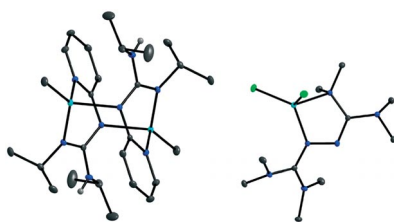
**H. H. Nguyen,\* K. Hazin, U. Abram\*** ..... 78–82

Synthesis and Characterization of Unusual Oxidorhenium(V) Cores 


**Keywords:** Rhenium / Oxido cores / Bridging ligands / Coordination modes

## Guanidine Ligands

The structures and dynamic behaviour of guanidine Zn complexes, in which the amino groups are directly involved in coordinative bonding, are analyzed in this work.



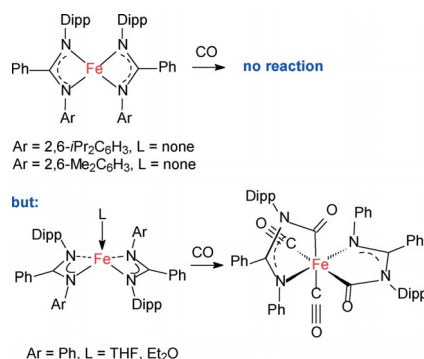
**M. Reinmuth, C. Neuhäuser, P. Walter, M. Enders, E. Kaifer, H.-J. Himmel\*** ..... 83–90

The Flexible Coordination Modes of Guanidine Ligands in Zn Alkyl and Halide Complexes: Chances for Catalysis 


**Keywords:** Zinc / Coordination modes / Guanidine ligands

## Amidinate Complexes

The influence of sterically demanding aryl substituents on the nitrogen atoms of amidinate ligands was investigated in paramagnetic bis(amidinate)  $\text{Fe}^{\text{II}}$  complexes. Reactivity towards Lewis bases and CO is almost completely suppressed with the most bulky ligand. Gradual restoration of reactivity is observed with sterically less demanding ligands.



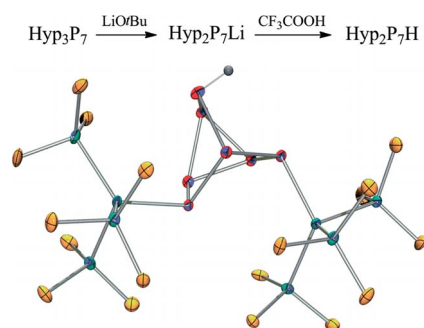
**E. Jellema, T. J. J. Sciarone,\* N. M. Navarrete, M. J. Hettinga, A. Meetsma, B. Hessen** ..... 91–100

Reactivity of Paramagnetic  $\text{Fe}^{\text{II}}$ –Bis(amidinate) Complexes 

**Keywords:** Iron / N ligands / Carbonylation / Lewis bases / Magnetic properties

## Heptaphosphanes

Cage-shaped heptaphosphanes  $\text{P}_7\text{R}_3$  that bear oligosilyl substituents R are easily modified with the help of Si–Si or Si–P bond-cleavage reactions by using  $\text{LiO}t\text{Bu}$  or  $\text{KO}t\text{Bu}$ .



**P. Noblet, V. Cappello, G. Tekautz, J. Baumgartner, K. Hassler\*** ..... 101–109

Heptaphosphanortricyclenes with Oligosilyl Substituents: Syntheses and Reactions

**Keywords:** Heptaphosphanes / Oligosilyl groups / X-ray structural analysis / NMR spectroscopy / Silicon



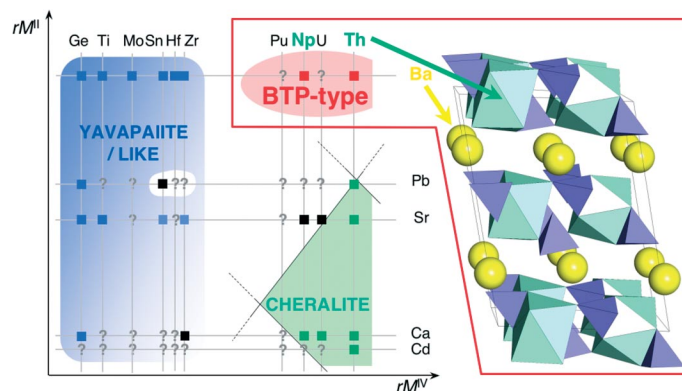
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## Layered Actinide Double Phosphates

