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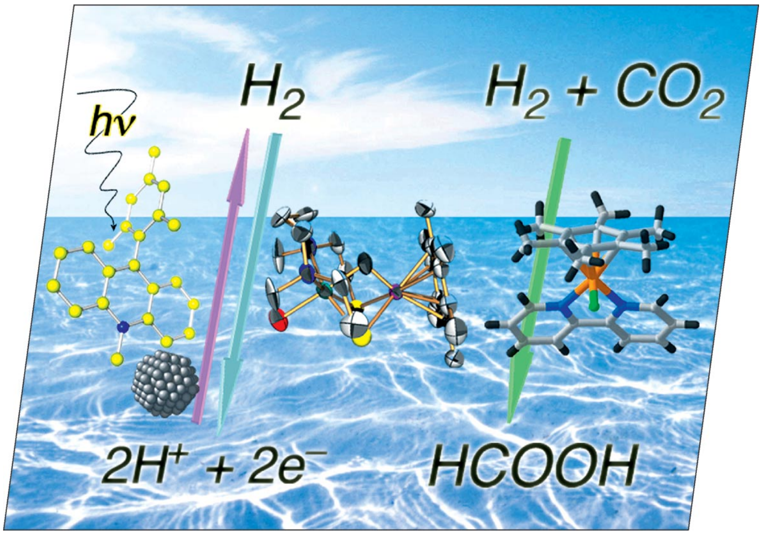
EUChemSoc

The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry.* Three further EUChemSoc Societies (Austria, Czech Republic and Sweden) are Associates of the two journals.

COVER PICTURE

The cover picture shows the photocatalytic production of hydrogen and the interconversion between hydrogen and formic acid with the use of catalysts. These processes have become important in the search for alternative energy resources that are renewable, in order to combat global environmental problems. Hydrogen is a clean energy source, and therefore its production and storage is a key to the future. Details are presented in the Microreview by S. Fukuzumi on p. 1351ff.



CONTENTS

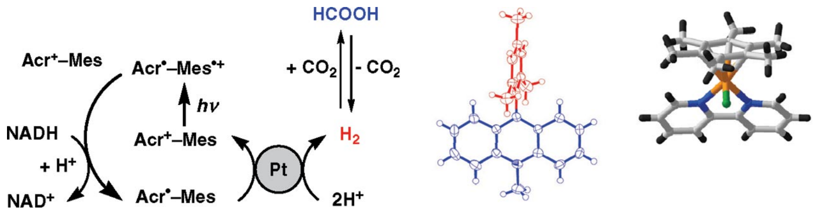
MICROREVIEW

Sustainable H_2 Storage

S. Fukuzumi* 1351–1362

Bioinspired Energy Conversion Systems for Hydrogen Production and Storage

Keywords: Artificial photosynthesis / Photoinduced electron transfer / Hydrogen production / Hydrogen storage / Sustainable chemistry



Recent developments in photocatalytic hydrogen production by using simplified artificial photosynthesis systems is described, together with those in hydrogen storage through the fixation of carbon dioxide with hydrogen. Hydrogen can be stored in the form of liquid formic acid, which can be converted back to hydrogen in the presence of an appropriate catalyst.

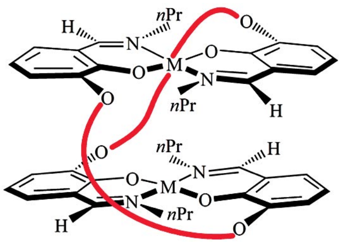
FULL PAPERS

Metallosupramolecular Chemistry

M. Isola,* F. Balzano, V. Liuzzo, F. Marchetti, A. Raffaelli, G. Uccello Barretta* 1363–1375

Coordination and Supramolecular Chemistry of New Bis-bidentate Schiff-Base Ligands

Keywords: Nickel / Copper / Schiff bases / Self-assembly / N,O ligands / Supramolecular chemistry



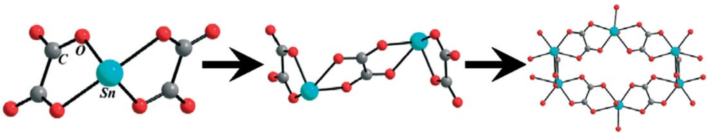
A series of bis-bidentate ligands containing two salicylaldiminato units connected to central polymethylene or α,α′-*ortho*-xylidene spacers form a range of structures including dinuclear double-stranded helicates with the metal atoms in the *trans*-square-planar geometry.

