Electron transfer (ET) is broadly described by Marcus-type theories, and plays a central role in many materials and catalytic systems and in biomolecules such as cytochromes. Classic ET processes are the self-exchange reactions between hydrated transition metal ions such as $\text{Fe}^{2+}(\text{aq}) + \text{Fe}^{3+}(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq}) + \text{Fe}^{2+}(\text{aq})$. A well-known anomaly of Marcus theory is $\text{Co}^{2+/3+}$ exchange, which proceeds $\sim 10^5$ times faster than predicted. $\text{Co}^{3+}(\text{aq})$ is a complex and reactive system widely thought to feature low-spin $\text{Co}^{3+}$. We studied the self-exchange process systematically for $\text{Cr}^{2+/3+}$, $\text{V}^{2+/3+}$, $\text{Fe}^{2+/3+}$, $\text{Co}^{2+/3+}$ using six distinct density functionals. We identify directly the $\sim 10^5$ anomaly of $\text{Co}^{2+/3+}$ from the electronic reorganization energies without use of empirical cross relations. Furthermore, when modeling $\text{Co}^{3+}$ as high-spin, the anomaly disappears, bringing all four processes on a linear trend within the uncertainty of experiment and theory. We studied both the acid-independent $[\text{Co(H}_2\text{O)}_6]^{3+}$ species that dominates at low pH, and the acid-dependent $[\text{Co(OH)(H}_2\text{O)}_5]^{2+}$ species that becomes important at higher pH, and use two distinct explicit second-sphere hydration models and models of perchlorate anion association. The high-spin state with weaker Co-O bonds is stabilized by vibrational energy and entropy by $\sim 11$ and $\sim 12$ kJ/mol, correcting gap estimates from absorption spectroscopy. High-spin $\text{Co}^{3+}(\text{aq})$ explains the full experimental data series of the $\text{M}(\text{aq})$. systems. Low-spin $\text{Co}^{3+}$ and high-spin $\text{Co}^{2+}$ involves changes in eg occupation upon electron transfer, with associated M-O bond changes and increased reorganization energy. In contrast, with high-spin $\text{Co}^{3+}(\text{aq})$ the redox-active electrons shuffle between t$_2$g orbitals to minimize structural changes, producing a relative rate in excellent agreement with experiment. This eg occupation effect explains most of the experimental differences in rate constants, with the remaining part explained by second-sphere hydration and anion effects. Our results consistently suggest that some high-spin $\text{Co}^{3+}(\text{aq})$ is active during the experiments.

Nature of Lone-Pair-Surface Bonds and Their Scaling Relations

We investigate the (surface) bonding of a class of industrially and biologically important molecules in which the chemically active orbital is a 2p electron lone pair located on an N or O atom bound via single bonds to H or alkyl groups. This class includes water, ammonia, alcohols, ethers, and amines. Using extensive density functional theory (DFT) calculations, we discover scaling relations (correlations) among molecular binding energies of different members of this class: the bonding energetics of a single member can be used as a descriptor for other members. We investigate the bonding mechanism for a representative ($\text{H}_2\text{O}$) and find the most important physical surface properties that dictate the strength and nature of the bonding through a combination of covalent and noncovalent electrostatic effects. We describe the importance of surface intrinsic electrostatic, geometric, and mechanical properties in determining the extent of the lone-pair-surface interactions. We study systems including ionic materials in which the surface positive and negative centers create strong local surface electric fields, which polarize the dangling lone pair and lead to a strong "electrostatically driven bond". We emphasize the importance of noncovalent electrostatic effects and discuss why a fully covalent picture, common in the current first-principles literature on surface bonding of these molecules, is not adequate to correctly describe the bonding mechanism and energy trends. By pointing out a completely different mechanism (charge transfer) as the major factor for binding N- and O-containing unsaturated (radical) adsorbates, we explain why their binding energies can be tuned independently from those of the aforementioned species, having potential implications in scaling-driven catalyst discovery.
Large Differences in the Optical Spectrum Associated with the Same Complex: The Effect of the Anisotropy of the Embedding Lattice

Transition-metal complexes with a well-defined geometry are usually considered to display almost the same properties independently of the system where they are embedded. Here we show that the above statement is not true depending on the anisotropy of the host lattice, which is revealed in the form of the electric field created by the rest of lattice ions over the complex. To illustrate this concept we analyze the origin of the surprisingly large differences in the d–d optical transitions of two systems containing square-planar CuF$_4^{2–}$ complexes, CaCuF$_4$, and center II in Cu$^{2+}$-doped Ba$_2$ZnF$_6$, even though the Cu$^{2+}$–F–distance difference is just found to be 1%. Using a minimalist first-principles model we show that the different morphology of the host lattices creates an anisotropic field that red-shifts the in vacuo complex transitions to the 1.25–1.70 eV range in CaCuF$_4$, while it blue-shifts them to the 1.70–3.0 eV region in Ba$_2$ZnF$_6$:Cu$^{2+}$. This particular example shows how the lattice anisotropy strongly alters the optical properties of a given transition-metal complex. This knowledge opens a new path to tune the spectra of this large family of systems.