G. Wallez,\* D. Begiroux,  
K. Popa, P. E. Raison, C. Apostolidis,  
P. Lindqvist-Reis, R. J. M. Konings,  
A. F. Popa ..... 110–115

$\text{BaAn}^{\text{IV}}(\text{PO}_4)_2$  ( $\text{An}^{\text{IV}} = \text{Th}, \text{Np}$ ) – A New Family of Layered Double Phosphates

**Keywords:** Phosphates / Actinides / Solid-state structures / Layered compounds / Raman spectroscopy



$\text{BaTh}(\text{PO}_4)_2$  and  $\text{BaNp}(\text{PO}_4)_2$  appear as the prototypes of a new family of double phosphates, which differ from cheralite by the ordering of the cations and from yava-

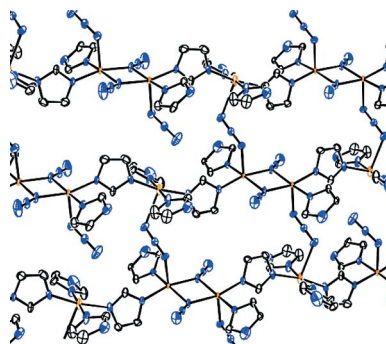
paiite by their higher coordination numbers (14 for Ba and 8 for Th/Np). This structure should also be compatible with  $\text{U}^{\text{IV}}$  and  $\text{Pu}^{\text{IV}}$ .

## Copper(II) Coordination Polymers

K. Sakai,\* T. Akutagawa,  
T. Nakamura ..... 116–120

An Imidazolate- and Azide-Bridged Copper(II) Coordination Polymer Consisting of Alternating Di- and Mononuclear Units

**Keywords:** Coordination polymers / Copper / N ligands / Azides / Magnetic properties



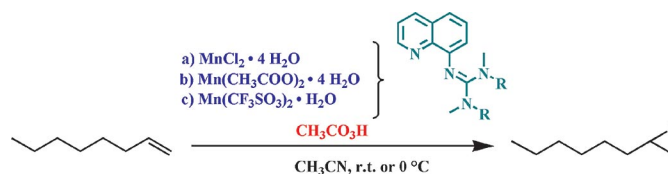
The novel copper(II) coordination polymer  $[\text{Cu}_3(\text{Him})_4(\text{im})_2(\text{N}_3)_4]_n$  is constructed with a combination of simple inorganic and organic bridging ligands, namely azide and imidazolate. It shows ferrimagnetic-like behaviour resulting from the coexistence of copper(II) di- and mononuclear units.

## (Guanidine)manganese Complexes

R. Wortmann, U. Flörke, B. Sarkar,  
V. Umamaheshwari, G. Gescheidt,  
S. Herres-Pawlis,\* G. Henkel\* .... 121–130

Synthesis and Characterisation of Novel (Guanidine)manganese Complexes and Their Application in the Epoxidation of 1-Octene

**Keywords:** Epoxidation / Manganese / Guanidine ligands / Alkenes



The synthesis and molecular structures of manganese complexes of the guanidine–pyridine hybrid ligands DMEGqu (**L1**) and TMGqu (**L2**) are reported. These novel complexes were proven to be active and

stable catalysts in the epoxidation of 1-octene with peracetic acid. Kinetic measurements exhibit that the epoxidation reaction proceeds on a time scale interesting for industrial application.

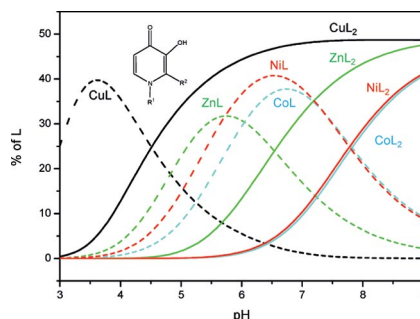
## Ni and Co Poisoning Control

C. Queiros, M. J. Amorim, A. Leite,  
M. Ferreira, P. Gameiro, B. de Castro,  
K. Biernacki, A. Magalhães, J. Burgess,  
M. Rangel\* ..... 131–140



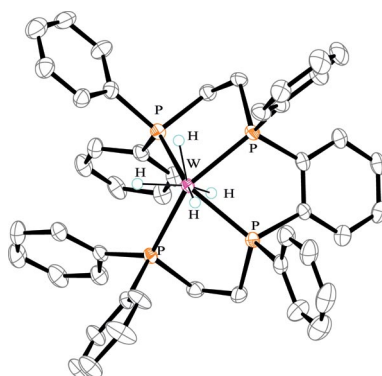
Nickel(II) and Cobalt(II) 3-Hydroxy-4-pyridinone Complexes: Synthesis, Characterization and Speciation Studies in Aqueous Solution