Oxalate Frameworks

P. Ramaswamy, A. Datta, S. Natarajan* 1376–1385

Hierarchical Structures in Tin(II) Oxalates

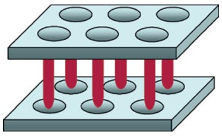
Keywords: Template synthesis / Lone pair / Hydrogen bonds / Tin / Oxalate



The figure shows representative tin(II) oxalate structures prepared by employing hydrothermal methods.

Magnetic Materials

A two-dimensional layer, formed by the 4.6.12-net connectivity, is penetrated by one-dimensional chain units forming a three-dimensional pillared-layer structure with two independent 12-ring channel systems. A schematic diagram of the pillared-layer structure is shown. Magnetic studies indicate antiferromagnetic behavior at high temperatures, with a small ferromagnetic polarization at low temperatures.

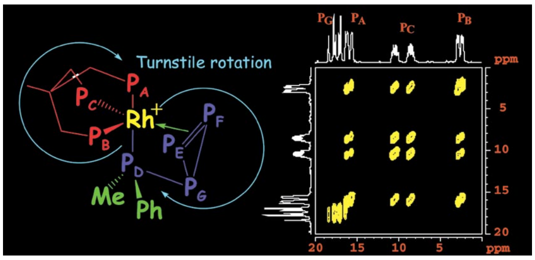


S. Mandal, D. Banerjee, S. V. Bhat,*
S. K. Pati,* S. Natarajan* ..... 1386−1391

Synthesis, Structure, and Magnetic Properties of a New Three-Dimensional Iron Phosphite, $[C_4N_2H_{12}][Fe_4(H_2O)_3(HPO_3)_7]\cdot(H_2O)_x$ $x = 0.6$

Keywords: Antiferromagnetism / Hydrothermal synthesis / Iron phosphite / Open frameworks

Fluxional Phosphane Complexes



2D ^1H NOESY and $^{31}P\{^1H\}$ EXSY NMR spectroscopy show that $[(triphos)Rh(\eta^1:\eta^2\text{-}P_4RR')]^{n+}$ complexes [triphos = $MeC(CH_2PPh_2)_3$; R = H, Me, Ph; R′ = lone pair, H, Me; n = 0, 1] are nonrigid on the NMR time-scale over the 253−318 K temperature range. A dynamic process that involves a slow scrambling motion where the P_4R unit tumbles with respect to the (triphos)Rh moiety accounts for the observed fluxionality. DFT calculations outline a possible turnstile mechanism involving the threefold and twofold rotors into which the complex is subdivided. The process goes through a transition state in which the axial and equatorial dispositions of the PRR′ and P=P donating groups of the P_4RR' ligand are inverted with respect to the ground state.

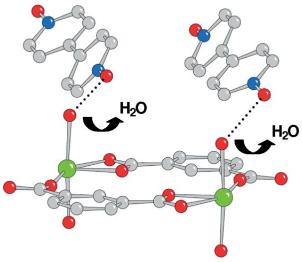
P. Barbaro, M. Caporali, A. Ienco,
C. Mealli, M. Peruzzini,*
F. Vizza .... 1392−1399

Dynamic Behaviour of the $[(Triphos)Rh(\eta^1:\eta^2\text{-}P_4RR')]^{n+}$ Complexes [Triphos = $MeC(CH_2PPh_2)_3$; R = H, Alkyl, Aryl; R′ = Lone Pair, H, Me; n = 0, 1]: NMR and Computational Studies

Keywords: Phosphorus / Rhodium / Tripodal phosphane ligands / Fluxionality / Density functional calculations / NMR spectroscopy

Supramolecular Isomerism

A one-pot reaction of three components [Mn^{II}, isophthalate dianion (isop) and 4,4′-dipyridyl N,N'-dioxide (dpyo)] in water/methanol (1:1) leads to two distinct structural isomers depending on the role played by dpyo molecule.