Large_difficulties_in_the_optical_spectrum_associated_to_the_same_complex_the_effect_of_the_anisotropy_of_the_embedding_lattice.pdf. Embargo ended: 11/07/2018

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Research output: Contribution to journal › Journal article – Annual report year: 2017 › Research › peer-review
A Quantitative Scale of Oxophilicity and Thiophilicity

Oxophilicity and thiophilicity are widely used concepts with no quantitative definition. In this paper, a simple, generic scale is developed that solves issues with reference states and system dependencies and captures empirically known tendencies toward oxygen. This enables a detailed analysis of the fundamental causes of oxophilicity. Notably, the notion that oxophilicity relates to Lewis acid hardness is invalid. Rather, oxophilicity correlates only modestly and inversely with absolute hardness and more strongly with electronegativity and effective nuclear charge. Since oxygen is highly electronegative, ionic bonding is stronger to metals of low electronegativity. Left-side d-block elements with low effective nuclear charges and electro-negativities are thus highly oxophilic, and the f-block elements, not because of their hardness, which is normal, but as a result of the small ionization energies of their outermost valence electrons, can easily transfer electrons to fulfill the electron demands of oxygen. Consistent with empirical experience, the most oxophilic elements are found in the left part of the d block, the lanthanides, and the actinides. The d-block elements differ substantially in oxophilicity, quantifying their different uses in a wide range of chemical reactions; thus, the use of mixed oxo- and thiophilic (i.e., “mesophilic”) surfaces and catalysts as a design principle can explain the success of many recent applications. The proposed scale may therefore help to rationalize and improve chemical reactions more effectively than current qualitative considerations of oxophilicity.
Electron Transfer and Solvent-Mediated Electronic Localization in Molecular Photocatalysis
This work provides a detailed mechanism for electron transfer in a heterodinuclear complex designed as a model system in which to study homogeneous molecular photocatalysis. With efficient Born–Oppenheimer molecular dynamics simulations, we show how intermediate, charge-separated states can mediate the electron transfer. We observe how Jahn–Teller distortion effects play out in solution, when the molecule has energetically close-lying states, and how this distortion is averaged out in the thermal sampling. Finally, we demonstrate how the solvent helps stabilize and localize the separated charge. The information on the electronic configuration and separate states is of key importance for designing next-generation photocatalysts.

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Contributors: Dohn, A. O., Kjær, K. S., Harlang, T. B., Canton, S. E., Nielsen, M. M., Møller, K. B.
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Theoretical Study of Spin Crossover in 30 Iron Complexes
Spin crossover was studied in 30 iron complexes using density functional theory to quantify the direction and magnitude of dispersion, relativistic effects, zero-point energies, and vibrational entropy. Remarkably consistent entropy–enthalpy compensation was identified. Zero-point energies favor high-spin by 9 kJ/mol on average; dispersion and relativistic effects both favor low-spin by 9 kJ/mol on average. These drivers dominate the thermodynamics (but not the transition nature) of SCO and should be considered in rational design of new spin crossover systems.

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Organisations: Department of Chemistry
Design of Single-Molecule Magnets: Insufficiency of the Anisotropy Barrier as the Sole Criterion

Determination of the electronic energy spectrum of a trigonal symmetry mononuclear Yb\textsuperscript{3+} single-molecule magnet (SMM) by high-resolution absorption and luminescence spectroscopies reveals that the first excited electronic doublet is placed nearly 500 cm\textsuperscript{-1} above the ground one. Fitting of the paramagnetic relaxation times of this SMM to a thermally activated (Orbach) model \( T = T_0 \times \exp \left[ \Delta_{\text{Orbach}}/(k_B T) \right] \) affords an activation barrier, \( \Delta_{\text{Orbach}} \), of only 38 cm\textsuperscript{-1}. This result is incompatible with the spectroscopic observations. Thus, we unambiguously demonstrate, solely on the basis of experimental data, that Orbach relaxation cannot \textit{a priori} be considered as the main mechanism determining the spin dynamics of SMMs. This study highlights the fact that the general synthetic approach of optimizing SMM behavior by maximization of the anisotropy barrier, intimately linked to the ligand field, as the sole parameter to be tuned, is insufficient because of the complete neglect of the interaction of the magnetic moment of the molecule with its environment. The Orbach mechanism is expected dominant only in the cases in which the energy of the excited ligand field state is below the Debye temperature, which is typically low for molecular crystals and, thus, prevents the use of the anisotropy barrier as a design criterion, for the realization of high-temperature SMMs. Therefore, consideration of additional design criteria that address the presence of alternative relaxation processes beyond the traditional double-well picture is required.
Growth of Highly Epitaxial YBa$_2$Cu$_3$O$_{7-\delta}$ Films from a Simple Propionate-Based Solution

Intensive investigations have been conducted to develop epitaxial oxide thin films with superior electromagnetic performance by low-cost chemical solution deposition routes. In this paper, a novel propionate-based precursor solution without involving any other additive was proposed and employed to grow superconducting YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) films on LaAlO$_3$ (LAO) single crystals. The precursor solutions are stable with a long shelf life of up to several months. Since the primary compositions are propionates after evaporating the solvent, the toxic reagents and evolved gases during solution synthesis and heat treatment can be eliminated completely. In this process, rapid pyrolysis and high conversion rate can also be achieved during growth of YBCO films in comparison with the conventional trifluoroacetate metal organic deposition routes. Remarkably, a 210 nm YBCO film exhibits high superconducting performance with a J$_c$ value of 3.7 MA/cm$^2$ at 77 K, self-field. Nucleation and growth behaviors in the chemical solution process have also been studied. It is revealed that the amount of liquid phase (Ba-Cu-O) is sufficient through the entire thickness within a very short time at high growth temperatures, which results in pronounced densification and fast conversion of the YBCO phase.

