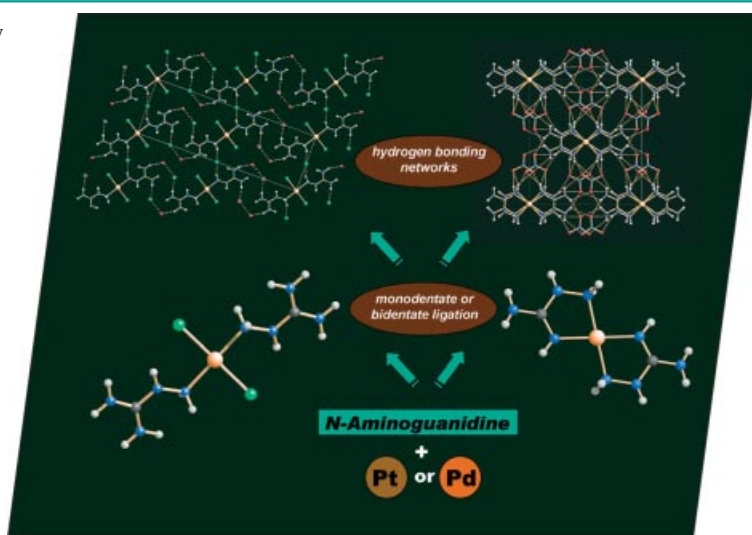




The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry*. Three further EUChemSoc Societies (Austria, Czech Republic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

## COVER PICTURE

The cover picture shows how aminoguanidine may behave as either a monodentate or bidentate ligand in square-planar complexes of platinum or palladium. In each case, the coordinating ligands can participate in extensive hydrogen-bonding networks. Details are discussed in the article by D. J. Aitken, J. Kozelka et al. on p. 3327 ff.



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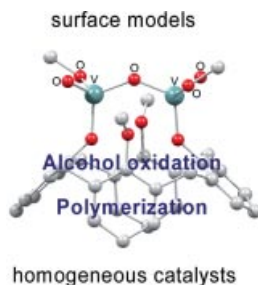
## MICROREVIEW

### Oxovanadium Calixarenes

C. Limberg\* ..... 3303–3314

Calixarene-Based Oxovanadium Complexes as Molecular Models for Catalytically Active Surface Species and Homogeneous Catalysts

**Keywords:** Vanadium / Oxo complexes / Models / Calixarenes / Catalysis



Oxovanadium calixarene complexes can be regarded as models for active surface species on vanadium oxide based heterogeneous catalysts, and their investigation thus contributes to a more comprehensive understanding of the effective mechanisms. In addition, they are interesting as homogeneous catalysts, for instance for aerobic alcohol oxidation and olefin polymerization.

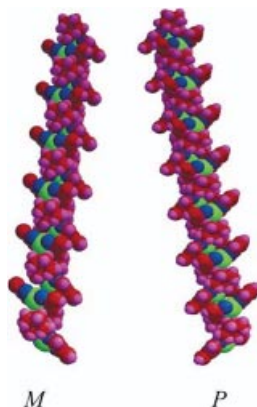
## SHORT COMMUNICATIONS

### Supramolecular Helical Assemblies

X.-F. Shan, L.-Z. Wu,\* X.-Y. Liu,  
L.-P. Zhang, C.-H. Tung ..... 3315–3319

C–H...Ni<sup>II</sup> Interaction-Driven Homochiral *M* and *P* Helices of Neutral (*R,R*)- and (*S,S*)-Bis(pyrrol-2-ylmethyleneamino)-cyclohexane Ni<sup>II</sup> Complexes

