

to fabricate crystalline undoped and doped ZnO namely the liquid phase epitaxy (LPE) of thin films on ZnO substrates (2) and synthesis of microcrystals from low-alkaline solutions using mild hydrothermal conditions(3). Photo- and radioluminescence spectra were measured at the undoped and doped with In, Ge, and Sb ZnO thin films and hydrothermal ZnO crystals respectively. The effect of doping, zinc source, and experimental parameters was studied on the phase composition, crystal morphology and size, and luminescence. Molecular imprinted polymer nanoparticles (nanoMIPs) are often referred to artificial receptors. Hybridmaterials based on doped hydrothermal ZnO nanocrystals and nanoMIPs are supposed to work as a specific, nontoxic, and multifunctional label for modern bio-analytics and diagnostics as well as in down stream processing in chemical and pharmaceutical industry.

References

- (1) S. Derenzo et al., Nucl. Instrum. Methods Phys. Res., Sect. A 2002, 486, 214.
- (2) D. Ehrentraut et al., J. Cryst. Growth 2006, 287, 367.
- (3) K. Byrappa, T. Adschiri, Prog. Cryst. Growth Char. Mater. 2007, 53, 117; D. Ehrentraut, K. Byrappa, J. Riegler et al., Cryst. Growth Des. 2007, in press.

Keywords: hydrothermal, luminescence, hybridmaterials

MS.05.1

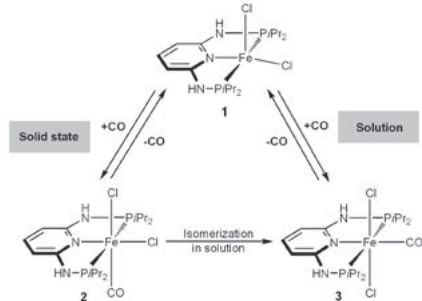
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Solid-state vs solution reactivity of iron complexes: Stereospecific and reversible CO binding

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Chemical transformations that occur in crystalline materials are very rare because most chemical reactions cause intramolecular reorganization, which typically results in the loss of crystallinity. We report here on novel solid-state (and solution) reactivities of iron complexes which maintain their crystallinity even upon CO uptake. When crystalline **1** is exposed to an atmosphere of CO, adsorption of the gas into the organoiron molecules was indicated by a color change of the material from light yellow to deep red, giving cis-[Fe(PNP)(CO)(Cl)₂] (**2**) as the sole product (Scheme 1). On the other hand, when CO was bubbled into a solution of **1** for two minutes, a blue solid precipitate was formed identified as the corresponding trans complex [Fe(PNP)(CO)(Cl)₂] (**3**). This process takes place stereospecifically and reversibly depending on the reaction conditions employed triggering changes in the color of the products, in the coordination geometry around the iron center, and in the spin states. Mechanistic aspects are discussed based on DFT calculations, solid-state NMR, and powder diffraction studies.



Keywords: gas sensors, CO binding, solid-state reactivity

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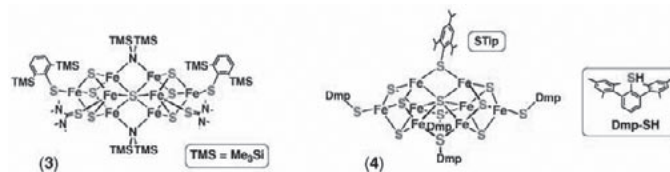
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A new synthetic route to iron-sulfide clusters modeling the active site of nitrogenase

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Recently, we developed a new method to synthesize Fe/S clusters, utilizing Fe{N(TMS)₂}₂ as the precursor. This route has allowed us to build Fe/S clusters in non-polar solvents, and resulted in a series of unprecedented cluster structures, which resemble closely the active sites of nitrogenase. We succeeded in reproducing the unusual [8Fe-7S] inorganic core structure of P-cluster (PN) of nitrogenase from a self-assembly reaction of Fe{N(TMS)₂}₂, SC(NMe₂)₂, HSTip, and S₈, which gave rise to [{N(TMS)₂}₂]{SC(NMe₂)₂}Fe₄S₃]₂(μ⁶-S){μ-N(TMS)₂}₂ (**1**). The cluster **1** consists of 6Fe(II)+2Fe(III) irons, while PN carries eight Fe(II)s. Although cluster **1** is unstable under the presence of thiols, it was possible to isolate (NEt₄)₂{N(TMS)₂}₂(SAr)Fe₄S₃]₂(μ⁶-S){μ-N(TMS)₂}₂ (**2**) and [(SAr){SC(NMe₂)₂}Fe₄S₃]₂(μ⁶-S){μ-N(TMS)₂}₂ (**3**) from careful treatments of (1) with corresponding thiolates and thiols. Yet another type of [8Fe-7S] cluster (**4**) was synthesized from the reaction of [Fe(Stip)]₂(μ-SDmp)₂ with S₈ in toluene, the structure of which links topologically FeMoco and P-cluster of nitrogenase and has an intriguing 5Fe(II)+3Fe(III) oxidation state with a doublet ground state.



Keywords: iron-sulfur cluster, nitrogenase, synthesis

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Advances in electrostatics and application to molecular reactivity

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Most important prerequisites for the reactivity of molecules are the prediction, interpretation and localization of the preferred sites of reactions. Molecular reactivity indicators generally correlate with the atomic charges, the molecular orbital densities and the electrostatic potential. Atomic bonding structures described in the theory of R.F.W. Bader gain acceptance in the field [1]. In this lecture, I will focus on the electrostatic potential, electric field and derived properties to rationalize the molecular interactions. The molecular surface of electrostatic potential defines the nucleophilic and electrophilic attack regions and the electric field assists in predicting the path of reactants in the vicinity of a molecule. The experimental approach of X-ray high resolution diffraction is used to derive these properties. Their computations are based on the Hansen-Coppens model of the electron density [2]. Molecular electrostatic potential

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surfaces and electric field lines are drawn and discussed in some cases of chemical reactivity prediction for molecules in the solid state. The topology of the electrostatic potential exhibits novel atomic basins where the total charge is zero. The quantum theory of Bader is used to establish the atomic bonding structures and chemical reactivity relationship. Finally, the interatomic force (pressure) [3] concept is introduced: the Ehrenfest and Feynman forces are computed for a set of chosen molecules to emphasize their contributions for a better molecular reactivity understanding.