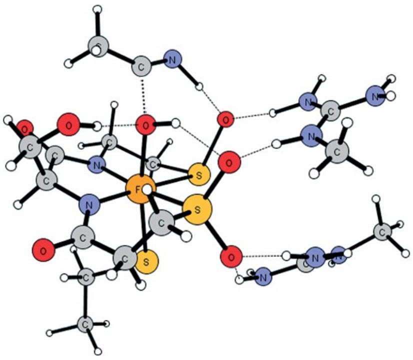
S. C. Manna, E. Zangrando, J. Ribas,
N. Ray Chaudhuri* .... 1400−1405

Supramolecular Isomerism in Coordination Polymers of Isophthalato-Bridged Mn^{II} Complexes Using 4,4′-Dipyridyl N,N'-Dioxide

Keywords: Manganese(II) / Isophthalate / 4,4′-Dipyridyl N,N'-dioxide / Supramolecular isomerism

Nitrile Hydratase Mechanism

Nitrile Hydratase (NHase) catalyzes conversion of nitriles by employing an unusual low-spin transition-metal complex. The precise reaction mechanism of NHase has not been elucidated yet. We have used quantum-chemical active-site models to investigate two proposed second-shell mechanisms. Energies and optimized transition states are reported.



K. H. Hopmann, F. Himo* .... 1406−1412

Theoretical Investigation of the Second-Shell Mechanism of Nitrile Hydratase

Keywords: Nitrile hydratase / Enzyme catalysis / Density functional theory / Reaction mechanism

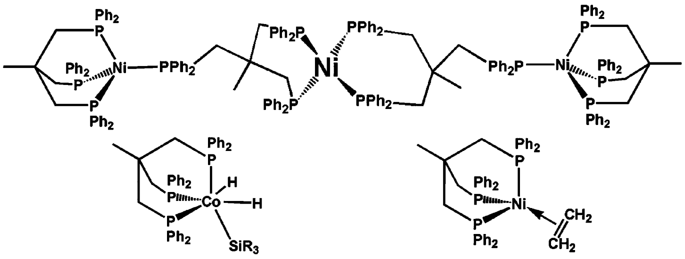
CONTENTS

tripod Chemistry

J. Mautz, K. Heinze, H. Wadepohl,
G. Huttner* 1413–1422

Reductive Activation of *tripod* Metal Compounds: Identification of Intermediates and Preparative Application

Keywords: Tripodal ligands / Cobalt / Nickel / Reductive activation / Oxidative addition / Silicon hydrides / Tin hydrides



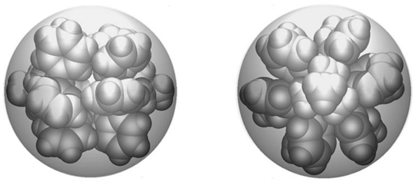
Reductive activation of [*tripod*$CoCl_2$] {*tripod* = $[CH_3C(CH_2PPh_2)_3]$} leads to a species that reacts with R_3EH (E = Si, Sn) to give [*tripod*$Co(H_2)(ER_3)$]. The compounds show a rather distorted coordination octahedron with P–Co–E angles of down to 140°. Upon reductive activation of $[(DME)NiBr_2]$ in the presence of *tripod* the complex [*tripod*$_4Ni_3$] is formed as the reactive species. The latter reacts with two-electron donor ligands to give the pseudo tetrahedral complexes [*tripod*Ni(L)].

tripod Chemistry

J. Mautz, G. Huttner* 1423–1434

Reductive Activation of *tripod* Metal Compounds: Preparative Application

Keywords: Tripodal ligands / Cobalt / Nickel / Reductive activation / Oxidative addition



[*tripod*Co=S=Co*tripod*]

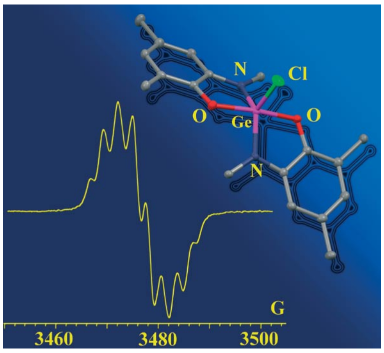
Halides of Ni^{II} and Co^{II} when reduced in the presence of *tripod* $[CH_3C(CH_2PPh_2)_3]$ produce reactive species. In general, with dichalcogenides REER (E = S, Se) they react to give compounds of type [*tripod*M(ER)] (M = Ni, Co). In the case of Co, dechalcogenation is often observed leading to [*tripod*Co=E=Co*tripod*] with a linear arrangement of the Co=E=Co group, very short Co–E bonds (Co–S = 205.3 pm, Co–Se = 216.3 pm) and almost globular shape.