**Keywords:** Nickel(II) complexes / C–H...Ni<sup>II</sup> interactions / Helical structures



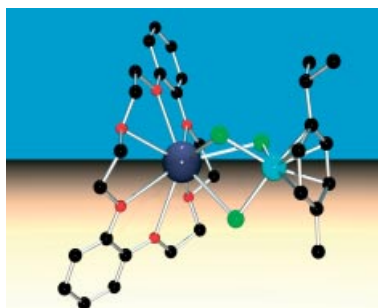
Reaction of (*R,R*)- and (*S,S*)-bis(pyrrol-2-ylmethyleneamino)cyclohexane with Ni<sup>II</sup>-(OAc)<sub>2</sub>·4H<sub>2</sub>O afforded enantiomeric nickel(II) Schiff-base complexes. Rare C–H...Ni<sup>II</sup> interactions were found to be responsible for the facile formation of the homochiral *M* and *P* helices of the neutral, chiral, mononuclear complexes in crystal lattices.

### Heterodimetallic Dinuclear Complexes

C. A. Vock, R. Scopelliti,  
P. J. Dyson\* ..... 3320–3322

Synthesis and Crystallographic Characterisation of the Heterodimetallic Complex [(Dibenzo-18-crown-6)K(μ-Cl)<sub>3</sub>Ru(η<sup>6</sup>-*p*-cymene)]

**Keywords:** Heterometallic complexes / Bridging ligands / Ruthenium / Crown compounds / X-ray crystallography



The first example of a triple-chlorido-bridged heterodimetallic dinuclear complex comprising an (η<sup>6</sup>-arene)Ru<sup>II</sup> fragment and a Group 1 metal crown ether fragment is presented. The solid-state structure was determined by X-ray crystallography. NMR investigations indicate the presence of a dynamic equilibrium in solution.

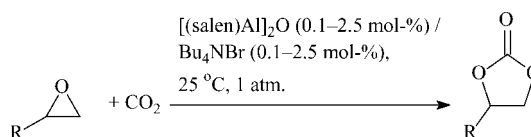
### Carbon Dioxide Fixation

J. Meléndez, M. North,\*  
R. Pasquale ..... 3323–3326



Synthesis of Cyclic Carbonates from Atmospheric Pressure Carbon Dioxide Using Exceptionally Active Aluminium(salen) Complexes as Catalysts

**Keywords:** Carbon dioxide fixation / Aluminium / Schiff bases / Epoxides / Catalysis

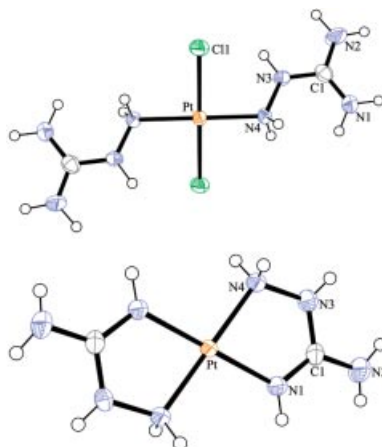


Dimetallic aluminium(salen) complexes show exceptionally high catalytic activity for the synthesis of cyclic carbonates from terminal epoxides at ambient temperature

and pressure. The process has the potential to contribute towards decreasing atmospheric carbon dioxide emissions from the burning of fossil fuels.

## FULL PAPERS

Aminoguanidine forms monodentate and bidentate complexes with  $\text{Pt}^{\text{II}}$  and  $\text{Pd}^{\text{II}}$ . A series of N4-bound monodentate and N1,N4-bound chelate complexes was synthesized and characterized by solution NMR and by X-ray crystallography. In the solid state, hydrogen-bonding networks were observed; all four nitrogens of the Amgu ligand are able to behave as hydrogen atom donors.