**Keywords:** Nickel / Cobalt / Toxicology / Pollution / N ligands / Ligand effects



The affinity of 3,4-HPO ligands towards  $\text{Co}^{\text{II}}$  and  $\text{Ni}^{\text{II}}$  allows their precipitation as neutral  $\text{ML}_2$  complexes. Although not suitable for oral use due to their higher affinity to  $\text{Fe}^{\text{III}}$ ,  $\text{Cu}^{\text{II}}$  and  $\text{Zn}^{\text{II}}$ , 3,4-HPO ligands may be of use in smart materials to prevent inhalation of nickel(II) or cobalt(II) particles in industrial environments as it is possible to vary the substituents without altering their chelating properties.

Reaction of  $[\text{WBr}_2(\kappa^4\text{-P4})]$  ( $\text{P4} = \text{meso-}o\text{-C}_6\text{H}_4(\text{PPhCH}_2\text{CH}_2\text{PPh}_2)_2$ ) with  $\text{NaBH}_4$  in ethanol at  $50^\circ\text{C}$  forms  $[\text{WH}_4(\kappa^4\text{-P4})]$ , which is one of the rare examples of a polyhydride complex containing a tetraphosphane co-ligand. Structure determination by single-crystal X-ray analysis and the reactivity of the complex towards  $\text{CS}_2$  and RNC are reported.



Q. X. Dai, H. Seino,\*

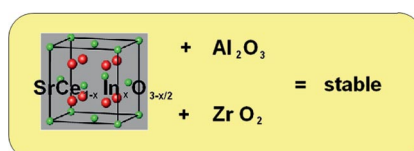
Y. Mizobe\* ..... 141–149

Preparation and Reactions of Molybdenum and Tungsten Hydride Complexes Containing the Tetraphosphane Ligand *meso-}o\text{-C}\_6\text{H}\_4(\text{PPhCH}\_2\text{CH}\_2\text{PPh}\_2)\_2*

**Keywords:** Molybdenum / Tungsten / Phosphane ligands / Hydride ligands

### Indium-Doped Strontium Cerate

The standard enthalpy of formation of  $\text{SrCe}_{0.5}\text{In}_{0.5}\text{O}_{2.75}$  has been determined by solution calorimetry for the first time. On the basis of the data obtained, it is possible to predict that  $\text{SrCe}_{0.5}\text{In}_{0.5}\text{O}_{2.75}$  is stable with respect to decomposition to binary oxides and it does not react with  $\text{Al}_2\text{O}_3$  or  $\text{ZrO}_2$ .



N. I. Matskevich,\* T. Wolf,

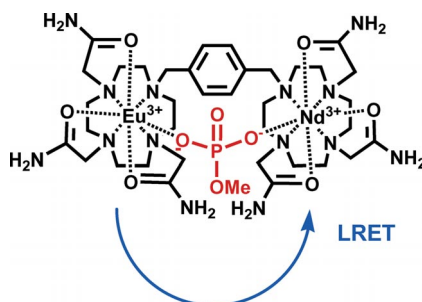
T. I. Chupakhina ..... 150–153

Thermodynamic Properties and Stability of In-Doped  $\text{SrCeO}_3$  Proton-Conducting Ceramics

**Keywords:** Thermodynamics / Proton-conducting ceramics / Strontium / Cerium / Solution calorimetry / Solid-phase synthesis

### Anion Sensors

Dinuclear  $\text{Eu}^{\text{III}}$  or  $\text{Tb}^{\text{III}}$  complexes bind to a series of biologically relevant anions with concomitant loss of water ligands. Anion binding induces characteristic changes in emission peak intensities for  $\text{Eu}^{\text{III}}$  analogs. A few anions promote luminescence resonance energy transfer between  $\text{Eu}^{\text{III}}$  and  $\text{Nd}^{\text{III}}$  centers.



C. M. Andolina,

J. R. Morrow\* ..... 154–164

Luminescence Resonance Energy Transfer in Heterodinuclear  $\text{Ln}^{\text{III}}$  Complexes for Sensing Biologically Relevant Anions

**Keywords:** Lanthanides / Luminescence resonance energy transfer / Anions / Sensors / DNA

\* Author to whom correspondence should be addressed.

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