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Halide Binding and Inhibition of Laccase Copper Clusters: The Role of Reorganization Energy

Laccase-like proteins are multicopper oxidases involved in several biological and industrial processes. Their application is commonly limited due to inhibition by fluoride and chloride, and as-isolated proteins are often substantially activated by heat, suggesting that multiple redox states can complicate characterization. Understanding these processes at the molecular level is thus desirable but theoretically unexplored. This paper reports systematic calculations of geometries, reorganization energies, and ionization energies for all partly oxidized states of the trinuclear copper clusters in realistic models with similar to 200 atoms. Corrections for scalar-relativistic effects, dispersion, and thermal effects were estimated. Fluoride, chloride, hydroxide, or water was bound to the T2 copper site of the oxidized resting state, and the peroxo intermediate was also computed for reference. Antiferromagnetic coupling, assigned oxidation states, and general structures were consistent with known spectroscopic data. The computations show that (i) ligands bound to the T2 site substantially increase the reorganization energy of the second reduction of the resting state and reduce the redox potentials, providing a possible mechanism for inhibition; (ii) the reorganization energy is particularly large for F- but also high for Cl-, consistent with the experimental tendency of inhibition; (iii) reduction leads to release of Cl- from the T2 site, suggesting a mechanism for heat/reduction activation of laccases by dissociation of inhibiting halides or hydroxide from T2.

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Organisations: Department of Chemistry, Physical and Biophysical Chemistry
Contributors: Kepp, K. P.
Spectroscopic Characterization of a Monomeric, Cyclopentadienyl-Based Rhenium(V) Dioxo Complex

Mononuclear, coordinatively unsaturated rhenium(V) dioxo species of the type XReO₂ (X = Me, substituted cyclopentadienyl) have long been postulated as intermediates in rhenium-catalyzed deoxydehydration, but their characterization was precluded because of aggregation into dimeric or oligomeric structures. Using the bulky 1,2,4-tri-tert-butylcyclopentadienyl (Cpttt) ligand, the rhenium(V) dioxo species (Cpttt)ReO₂ could now be observed, in equilibrium with the dimeric form [(Cpttt)Re(O)μ-O]₂, and characterized by NMR, IR, and UV-Vis spectroscopies, as well as electrospray ionization mass spectrometry. (Cpttt)ReO₂ is shown to be the primary product of reduction of the rhenium(VII) complex (Cpttt)ReO₃ with PPh₃ and demonstrated to react with ethylene glycol significantly faster than its dimeric counterpart, supporting its role as an intermediate in rhenium-catalyzed deoxydehydration reactions.

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Incorporation of Monovalent Cations in Sulfate Green Rust

Green rust is a naturally occurring layered mixed-valent ferrous-ferric hydroxide, which can react with a range of redox-active compounds. Sulfate-bearing green rust is generally thought to have interlayers composed of sulfate and water. Here, we provide evidence that the interlayers also contain monovalent cations, using X-ray photoelectron spectroscopy and synchrotron X-ray scattering. For material synthesized with Na⁺, K⁺, Rb⁺, or Cs⁺, interlayer thickness derived from basal plane spacings correlates with the radius of the monovalent cation. In addition, sequential washing of the materials with water showed that Na⁺ and K⁺ were structurally fixed in the interlayer, whereas Rb⁺ and Cs⁺ could be removed, resulting in a decrease in the basal layer spacing. The incorporation of cations in the interlayer opens up new possibilities for the use of sulfate green rust for exchange reactions with both anions and cations: e.g., radioactive Cs.

Magnetic Interactions Through Fluoride: Magnetic and Spectroscopic Characterization of Discrete, Linearly Bridged \([\text{Mn}^\text{III} \_2(\mu-\text{F})_2(\text{Me}_3\text{tacn})_2][\text{PF}_6]\)

The nature of the magnetic interaction through fluoride in a simple, dinuclear manganese(III) complex (1), bridged by a single fluoride ion in a perfectly linear fashion, is established by experiment and density functional theory. The magnitude of the antiferromagnetic exchange interaction and the manganese(III) zero-field-splitting parameters are unambiguously determined by inelastic neutron scattering to yield \(J = 33.0(2)\, \text{cm}^{-1}\) \((\tilde{H} = \tilde{S}_1 \cdot \tilde{S}_2\) Hamiltonian definition) and single-ion \(D = -4.0(1)\, \text{cm}^{-1}\). Additionally, high-field, high-frequency electron paramagnetic resonance and magnetic measurements support the parameter values and resolve \(|E| = 0.04\, \text{cm}^{-1}\). The exchange coupling constant \((J)\) is 1 order of magnitude smaller than that found in comparable systems with linear oxide bridging but comparable to typical magnitudes through cyanide, thus underlining the potential of fluoride complexes as promising building blocks for novel magnetic systems.
Quantifying Local and Cooperative Components in the Ferroelectric Distortion of BaTiO$_3$: Learning from the Off-Center Motion in the MnCl$_6^{5–}$ Complex Formed in KCl:Mn$^+$

The delicate balance between cooperative and local contributions in the ferroelectric distortions of BaTiO$_3$ is explored by means of ab initio calculations. As a salient feature, it is found that a single Ti$^{4+}$ ion in BaTiO$_3$ is not allowed to move off-center at ambient pressure, while this is no longer true if the lattice is expanded by only ~5%, stressing the high sensitivity of the local contribution to chemical and hydrostatic pressures. In order to further understand the effect of local contributions on the phase transition mechanism of ferroelectrics, we have investigated the surprising C$_3v$ → C$_4v$ → Oh local transformations occurring in the 10–50 K temperature range for the MnCl$_6^{5–}$ complex formed in KCl:Mn$^+$ that mimic the behavior of BaTiO$_3$. From Boltzmann analysis of the vibronic levels derived from ab initio calculations and considering decoherence introduced by random strains, the present calculations reproduce the experimental phase sequence and transition temperatures. Furthermore, our calculations show that the off-center instability in KCl:Mn$^+$ would be suppressed by reducing by only 1% the lattice parameter, a situation that then becomes comparable to that found for BaTiO$_3$ at ambient pressure. The present results thus stress the deep link between the structural phase transitions of ferroelectric materials and local phase transitions displayed by transition-metal impurities in insulators.