[1] R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*. Oxford University Press, Oxford, 1990.

[2] N. Bouhmaida, M. Dutheil, N. E. Ghermani & P. Becker, *J. Chem. Phys.*, 2002, 116, No14, 6196.

[3] N. Bouhmaida & N. E. Ghermani *PCCP*, 2008, in press.

Keywords: molecular reactivity, electrostatic potential and electric field, ehrenfest & feynman forces.

MS.05.4

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Structural chemistry of 2-aza-1,3-dienes

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Since the solution of crystal structure of leading compound 1 ($\text{Ph}_2\text{C}(1)=\text{N}-\text{C}(2)(\text{H})=\text{C}(3)\text{X}_2$, $\text{X}=\text{Cl}$) we focused our attention on its capability of acting as a target for both the nucleophilic and the electrophilic attacks. One of the phenyl groups is roughly coplanar with azadienic chain suggesting so an extended pi-conjugation. The calculated electronic structure of 1 (B3LYP/6-311G) is compatible with that of butadiene, but shows a significant contribution of Cl atoms to the HOMO. The first nucleophilic attack occurs on C(2) atom with alkoxydes, cyanide and pyrrol anion, but C(3) carbon is preferred with thiolates and OPh. Such a regio - selectivity is rationalized by the hardness of incoming nucleophile calculated with DFT (hard nucleophile attacks on C(2) and the soft one on C(3)). A mentioned pi-conjugation of one phenyl ring with azadienic chain seems to operate in several molecules with $\text{X} = \text{Cl}, \text{OPh}, \text{SPh} \dots$ where the dihedral angles $\text{Ph}/\text{C}(1)\text{NC}(2)\text{C}(3)$ fall in the range of 10 to 38 deg. This effect is much stronger for free molecules (gas phase) as calculated with DFT (range of angles is 1 to 8 deg). Thus, the packing in the crystals partially leaves this conjugation. An oxidative addition is observed. The terminal chloride in Pt sigma-alkenyl complex may be substituted with a neutral (xylyl)NC ligand rising a spectacular linear pi-system delocalized on some 20 atoms. Substituted azadienes with $\text{X} = \text{SPh}$ and SiPr act as the ligands in complexes with Re, Mn, Cu, Hg, Pt and Pd. Generally, the chelates with five membered S_2N -metallacycles are formed. Orthometallation reactions predicted by DFT calculations are also observed in some cases.

Keywords: azadienes, chemical hardness, organometallics

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Iridium catalyzed hydrogenation with chiral ferrocenyl P-S ligands. X-ray structure of precatalysts

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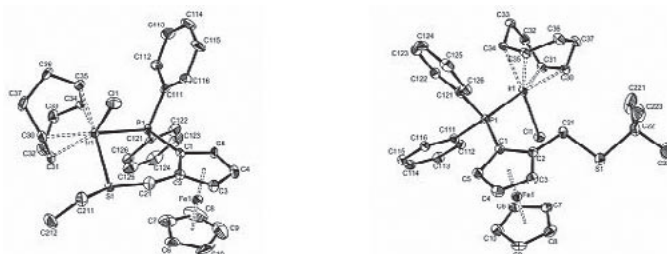
Iridium complexes of the new chiral ferrocenyl (P,S)R ligands $\text{CpFe}[1,2-\text{C}_5\text{H}_3(\text{PPh}_2)(\text{CH}_2\text{SR})]$ ($\text{R} = \text{Et}, \text{tBu}, \text{Ph}, \text{etc.}$), were successfully used in the hydrogenation of diphenylacetylene and in asymmetric hydrogenation simple ketones with high activities (turnover numbers up to 915 and global turnover frequencies up to ca. 250 h^{-1}) and enantioselectivities (ee up to 99%). The X-ray structural characterization of the precatalyst Ir complexes allowed to reveal that the coordination geometry of chlorocyclooctadieneiridium ligand adducts is delicately controlled by the nature of the R substituent, yielding five or four-coordinate complexes featuring then a dangling thioether group. Moreover, the ligand chirality controls the geometry at the sulfur and iridium atoms, producing single diastereomers.

Ref.

Malacea et al., *Eur. J. Inorg. Chem.*, 2006, 1803-1816.

Malacea, et al., *Dalton Trans.*, 2006, 3350-3359.

Le Roux et al., *Advanced Synthesis and Catalysis*, 2007, 349, 1064-1073.



Keywords: structural ferrocene chemistry, asymmetric catalysis by iridium, catalysts optimization

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Macromolecular refinement at subatomic resolution with interatomic scatterers

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The study of accurate electron-density distributions in molecular crystals at subatomic resolution (better than 1.0 \AA) requires more detailed models than those based on independent spherical atoms. We present a simple model composed of conventional independent spherical atoms augmented by additional scatterers to model bonding effects at high resolution. Refinement of these mixed models for several benchmark data sets gives results that are comparable in quality with the results of multipolar refinement and superior to those for conventional models. The application of this method to several data sets of both small molecules and macromolecules will be described as well as its implementation in the general-purpose macromolecular refinement module, phenix.refine, in the PHENIX software package.