Di- and Tetravalent Germanium

A. V. Piskunov,* I. A. Aivaz'yan,
A. I. Poddel'sky, G. K. Fukin,
E. V. Baranov, V. K. Cherkasov,
G. A. Abakumov 1435–1444

New Germanium Complexes Containing Ligands Based on 4,6-Di-*tert*-butyl-*N*-(2,6-diisopropylphenyl)-*o*-iminobenzoquinone in Different Redox States

Keywords: Germanium / Metallacycles / N,O ligands / EPR spectroscopy / X-ray diffraction



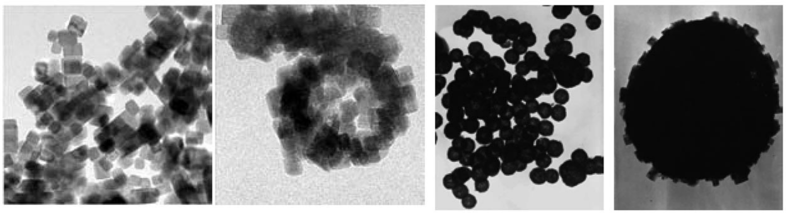
It has been shown that a bulky aryl-substituted *o*-iminoquinone can serve as a versatile ligand that can be used to synthesize both divalent and tetravalent germanium amidophenolate derivatives. At the same time, the ligand coordinated to the germanium atom can be transformed from the dianion to the radical anion or protonated anion forms.

Indium Nano/microstructures

L.-Y. Chen, Y.-G. Zhang, W.-Z. Wang,
Z.-D. Zhang* 1445–1451

Tunable Synthesis of Various Hierarchical Structures of $In(OH)_3$ and In_2O_3 Assembled by Nanocubes

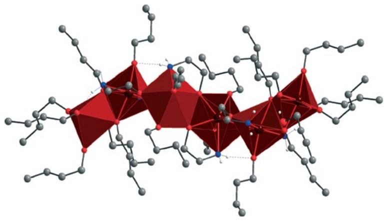
Keywords: Indium / Crystal growth / Hydrothermal synthesis / Photoluminescence



$In(OH)_3$ and C-In_2O_3 nano/microstructures with different morphologies were prepared by a simple hydrothermal method with the assistance of ethylenediamine conditions.

Metal Alkoxide Chemistry

Amino alcoholate derivatives of metal alkoxides are interesting precursors for sol-gel reactions. New structural data of mono- and disubstituted titanium and zirconium alkoxide precursors are presented. Furthermore, a few oxo clusters obtained by partial hydrolysis are characterized. Some of the solid-state structures are rather complex due to association processes.



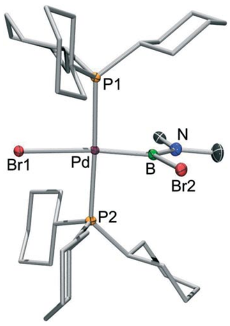
H. Fric, M. Puchberger,
U. Schubert* 1452–1461

Contributions to the Structural Chemistry of 2-Amino Alcoholate Derivatives of Titanium and Zirconium Alkoxides and Their Partial Hydrolysis Products

Keywords: Titanium / Zirconium / Aminoethanolate ligands / Partial hydrolysis

Bromo(boryl)palladium Complexes

A series of palladium boryl complexes were synthesized by oxidative addition of bromoboranes to a Pd^0 precursor. X-ray analysis of the two compounds reveals a distorted square-planar geometry at the Pd centres with the phosphane ligands *trans* to each other. The long Pd–Br bond reflects the strong *trans* influence of the boryl moiety.