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Synthesis and Characterization of Divalent Manganese, Iron, and Cobalt Complexes in Tripodal Phenolate/N-Heterocyclic Carbene Ligand Environments

Two novel tripodal ligands, (BIMPNMes,Ad,Me)$_–$ and (MIMPNMes,Ad,Me)$_2$–, combining two types of donor atoms, namely, NHC and phenolate donors, were synthesized to complete the series of N-anchored ligands, ranging from chelating species with tris(carbene) to tris(phenolate) chelating arms. The complete ligand series offers a convenient way of tuning the electronic and steric environment around the metal center, thus, allowing for control of the complex’s reactivity. This series of divalent complexes of Mn, Fe, and Co was synthesized and characterized by 1H NMR, IR, and UV/vis spectroscopy as well as by single-crystal X-ray diffraction studies. Variable-temperature SQUID magnetization
measurements in the range from 2 to 300 K confirmed high-spin ground states for all divalent complexes and revealed a trend of increasing zero-field splitting $|D|$ from Mn(II), to Fe(II), to Co(II) complexes. Zero-field $^{57}$Fe Mössbauer spectroscopy of the Fe(II) complexes 3, 4, 8, and 11 shows isomer shifts $\delta$ that increase gradually as carbenes are substituted for phenolates in the series of ligands. From the single-crystal structure determinations of the complexes, the different steric demand of the ligands is evident. Particularly, the molecular structure of 1 in which a pyridine molecule is situated next to the Mn–Cl bond and those of azide complexes 2, 4, and 6 demonstrate the flexibility of these mixed-ligand derivatives, which, in contrast to the corresponding symmetrical TIMENR ligands, allow for side access of, e.g., organic substrates, to the reactive metal center.

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Cu$^{2+}$ in Layered Compounds: Origin of the Compressed Geometry in the Model System K$_2$ZnF$_4$:Cu$^{2+}$
Many relevant properties (including superconductivity and colossal magnetoresistance) of layered materials containing Cu$^{2+}$, Ag$^{2+}$, or Mn$^{3+}$ ions are commonly related to the Jahn–Teller instability. Along this line, the properties of the CuF$_6^{4-}$ complex in the K$_2$ZnF$_4$ layered perovskite have recently been analyzed using a parametrized Jahn–Teller model with an imposed strain [Reinen, D. Inorg. Chem.2012, 51, 4458]. Here, we present results of ab initio periodic supercell and cluster calculations on K$_2$ZnF$_4$:Cu$^{2+}$, showing unequivocally that the actual origin of the unusual compressed geometry of the CuF$_6^{4-}$ complex along the crystal c axis in that tetragonal lattice is due to the presence of an electric field due to the crystal surrounding the impurity. Our calculations closely reproduce the experimental optical spectrum. The calculated values of the equilibrium equatorial and axial Cu$^{2+}$–F$^-$ distances are, respectively, $R_{ax} = 193$ pm and $R_{eq} = 204$ pm, and so the calculated distortion $R_{ax} - R_{eq} = 11$ pm is three times smaller than the estimated through the parametrized Jahn–Teller model. As a salient feature, we find that if the CuF$_6^{4-}$ complex would assume a perfect octahedral geometry ($R_{ax} = R_{eq} = 203$ pm) the antibonding $\Delta_{1g}^\prime(\sim 3z^2 - r^2)$ orbital is placed above $\Delta_{1g}^\prime(\sim x^2 - y^2)$, with a transition energy $E(\Delta_{1g}^\prime \rightarrow \Delta_{1g}^\prime) = 0.34$ eV. This surprising fact stresses that about half the experimental value $E(\Delta_{1g}^\prime \rightarrow \Delta_{1g}^\prime) = 0.70$ eV is not due to the small shortening of the axial Cu$^{2+}$–F$^-$ distance, but it comes from the electric field, $E_F(r)$, created by the rest of the lattice ions on the CuF$_6^{4-}$ complex. This internal field, displaying tetragonal symmetry, is thus responsible for the compressed geometry in K$_2$ZnF$_4$:Cu$^{2+}$ and the lack of symmetry breaking behind the ligand relaxation. Moreover, we show that the electronic energy gain in this process comes from bonding orbitals and not from antibonding ones. The present results underline the key role played by ab initio calculations for unveiling all the complexity behind the properties of the model system K$_2$ZnF$_4$:Cu$^{2+}$, opening at the same time a window for improving our knowledge on d$^9$, d$^7$, or d$^4$ ions in other layered compounds.