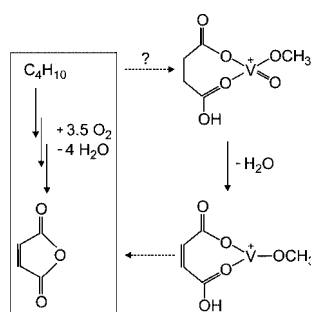
### Aminoguanidine Coordination Modes

D. J. Aitken,\* A. Albinati, A. Gautier,  
H.-P. Husson, G. Morgant, D. Nguyen-Huy,  
J. Kozelka,\* P. Lemoine, S. Ongeri,  
S. Rizzato, B. Viosat ..... 3327–3334

Platinum(II) and Palladium(II) Complexes  
with *N*-Aminoguanidine

**Keywords:** Platinum / Palladium / N li-  
gands / Coordination modes

Electrospray ionization is used for the investigation vanadium(V) complexes of maleic and succinic acid. The fragmentation patterns of the mass-selected ions *inter alia* reveal a hitherto unrecognized connection between succinato and maleato complexes, which may be relevant in the context of vanadium-oxide-mediated formation of maleic acid upon partial oxidation of  $\text{C}_4$ -hydrocarbons.

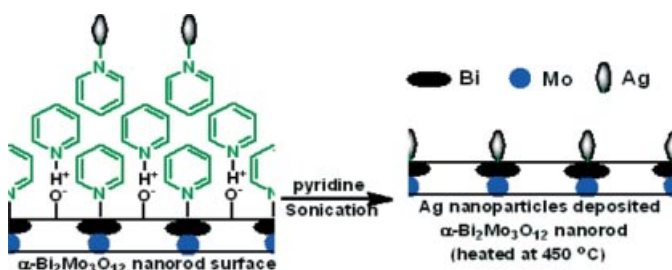


### Gas-Phase Fragmentation

M. Kaczorowska, H. Schwarz,  
D. Schröder\* ..... 3335–3341

Gas-Phase Fragmentation Behavior of  
Vanadium(V) Complexes Containing One  
Molecule of a  $\text{C}_4$ -Dicarboxylic Acid

**Keywords:** Carboxylato complexes / Va-  
nadium / Electrospray ionization / Maleic  
anhydride / Mass spectrometry



### Hybrid Nanocomposites

A. V. Ghule, K. Ghule, S.-H. Tzing,  
Y.-C. Ling\* ..... 3342–3349

Synthesis and Characterization of Silver-  
Nanoparticle-Deposited  $\alpha\text{-Bi}_2\text{Mo}_3\text{O}_{12}$   
Nanorods

**Keywords:** Nanoparticles / Ultrasound /  
Deposition / Nanorods / Surface analysis /  
Electron microscopy

Silver nanoparticles with an average size of about 10 nm were uniformly deposited on the surface of  $\alpha\text{-Bi}_2\text{Mo}_3\text{O}_{12}$  nanorods by using power ultrasound. Pyridine as a me-

dium assisted the deposition process of the Ag nanoparticles, whereas Bi was observed to be the preferred binding site on the surface of the nanorods.

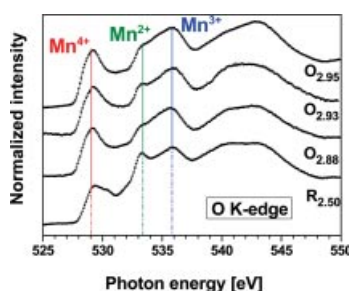
### Magnetic Perovskites

J. M. Alonso, R. Cortés-Gil,  
L. Ruiz-González, J. M. González-Calbet,\*  
A. Hernando, M. Vallet-Regí, M. E. Dávila,  
M. C. Asensio ..... 3350–3355

Influence of the Synthetic Pathway on the  
Properties of Oxygen-Deficient Mangan-  
ese-Related Perovskites

**Keywords:** Mixed-valent compounds /  
Perovskite phases / Magnetic properties /  
X-ray absorption near-edge spectroscopy  
(XANES) / Topotactic reaction

Oxygen-deficient manganites, with the same composition but different oxidation states of Mn, were stabilized through a reversible topotactic process using different pathways. Dramatic changes in the magnetic behaviour were observed due to the stabilization of different Mn oxidation states.



