

PREDICTING STRUCTURES AND ENERGETICS IN TRANSITION METAL POLYHYDRIDE COMPLEXES

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Density functional calculations make excellent predictions for the geometry and energy of stable structures for the tetrahydrides of cyclopentadienyl osmium phosphines and arsines and for the tetrahydrides of tris(pyrzoly)borato iridium. The latter seven-coordinate species are predicted to have an edge-bridged octahedral structure (C_s symmetry) rather than the expected face-bridged structure (C_{3v} symmetry). The calculations predict several other low energy structures that can be invoked to explain this species spectroscopy.

Keywords: POLYHYDRIDES QUANTUM CHEMISTRY DENSITY FUNCTIONAL THEORY

NEW METAL HYDRIDES CONTAINING TRANSITION METAL HYDROGEN COMPLEXES

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Metal hydrides containing transition metal hydrogen complexes provide new opportunities for efficient and safe hydrogen storage. Their hydrogen-to-metal ratios reach values of up to $H/M = 4.5$ ($BaReH_9$) and thus surpass the hydrogen-to-carbon ratios of hydrocarbons (methane : $H/C = 4$); their hydrogen volume efficiencies exceed that of liquid hydrogen by a factor of up to two (Mg_2FeH_6), their weight efficiencies exceed 5% (Mg_2MnH_7), and their hydrogen dissociation temperatures under 1 bar hydrogen pressure range from about 100°C ($NaKReH_9$) to 400°C ($CaMgNiH_4$). Their crystal chemistry is extremely rich and shows a large inventory of transition metal hydrido complexes that often conform to the 18-electron rule. The aim of current work is to find lighter and cheaper metal hydrides that decompose at or near ambient conditions, to develop new predictive concepts, to find new synthetic routes, and to understand the factors that govern metal hydride formation, hydrogen contents and thermal stability. In this talk some aspects of that work will be highlighted. Given the absence of suitable single crystals, most structure work has to be performed on polycrystalline samples. The importance of advanced radiation sources (synchrotrons and high-flux neutron sources), modern diffraction equipment and advances in powder diffraction methodology will be underlined.

Keywords: HYDRIDES HYDRIDO COMPLEXES TRANSITION METAL

INTERCONVERSION OF DIHYDROGEN AND HYDRIDE LIGANDS IN TRANSITION METAL COMPLEXES

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A particularly important aspect of the chemistry of dihydrogen ligands in transition metal complexes are the direct interactions between dihydrogen and hydride ligands, which can result in rapid exchange or interconversion among these species. The dynamics of this process can be faster than what can be probed by NMR, and may well contribute to the very large thermal ellipsoid observed in diffraction experiments on such compounds. We have carried out detailed inelastic neutron scattering (INS) studies over a wide range of temperatures on systems, where extremely rapid dihydrogen-hydride exchange is deduced from NMR. These include the series $IrXH_2(H_2)(P^iPr_3)_3$ here X is a halide, the Fe complex $FeH_2(H_2)(PEtPh_2)_2$, as well as the Rh complex $Tp^+RhH_2(H_2)$. The results show that the presence of dihydrogen-hydride exchange is evident in the high temperature quasielastic neutron scattering spectrum from these ligands. Both average jump distances for the motion of the hydrogens in this process and the associated activation energies have been derived from the neutron scattering data and can be related to structural and energetic results obtained from diffraction and theoretical studies.

The work described in this talk is part of several close collaborations, primarily with the groups of M. B. Hall and C. M. Jensen, and with E. Clot, A. Albinati and others.

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Keywords: DIHYDROGEN, TRANSITION METAL COMPLEXES, DYNAMICS

2D-3D TRANSITIONS IN LUNG SURFACTANT

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The primary function of lung surfactant is to form monolayers at the alveolar interface capable of lowering the normal surface tension to near zero. To accomplish this process, the surfactant must maintain a coherent, tightly packed monolayer that avoids collapse during expiration. Utilizing different microscopy techniques, we have observed that the positively charged amino-terminal peptide sequence SP-B1-25 in simple phospholipid and model lung surfactant monolayers promote the protrusion of folds into the subphase at low surface tensions. The folds remain attached to the monolayer, appear to be identical in composition to unfolded monolayer, and reversibly reincorporated upon expansion. Without SP-B, an unsaturated lipid-rich phase is irreversibly 'squeezed-out' of the monolayer at higher surface tensions. These folded reservoirs reconcile how lung surfactant can achieve both low surface tensions upon compression and rapid respreading upon expansion, and have important implications concerning the design of replacement lung surfactants. The 2D to 3D folding transition has also been observed in simple lipid systems, though never in pure DPPC monolayers. The addition of 'wedge' molecules like palmitic acid or hexadecanol to DPPC monolayers, however, yields folding transitions in these mixed lipid monolayers upon collapse. Using x-ray scattering techniques, we have probed how the presence of 'wedge' molecules affects the packing of the lipids. The alteration of the mechanical properties of the monolayer by the presence of the 'wedge' molecules may be responsible for the ability of the mixed film to collapse via folding. A theoretical model for the folding transition will be presented.

Keywords: LANGMUIR MONOLAYER, COLLAPSE, FOLDING INSTABILITY