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Contributors: Aramburu, J. A., García Lastra, J. M., García-Fernández, P., Barriuso, M. T., Moreno, M.
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The structure of ferric iron (Fe^{3+}) dimers in aqueous solutions has long been debated. In this work, we have determined the dimer structure in situ in aqueous solutions using extended X-ray absorption fine structure (EXAFS) spectroscopy. An Fe K-edge EXAFS analysis of 0.2 M ferric nitrate solutions at pH 1.28–1.81 identified a Fe–Fe distance at ∼3.6 Å, strongly indicating that the dimers take the μ-oxo form. The EXAFS analysis also indicates two short Fe–O bonds at ∼1.80 Å and ten long Fe–O bonds at ∼2.08 Å, consistent with the μ-oxo dimer structure. The scattering from the Fe–Fe paths interferes destructively with that from paths belonging to Fe(OH)^{2+}\text{6}\text{3+} monomers that coexist with the dimers, leading to a less apparent Fe shell in the EXAFS Fourier transform. This might be a reason why the characteristic Fe–Fe distance was not detected in previous EXAFS studies. The existence of μ-oxo dimers is further confirmed by Mössbauer analyses of analogous quick frozen solutions. This work also explores the electronic structure and the relative stability of the μ-oxo dimer in a comparison to the dihydroxo dimer using density function theory (DFT) calculations. The identification of such dimers in aqueous solutions has important implications for iron (bio)inorganic chemistry and geochemistry, such as understanding the formation mechanisms of Fe oxyhydroxides at molecular scale.
model system NaCl:Ni+. This system is particularly puzzling because, according to experimental data, its barrier is much smaller than that for other d⁹ and d⁷ ions in similar lattices. All calculations performed on the model system lead, in fact, to values |B| ≤ 160 cm⁻¹, which are certainly smaller than B = 500 cm⁻¹ derived for NaCl:M²⁺ (M = Ag, Rh) or B = 1024 cm⁻¹ obtained for KCl:Ag⁺. As a salient feature, analysis of calculations carried out as a function of the Qθ (3z² – r²) coordinate unveils the microscopic origin of the barrier. It is quantitatively proven that the elongated geometry observed for NaCl:Ni⁺ is due to the 3d–4s vibronic admixture, which is slightly larger than the anharmonicity in the e_g JT mode that favors a compressed geometry. The existence of these two competing mechanisms explains the low value of B for the model system, contrary to cases where the complex formed by d⁹ or d⁷ ions is elastically decoupled from the host lattice. Although the magnitude of B for NaCl:Ni⁺ is particularly small, the tunneling splitting, 3Γ, is estimated to be below 9 cm⁻¹, thus explaining why the coherence is easily destroyed by random strains and thus a static JT effect is observed experimentally. As a main conclusion, the barrier in JT systems cannot be understood neglecting the tiny changes of the electronic density involved in small distortions. The present calculations reasonably explain the experimental g tensor of NaCl:Ni⁺, pointing out that the d–d transitions in NiCl₆⁵⁻ are much smaller than those for CuCl₆⁴⁻ and the optical electronegativity of Ni⁺ is only around 1.

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Structure and Magnetic Properties of Cu₃Ni₂SbO₆ and Cu₃Co₂SbO₆ Delafossites with Honeycomb Lattices
The crystal structures of two Delafossites, Cu₃Ni₂SbO₆ and Cu₃Co₂SbO₆, are determined by high-resolution synchrotron powder X-ray diffraction. The Ni and Co are ordered with respect to Sb in the layer of edge sharing octahedra, forming magnetic layers with honeycomb geometry. High-resolution electron microscopy confirms ordering, and selected-area electron diffraction patterns identify examples of the stacking polytypes. Low temperature synthetic treatments result in disordered stacking of the layers, but heating just below their melting points results in nearly fully ordered stacking variants. The major variant in both cases is a monoclinic distortion of a 6-layer Delafossite polytype, but a significant amount of a 2-layer polytype is also present for the Ni case. The antiferromagnetic ordering with transitions, at 22.3 and 18.5 K for Ni and Co variants, respectively, is investigated by temperature and field dependent magnetization, as well as specific heat. The sharp magnetic transitions support the presence of well developed 2:1 ordering of the Co:Sb or Ni:Sb ions in the honeycomb layers. Neutron diffraction measurements at 4 K are used to determine the magnetic structures. For both the Ni and Co phases, the propagation vector is k = [100], and can be described as alternating ferromagnetic chains in the metal-oxide plane giving an overall antiferromagnetic “zigzag” alignment. While orientation of the magnetic moments of the Co is along the b-axis, the Ni moments are in the ac plane, approximately parallel to the stacking direction. Bulk magnetization properties are discussed in terms of their magnetic structures.

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**A Copper(II) Thiolate from Reductive Cleavage of an S-Nitrosothiol**

S-Nitrosothiols RSNO represent circulating reservoirs of nitric oxide activity in the plasma and play intricate roles in protein function control in health and disease. While nitric oxide has been shown to reductively nitrosylate copper(II) centers to form copper(I) complexes and ENO species (E = R2N, RO), well-characterized examples of the reverse reaction are rare. Employing the copper(I) beta-diketiminate [Me2NN]Cu, we illustrate a clear example in which an RS NO bond is cleaved to release NO g with formation of a discrete copper(II) thiolate. The addition of Ph3CSNO to [Me2NN]Cu generates the three-coordinate copper(H) thiolate [Me2NN]CuSCPh3, which is unstable toward free NO.