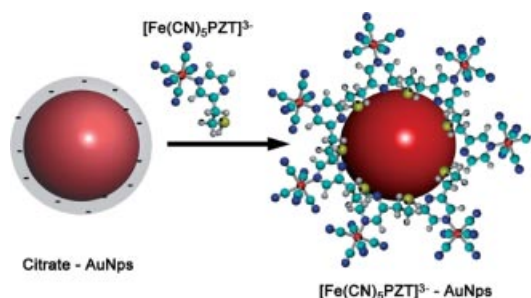
# CONTENTS

## Metal Nanoparticles

S. H. Toma, J. A. Bonacin, K. Araki,  
H. E. Toma\* ..... 3356–3364

Controlled Stabilization and Flocculation of Gold Nanoparticles by Means of 2-Pyrazin-2-ylethanethiol and Pentacyanidoferrate(II) Complexes

**Keywords:** Aggregation / Colloids / Semi-empirical calculations / Raman spectroscopy / UV/Vis spectroscopy / Charge transfer



Coordination of pentacyanidoferrates and 2-pyrazin-2-ylethanethiol exerts a strong influence on the flocculation of gold nano-

particles, giving rise to contrasting SERS effects.

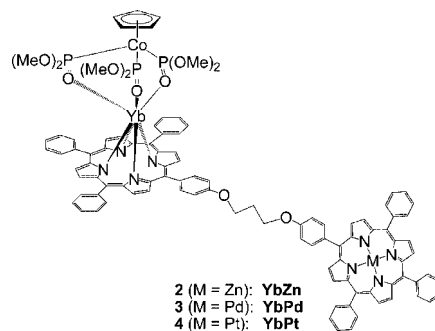
## Heterodimetallic Bisporphyrins

F.-L. Jiang, W.-K. Wong,\* X.-J. Zhu,  
G.-J. Zhou, W.-Y. Wong, P.-L. Wu,  
H.-L. Tam, K.-W. Cheah, C. Ye,  
Y. Liu\* ..... 3365–3374



Synthesis, Characterization, and Photophysical Properties of Some Heterodimetallic Bisporphyrins of Ytterbium and Transition Metals – Enhancement and Lifetime Extension of Yb<sup>3+</sup> Emission by Transition-Metal Porphyrin Sensitization

**Keywords:** Lanthanides / Optical limiting / Photoluminescence / Porphyrins / Transition metals



A series of heterodimetallic bisporphyrins of ytterbium and transition metals (**YbZn**, **YbPd**, and **YbPt**) have been synthesized and fully characterized. Their near-infrared photophysical studies show that the transition-metal porphyrinate unit enhances the Yb<sup>III</sup> emission and the Yb<sup>III</sup> lifetimes

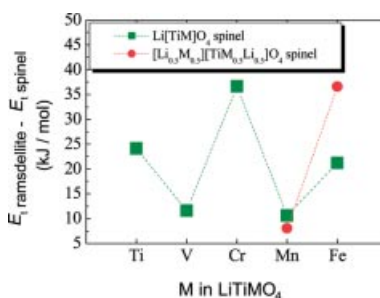
of **YbPd** and **YbPt** are extended because of sensitization of the <sup>3</sup>Pd(TPP)\* and <sup>3</sup>Pt(TPP)\* cores, respectively. The two-photon absorption and optical limiting properties of these mixed-metal complexes have also been investigated.