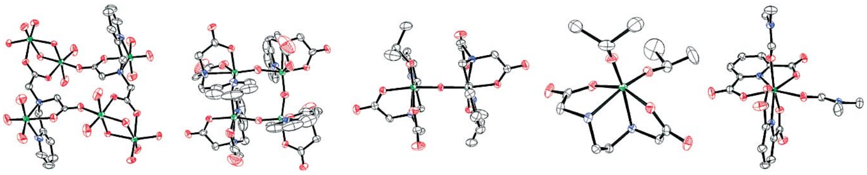


H. Braunschweig,* K. Gruss, K. Radacki,
K. Uttinger 1462–1466

Oxidative Addition of B–Br Bonds to Pd^0: Synthesis and Structure of *trans*-Bromo(boryl)palladium Complexes

Keywords: Boron / Boryl complexes / Oxidative addition / Palladium

Bis(carboxylato) Complexes of Ti^{IV}



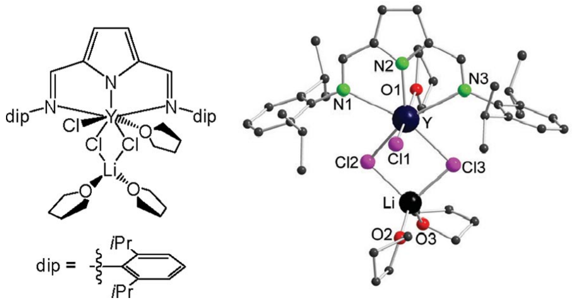
Ti^{IV} complexes of bis(carboxylato) ligands of different nuclearities and bridging modes were formed. An $[O_2NO_2]$ ligand led to an $L_2Ti(dmf)_2$ octacoordinate complex, whereas $[O_2NNO_2]$ ligands led to either a mononuclear or a unique hexanuclear isopropoxido complex at room temp., depending on the particular ligand. Slight heating resulted in *O*-bridged species with Ti–O π interactions, when allowed by steric crowding.

M. Shavit, E. Y. Tshuva* 1467–1474

Preparation and X-ray Structures of Ti^{IV} Complexes of Bis(carboxylato) Ligands – Formation of Mono-, Di-, Tetra-, and Hexanuclear Complexes with or without OR and μ-O Ligands

Keywords: Titanium(IV) / Carboxylato ligands / Oxido ligands / Cluster compounds / Coordination modes

Amido Complexes



New 2,5-bis{[(2,6-diisopropylphenyl)imino]methyl}pyrrolyl compounds of alkaline and rare earth metals are presented.

N. Meyer, M. Kuzdrowska,
P. W. Roesky* 1475–1479

(2,5-Bis{[(2,6-diisopropylphenyl)imino]methyl}pyrrolyl)yttrium and -lutetium Complexes – Synthesis and Structures

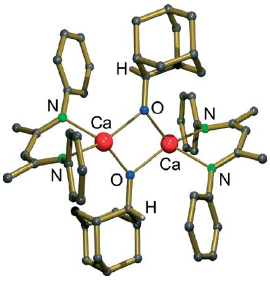
Keywords: Lutetium / N ligands / Potassium / Pyrrole / Yttrium

Organocalcium Catalysis

J. Spielmann, S. Harder* 1480–1486

Reduction of Ketones with Hydrocarbon-Soluble Calcium Hydride: Stoichiometric Reactions and Catalytic Hydrosilylation

Keywords: Alkaline earth metals / Calcium / Hydride / Catalysis / Hydrosilylation



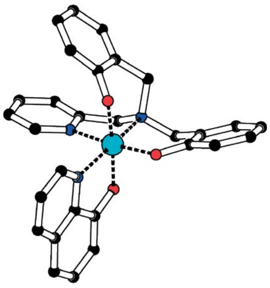
The chemoselectivity of the reaction of the hydrocarbon-soluble calcium hydride complex [(DIPP-nacnac)CaH·thf]$_2$ with several ketones has been investigated. Whereas reactions with α-hydrogen containing ketones are often unselective, the Ca-mediated hydrosilylation of these ketones are surprisingly chemoselective. This can be explained by assuming a mechanism which involves a hypervalent six-coordinate silicon center.

Tripodal Ligands

R. van Gorkum, J. Berding, A. M. Mills, H. Kooijman, D. M. Tooke, A. L. Spek, I. Mutikainen, U. Turpeinen, J. Reedijk, E. Bouwman* 1487–1496

The Synthesis, Structures and Characterisation of New Mixed-Ligand Manganese and Iron Complexes with Tripodal, Tetradentate Ligands

Keywords: Tripodal ligands / Iron / Manganese



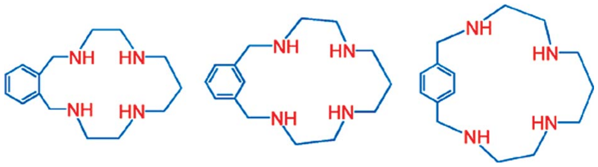
A number of structures of Mn^{III} and Fe^{III} complexes with the general formula [M(tripod)(anion)] is reported. A clear correlation between the ligand sets and the electron density of the metal centre in the complexes could be made, corroborated by UV/Vis data and the CV measurements.