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Fluoride Bridges as Structure-Directing Motifs in 3d-4f Cluster Chemistry

The use of kinetically robust chromium(III) fluorido complexes as synthons for mixed 3d-4f clusters is reported. The tendency toward linear \{Cr^{III}–F–Ln^{III}\} units dictates the cluster topology. Specifically, we show that reaction of cis-[Cr^{III}F_2(NN)]NO_3 (NN = 1,10-phenanthroline ("phen") or 2,2'-bipyridine ("bpy")) with Ln(NO_3)_3·xH_2O produces isostructural series of molecular \{Ln_2Cr_2\} squares (1–9) with linear fluoride bridges. In a parallel fashion, fac-[Cr^{III}F_3L], where L = N,N',N'-trimethyl-1,4,7-triazacyclononane ("Me_3tacn"), reacts with Nd(NO_3)_3·6H_2O to form a fluoride-centered pentanuclear complex and fac-[Cr^{III}F_3L'], with L' = 1,1,1-tris((methylamino)methylethane) ("Me_3tame"), reacts with [Ln(hfac)_3(H_2O)_2] (hfacH = 1,1,1,5,5,5-hexafluoroacetylacetone) to yield an isostructural series of \{Ln_3Cr_2\} (10–14) trigonal bipyramids with no central ligand. The formation of the latter is accompanied by a partial solvolysis of the Cr(III) precursor but without formation of insoluble LnF_3. The magnetic properties of the gadolinium-containing clusters allow quantification of fluoride-mediated, antiferromagnetic Gd–Cr exchange interactions of magnitude between 0.14 cm\(^{-1}\) and 0.71 cm\(^{-1}\) (\(\hat{H} = J_{12}\hat{S}_1\cdot\hat{S}_2\) formalism) and vanishingly small \(J_{Gd–Gd}\) of 0.06(0) cm\(^{-1}\). The large spin and small anisotropy together with weak exchange interactions in the \{Gd_3Cr_2\} (11) cluster give rise to a very large magneto-caloric effect of \(\Delta S_m = 28.7\) J kg\(^{-1}\) K\(^{-1}\) (\(\mu_0H = 90\) to 0 kOe).

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Spin 1/2 Delafossite Honeycomb Compound Cu5SbO6

Cu5SbO6 is found to have a monoclinic, Delafossite-derived structure consisting of alternating layers of O–Cu(I)–O sticks and magnetic layers of Jahn–Teller distorted Cu(II)O6 octahedra in an edge sharing honeycomb arrangement with Sb(V)O6 octahedra. This yields the structural formula Cu(I)3Cu(II)2Sb(V)O6. Variants with ordered and disordered layer stacking are observed, depending on the synthesis conditions. The spin 1/2 Cu2+ ions form dimers in the honeycomb layer. The magnetic susceptibility measured between 5 and 300 K is characteristic of the presence of a singlet–triplet spin gap of 189 K. High resolution synchrotron X-ray diffraction studies indicate that changes in the intra- or interdimer distances between 300 and 20 K, such as might indicate an increase in strength of the Peierls-like distortion through the spin gap temperature, if present, are very small. A comparison to the NaFeO2-type Cu2+ honeycomb compounds Na3Cu2SbO6 and Na2Cu2TeO6 is presented.

General Information

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Synthesis and Characterization of \((\text{smif})_2M-n\) (n=0, M = V, Cr, Mn, Fe, Co, Ni, Ru; n =+1, M = Cr, Mn, Co, Rh, Ir; smif=1,3-di-(2-pyridyl)-2-azaallyl)

A series of Werner complexes featuring the tridentate ligand smif, that is, 1,3-di-(2-pyridyl)-2-azaallyl, have been prepared. Syntheses of \((\text{smif})_2M\) (1-M; M = Cr, Fe) were accomplished via treatment of \(M(\text{NSiMe}_3)(2)(\text{THF})(n)\) (M = Cr, n = 2; Fe, n = 1) with 2 equiv of \((\text{smif})H\) (1,3-di-(2-pyridyl)-2-azapropene); ortho-methylated \((\text{oMes})\text{smif}(2)Fe\) (2-Fe) and \((\text{oMe})\text{smif}(2)Fe\) (3-Fe) were similarly prepared. Metatheses of \(MX_2\) variants with 2 equiv of \(\text{Li(smif)}\) or \(\text{Na(smif)}\) generated 1-M (M = Cr, Mn, Fe, Co, Ni, Zn, Ru). Metathesis of \(VCl_3(\text{THF})(3)\) with 2 \(\text{Li(smif)}\) with a reducing equiv of \(\text{Na/Hg}\) present afforded 1-V, while 2 \(\text{Na(smif)}\) and \(\text{IrCl}_3(\text{THF})_3\) in the presence of \(\text{NaBPh}_4\) gave \(\{(\text{smif})(2)\text{Ir}\}B\text{Ph}_4\) (1(+)-Ir). Electrochemical experiments led to the oxidation of 1-M (M = Cr, Mn, Co) by \(\text{AgOTf}\) to produce \(\{(\text{smif})(2)\text{M}\}\text{OTf}\) (1(+)-M), and treatment of \(\text{Rh}-2(\text{O}_2\text{CCF}_3)(4)\) with 4 equiv \(\text{Na(smif)}\) and 2 \(\text{AgOTf}\) gave 1(+)-Rh. Characterizations by NMR, EPR, and UV-vis spectroscopies, SQUID magnetometry, X-ray crystallography, and DFT calculations are presented. Intraligand (IL) transitions derived from promotion of electrons from the unique \(\text{CNCnb}\) (nonbonding) orbitals of the smif backbone to ligand \(\pi^*\)-type orbitals are intense (epsilon approximate to 10 000-60 000 M(1)cm(-1)), dominate the UV-visible spectra, and give crystals a metallic-looking appearance. High energy K-edge spectroscopy was used to show that the smif in 1-Cr is redox noninnocent, and its electron configuration is best described as \((\text{smif}(-))(\text{smif}(-))\text{Cr(III)}\); an unusual S = 1 EPR spectrum (X-band) was obtained for 1-Cr.