## Ramsdellites for Lithium Batteries

A. Kuhn, P. Díaz-Carrasco,  
M. E. Arroyo y de Dompablo,\*  
F. García-Alvarado\* ..... 3375–3384

On the Synthesis of Ramsdellite LiTiMO<sub>4</sub> (M = Ti, V, Cr, Mn, Fe): An Experimental and Computational Study of the Spinel–Ramsdellite Transformation

**Keywords:** Titanates / Phase transitions / Ab initio calculations / Solid-state reactions / Electrochemistry

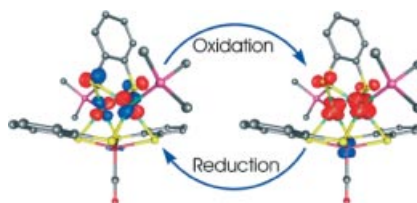


The LiTiMO<sub>4</sub> (spinel) ↔ LiTiMO<sub>4</sub> (ramsdellite) transformation is investigated by a combination of computational and experimental techniques for M = Ti, V, Cr, Mn, and Fe in order to understand the characteristics of this transformation.

## [NiFe] Hydrogenase Model Complex

F. Lauderbach, R. Prakash,\* A. W. Götz,\*  
M. Munoz, F. W. Heinemann, U. Nickel,  
B. A. Hess, D. Sellmann ..... 3385–3393

Alternative Synthesis, Density Functional Calculations and Proton Reactivity Study of a Trinuclear [NiFe] Hydrogenase Model Compound

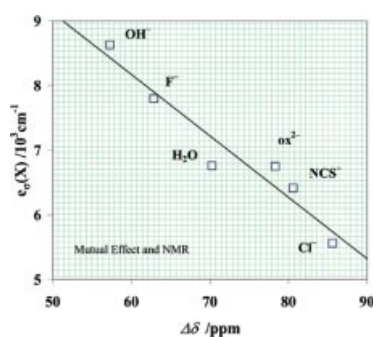


Reversible oxidation of a trinuclear [NiFe] hydrogenase model compound (see picture) can be employed electrochemically for the reduction of protons to dihydrogen at a mild reduction potential. Density functional theory calculations give an insight into the redox process. The trinuclear compound can be synthesized from simple metal salts without use of any precursor complexes.

**Keywords:** Constant potential coulometry / Density functional calculations / Iron / Nickel / NiFe hydrogenases / S ligands



The effect of the co-ligand (X) on the  $^2\text{H}$  NMR chemical shift difference ( $\Delta\delta$ ) for  $\text{trans-}[\text{CrX}_2(\text{D}_4\text{3,2,3-tet})]^{n+}$  and  $\text{cis-}\alpha\text{-}[\text{CrX}_2(\text{D}_4\text{trien})]^{n+}$  is found to correlate well with the reported  $e_\sigma(\text{X})$  values of these co-ligands, thereby demonstrating the first example of the co-ligand effect or a mutual influence of ligands associated with variation of the Cr–N and Cr–X bonds in *cis*- and *trans*- $[\text{CrX}_2\text{N}_4]$ -type complexes.



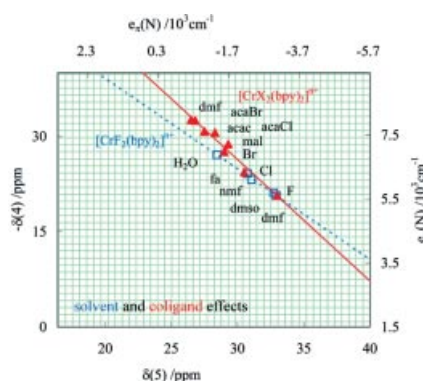
Y. Yamaguchi-Terasaki, T. Fujihara,  
S. Kaizaki\* ..... 3394–3399

Mutual Influences of Ligands as Revealed by  $^2\text{H}$  NMR Shifts and the Angular Overlap Model Parameters: *trans*- and *cis*- $[\text{CrX}_2(\text{N})_4]$ -Type Complexes with Aliphatic Amine Ligands

**Keywords:** Chromium complexes / Ligand effects / N ligands / NMR spectroscopy / Angular overlap model parameters

## Ligand Effects

The dependence of the  $^2\text{H}$  NMR shifts of  $\text{cis-}[\text{CrX}_2(\text{D}_4\text{bpy})_2]^{n+}$  and  $\text{fac-}[\text{CrX}_3(\text{D}_{12}\text{tpa})]^{n+}$  on the co-ligands X allows the ordering of the AOM parameter for monodentate and/or didentate ligands, from which the ranking of the two-dimensional spectrochemical series for  $\text{Cl}^-$  and  $\text{Br}^-$  is found to differ from that in the aliphatic amine complexes. This change is explained in terms of the hard/soft acid/base (HSAB) concept.