Changing Macrocyclic Cavity

B. Verdejo, M. García Basallote,* A. Ferrer, M. Angeles Mañez, J. C. Hernández, M. Chadim, J. Hodačová,* J. M. Llinares, C. Soriano, E. García-España* 1497–1507

Equilibrium and Kinetic Properties of Cu^{II} Cyclophane Complexes: The Effect of Changes in the Macrocyclic Cavity Caused by Changes in the Substitution at the Aromatic Ring

Keywords: Cyclophanes / Copper(II) complexes / Protonation constants / Kinetics / Macrocyclic ligands



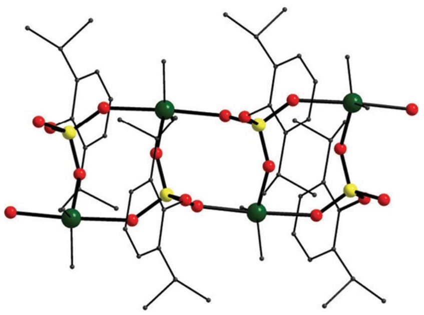
Studies on the stability and decomposition kinetics of three Cu^{II} complexes with cyclophane ligands that differ only in their substitution at the aromatic ring reveal the existence of gradual but significant changes in the thermodynamic and kinetic properties of these complexes.

Structurally Diverse Organostannanes

R. Murugavel,* S. Shanmugan, S. Kuppuswamy 1508–1517

Structural Diversity in Organotin Compounds Derived from Bulky Monoaryl Phosphates: Dimeric, Tetrameric, and Polymeric Tin Phosphate Complexes

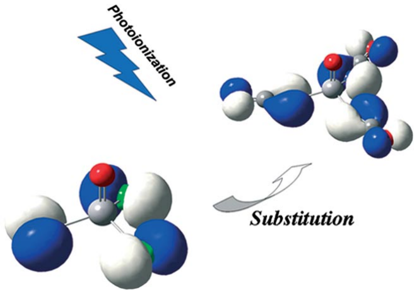
Keywords: Organotin compounds / Polymers / Cluster compounds / Precursors / X-ray structures



The reactions of sterically hindered monoaryl phosphates (RO)P(O)(OH)$_2$ with organotin halides and oxides were investigated and series of new organooxo tin derivatives were isolated and structurally characterized. A stoichiometry control operates to favor the isolation of two different types of 1D polymeric structure. Color code: green: Sn; yellow: P; red: O.

Gas-Phase OV(NCO)$_3$

OV(NCO)$_3$ was generated in the gas phase for the first time. The compound and its electronic structure have been investigated with photoionization mass spectroscopy, quantum chemical calculations, and ultraviolet photoelectron spectroscopy.

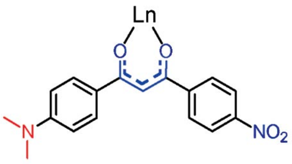


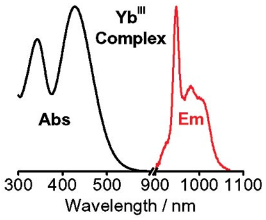
M. Ge,* W. Wang, S. Yin, C. O. Della Védova **1518–1522**

Gas-Phase Generation and Electronic Structure Investigation of Oxidovanadium Triisocyanate, OV(NCO)$_3$

Keywords: Vanadium / Photoelectron spectroscopy / Electronic structure / Mass spectrum

IR Lanthanide Luminescence





The presence of both an electron-donor and an electron-acceptor group in a 1,3-diketonato ligand created a low-energy charge-transfer absorption transition which was used for visible-light excitation of infrared luminescence of lanthanide ions.

N. M. Shavaleev, R. Scopelliti, F. Gumy, J.-C. G. Bünzli* **1523–1529**

Visible-Light Excitation of Infrared Lanthanide Luminescence via Intra-Ligand Charge-Transfer State in 1,3-Diketonates Containing Push-Pull Chromophores

Keywords: Lanthanide / Luminescence / Near infrared / Energy transfer / 1,3-Diketonate / Chromophore