Bond Shortening (1.4 Å) in the Singlet and Triplet Excited States of \([\text{Ir}_2(\text{dimen})_4]^{2+}\) in Solution Determined by Time-Resolved X-ray Scattering
Ground- and excited-state structures of the bimetallic, ligand-bridged compound \( \text{Ir}_2(\text{dimen})_4^{2+} \) are investigated in acetonitrile by means of time-resolved X-ray scattering. Following excitation by 2 ps laser pulses at 390 nm, analysis of difference scattering patterns obtained at eight different time delays from 250 ps to 300 ns yields a triplet excited-state distance between the two Ir atoms of 2.90(2) Å and a triplet excited-state lifetime of 410(70) ns. A model incorporating the presence of two ground-state structures differing in Ir–Ir separation is demonstrated to fit the obtained data very well, in agreement with previous spectroscopic investigations. Two ground-state isomers with Ir–Ir separations of 3.60(9) and 4.3(1) Å are found to contribute equally to the difference scattering signal at short time delays. Further studies demonstrate the feasibility of increasing the effective time resolution from the ∼100 ps probe width down to the 10 ps regime by positioning the laser pump pulse at selected points in the X-ray probe pulse. This approach is used to investigate the structures of both the singlet and the triplet excited states of \( \text{Ir}_2(\text{dimen})_4^{2+} \).

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Light-Induced Copper(II) Coordination by a Bicyclic Tetraaza Chelator through a Ligand-to-Metal Charge-Transfer Reaction
To enable utilization of the broad potential of copper isotopes in nuclear medicine, rapid and robust chelation of the copper is required. Bowl adamanzanes (bicyclic tetraaza ligands) can form kinetically stable copper complexes, but they are usually formed at low rates unless high pH values and high temperatures are applied. We have investigated the effects of the variation in the pH, different anions, and UV irradiation on the chelation rate. UV spectra of mixtures of Cu(II) and \( [24.31] \text{adz} \) in water show the existence of a long-lived two-coordinated copper(II) intermediate (only counting coordinated amine groups) at pH above 6. These findings are supported by pH titrations of mixtures of Cu(II) and \( [24.31] \text{adz} \) in water. Irradiation of this complex in the ligand-to-metal charge-transfer (LMCT) band by a diode-array spectrophotometer leads to photodeprotonation and subsequently to formation of the four-coordinated copper(II) complex at a rate up to 7800-fold higher at 25 °C than in the dark. Anions in the solution were found to have three major effects: competitive inhibition due to Cu(II) binding anions, inhibition of the photoinduced transchelation from UV-absorbing anions, and photoredox inhibition from acido ligands capable of acting as electron donors in LMCT reactions. Dissolved O2 was also found to result in photoredox inhibition.

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Magnetic Properties of a Manganese(III) Chain with Monoatomic Bridges: catena-MnF(salen)

In the solid state, MnF(salen) forms chains wherein fairly linear fluoride bridges between high-spin Mn$^{III}$ centers are observed. We interpret the magnetic properties of these chains by use of the classical Fisher model and by use of the high-temperature expansion approach, as well as by exact matrix diagonalization of the spin Hamiltonian, of model rings. In solution, electron paramagnetic resonance shows the chains to be symmetrically cleaved to monomeric MnF(salen).

Enzymatic versus Inorganic Oxygen Reduction Catalysts: Comparison of the Energy Levels in a Free-Energy Scheme

In this paper, we present a method to directly compare the energy levels of intermediates in enzymatic and inorganic oxygen reduction catalysts. We initially describe how the energy levels of a Pt(111) catalyst, operating at pH = 0, are obtained. By a simple procedure, we then convert the energy levels of cytochrome c oxidase (CcO) models obtained at physiological pH = 7 to the energy levels at pH = 0, which allows for comparison. Furthermore, we illustrate how different bias voltages will affect the free-energy landscapes of the catalysts. This allows us to determine the so-called theoretical overpotential of each system, which is shown to be significantly lower for the enzymatic catalysts compared to the inorganic Pt(111) catalyst. Finally, we construct theoretical polarization curves for the CcO models, in order to illustrate the effect of the low overpotentials on turnover rates per site.

The synthesis and characterization of an organometallic trinuclear oxo-bridged niobium cluster complex with perpendicularly coordinated mu(3)eta(2):eta(2)(perpendicular to)-acetonitrile ligand in aqueous solution is reported. Reaction of NbCl5 in acetonitrile with aluminum under argon followed by reaction with aqueous hydrochloric acid affords, after suitable workup, the isolation of the organometallic [Nb-3(mu-eta(2):eta(2)-NCCH3)O-3(H2O)(9)](6+) aqua ion by cation-exchange chromatography. The purple niobium aqua ion in 2 M HCl shows a small peak at 365 nm (epsilon similar to 511 M-1 cm(-1) per Nb) and a broad peak at 565 nm (epsilon similar to 335 M-1 cm(-1)) in the UV-visible region. It is electron paramagnetic resonance (EPR)-active (g = 1.98), but no hyperfine interaction with the Nb-93 nuclear spin (I = 9/2) was observed. The cyclic voltammogram of [Nb-3(mu-eta(2):eta(2)-NCCH3)O-3(H2O)(9)](6+) in 4 M HCl on edge-plane pyrolytic graphite electrode at 50 mV s(-1) in the potential range -1.2 V to +1.1 V (vs SCE) exhibits three anodic peaks at -0.12, +0.53, and +0.85 V and a large cathodic peak at -0.91 V with a slight shoulder at about -0.8 V. The purple aqua ion reacted with potassium thiocyanate to give the green thiocyanate derivative, which was crystallized as ((CH3)(3)NH)(3)[Nb-3(mu-eta(2):eta(2)-NCCH3)O-3(NCS)(9)]center dot 2.5H(2)O (1) and subjected to X-ray structure analysis. Density-functional theory (DFT) calculations fully supported the structure of the cluster.
Crystal Structures of Titanate Nanotubes: A Raman Scattering Study