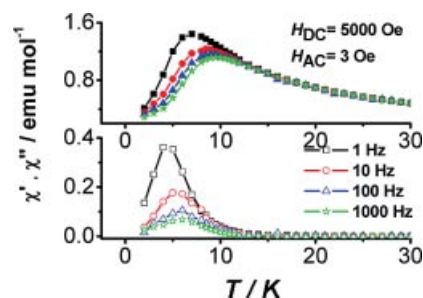
Y. Terasaki, T. Fujihara,  
S. Kaizaki\* ..... 3400–3404

Mutual Influences of Ligands as Revealed by the  $^2\text{H}$  NMR Chemical Shifts and the Angular Overlap Model Parameters: *cis*- $[\text{CrX}_2(\text{N})_4]$  and *fac*- $[\text{CrX}_3(\text{N})_3]$ -Type Complexes with Aromatic Amines

**Keywords:** Chromium complexes / Ligand effects / N ligands / NMR spectroscopy / Angular overlap model parameters

## Molecular Magnetism

A new lanthanide citrate  $[\text{Dy}(\text{citrate})(\text{H}_2\text{O})]_n$  (**1**) was hydrothermally synthesized and structurally characterized. The structure of **1** exhibits a 2D layer structure. The photoluminescence spectrum shows blue luminescence in the solid state at room temperature. Owing to the special frustration structure, unusual magnetic relaxation was found in compound **1**.



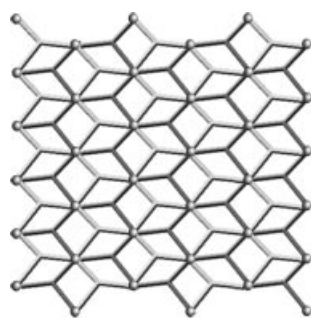
F.-Y. Li, L. Xu,\* G.-G. Gao,  
L.-H. Fan, B. Bi ..... 3405–3409

Unusual Magnetic Behavior of a 2D Citrate-Bridged Dysprosium(III) Coordination Polymer

**Keywords:** Lanthanides / Coordination chemistry / Magnetic properties / Hydrothermal synthesis

## Lanthanide–Organic Frameworks

Three novel LnOFs  $[\text{Ln}(\text{pza})(\text{OH})(\text{H}_2\text{O})]_n$  ( $\text{Ln} = \text{Y}, \text{Er}$  and  $\text{Yb}$ ) with helical chains and 2D  $(4^3)_2(4^6, 6^6, 8^3)$  topology were obtained by hydrothermal synthesis. The up-conversion properties resulting from two-photon excitation of Y: Er, Yb codoped coordination polymer and the magnetic properties of the Er and Yb complexes are investigated.



D. Weng, X. Zheng,\* X. Chen,  
L. Li, L. Jin\* ..... 3410–3415

Synthesis, Upconversion Luminescence and Magnetic Properties of New Lanthanide–Organic Frameworks with  $(4^3)_2(4^6, 6^6, 8^3)$  Topology

**Keywords:** Lanthanide–organic frameworks / Codoped coordination polymers / Upconversion properties / Magnetic properties

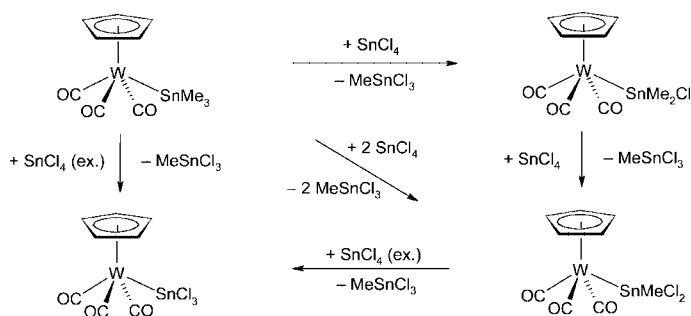
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## Organotin Complexes

H. Braunschweig,\* H. Bera, B. Geibel,  
R. Dörfler, D. Götz, F. Seeler, T. Kupfer,  
K. Radacki ..... 3416–3424

Synthesis of Half-Sandwich Tungsten  
Chlorogermyl and Chlorostannyl Com-  
plexes

**Keywords:** Half-sandwich complexes /  
Tungsten complexes / Germanes / Stann-  
anes / Stannylcyclopentadienes



A chlorination system is established, which enables a controlled and successive chlorination of a trimethylstannyl tungsten complex to the trichlorostannyl derivative via the isolable mono- and double-chlorinated compounds by use of  $\text{SnCl}_4$ . In addition, we proved that alkali salt elimination has

to be regarded as a straightforward route to synthesize a range of diorgano chlorogermyl and chlorostannyl tungsten complexes of the general formula  $[(\eta^5\text{-C}_5\text{R}'_5)\text{L}(\text{OC})_2\text{W}(\text{ER}_2\text{Cl})]$  ( $\text{R}' = \text{H, Me}$ ;  $\text{L} = \text{CO, PPh}_3$ ;  $\text{E} = \text{Ge, Sn}$ ;  $\text{R} = \text{Me, Bu}$ ).

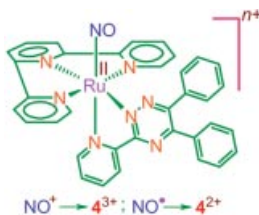
## Nitrosyl Complexes

S. Maji, C. Chatterjee, S. M. Mobin,  
G. K. Lahiri\* ..... 3425–3434



Synthesis and Spectro-electrochemical As-  
pects of  $[\text{Ru}^{\text{II}}(\text{trpy})(\text{pdt})(\text{X})]^n+$  ( $\text{trpy} =$   
 $2,2':6',2''\text{-Terpyridine}$ ,  $\text{pdt} = 5,6\text{-Diphen-}$   
 $\text{yl-3-pyridyl-as-triazine}$ ,  $\text{X} = \text{Cl}^-, \text{CH}_3\text{CN},$   
 $\text{NO}_2^-, \text{NO}^+, \text{NO}^-$ ) – Electrophilicity of  
 $\{\text{Ru}^{\text{II}}\text{-NO}^+\}$  and Photolability of  
 $\{\text{Ru}^{\text{II}}\text{-NO}\}$

**Keywords:** Ruthenium / Nitrosyl complex /  
Spectroscopy / Electrochemistry / Reac-  
tivity



Moderately electrophilic nitrosyl ( $\nu\text{NO}^+ =$   
 $1944 \text{ cm}^{-1}$ ) in  $4^{3+}$  transforms to the cor-  
responding nitro species in  $\text{CH}_3\text{CN}$  under  
alkaline conditions with a pseudo-first-  
order rate constant ( $k/s$ ) of  $4.13 \times 10^{-4}$  at  
298 K and on exposure of light  $4^{2+}$  un-  
dergoes slow photocleavage of the  
 $\text{Ru}^{\text{II}}\text{-NO}\cdot$  bond in  $\text{CH}_3\text{CN}$  with a  $k_{\text{NO}}$  of  
 $4.4 \times 10^{-3} \text{ min}^{-1}$  ( $t_{1/2} \approx 157 \text{ min}$ ).

If not otherwise indicated in the article, papers in issue 20 were published online on July 4, 2007