Crystal structures of titanate nanotubes prepared from a NaOH treatment of TiO2 with subsequent acid washing were discussed from a viewpoint of vibrational spectroscopy. The correlation between the vibrational feature and the polymerization nature of the TiO6 octahedron was established by analyzing Raman scattering data of crystalline TiO2 (anatase and rutile) and layered protonic titanates. Then, the polymerization nature of TiO6 octahedra in the titanate nanotubes was identified by comparing their Raman scattering spectra with those of the crystalline TiO2 and layered protonic titanates. It demonstrated that the titanate nanotubes consist of two-dimensional TiO6 octahedral host layers with a lepidocrocite (gamma-FeOOH)-type layered structure. This conclusion was confirmed further by considering the Raman scattering properties of a restacked titanate prepared by assembling TiO6 octahedral layers derived from the original scroll-like titanate nanotubes. Our findings offered a convenient approach to validate the crystal structures of the products from an alkaline treatment of TiO2 under different experimental conditions.

Microstructures, Surface Properties and Topotactic Transitions of gamma-MnOOH Nanorods

Single crystalline monoclinic Manganite (gamma-MnOOH) nanorods have interesting surface properties and thermal behaviors that are distinctive from those of the bulk counterparts.
Preparation of Nb-Substituted Titanates by a Novel Sol-Gel Assisted Solid State Reaction

Single-phase layered Nb-substituted titanates, Na2Ti3-xNbxO7 (x = 0-0.06) and Cs0.7Ti1.8-xNbxO4 (x = 0-0.03), were for the first time synthesized by a novel sol-gel assisted solid state reaction (SASSR) route. Conventional solid state reactions as well as sol-gel synthesis did not succeed in producing phase pure Nb-substituted titanates. In the SASSR synthesis route we combine the advantages of traditional sol-gel technique (i.e., homogeneous products formed at low temperatures) and solid state reaction (i.e., formation of stable, crystalline phases) for preparing single-phase niobium-substituted layered titanates. The obtained products were characterized by X-ray powder diffraction, scanning electron microscopy, inductively coupled plasma-atomic emission spectrometry, Raman spectroscopy, and thermogravimetric analysis. Results indicate that the Ti(IV) in the host layer of the samples could be partially replaced by Nb(V) without structural deterioration. After proton-exchange, more water molecules were intercalated into the interlayer of H0.7Ti1.8-xNbxO4 center dot nH(2)O with increasing niobium content, whereas the interlayer distance of H2Ti3-xNbxO7 (x = 0-0.06) was unchanged.

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Single-Ion Anisotropy and Exchange Interactions in the Cyano-Bridged Trimers (MnIII2MIII(CN)6 (MIII = Co, Cr, Fe) Species Incorporating [Mn(5-Brsalen)]+ Units: An Inelastic Neutron Scattering and Magnetic Susceptibility Study

The electronic structures of the compounds K[(5-Brsalen)2(H2O)2-Mn2MIII(CN)6] ·2H2O (MIII = CoIII, CrIII, FeIII) have been determined by inelastic neutron scattering (INS) and magnetic susceptibility studies, revealing the manganese(III) single-ion anisotropy and exchange interactions that define the low-lying states of the Mn-MIII-Mn trimeric units. Despite the presence of an antiferromagnetic intertrimer interaction, the experimental evidence supports the classification of both the Cr(III) and Fe(III) compounds as single-molecule magnets. The value of 17(2) cm-1 established from AC susceptibility measurements for a spin-reversal barrier of K[(5-Brsalen)2(H2O)2-Mn2Cr(CN)6] ·2H2O may be readily rationalized in terms of the energy level diagram determined directly by INS. AC susceptibility measurements on samples of K[(5-Brsalen)2(H2O)2-Mn2Fe(CN)6] ·2H2O are contrary to those previously reported, exhibiting but the onset of peaks below temperatures of 1.8 K at oscillating frequencies in the range of 100-800 Hz. INS measurements reveal an anisotropic ferromagnetic manganese(III)-iron(III) exchange interaction, in accordance with theoretical expectations based on the unquenched orbital angular momentum of the [Fe(CN)6]3- anion, giving rise to an Ms similar to +/-9/2 ground state, isolated by similar to 11.5 cm-1 from the higher-lying levels. The reported INS and magnetic data should now serve as a benchmark against which theoretical models that aim to inter-relate the electronic and molecular structure of molecular magnets should be tested.

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Organisations: University of Copenhagen, Paul Scherrer Institute, Moldova Academy of Sciences - Institute of Applied Physics, Institut Laue-Langevin
Syntheses, Structures, and Magnetic Properties of Nickel-Doped Lepidocrocite Titanates

Ni-doped titanate CsxTi2−x/2Nix/2O4 and its protonic derivative HxTi2−x/2Nix/2O4·xH2O (x = 0.7) were synthesized and characterized by means of synchrotron X-ray diffraction, Raman scattering, X-ray photoelectron spectroscopy (XPS), and magnetic measurements. CsxTi2−x/2Nix/2O4 crystallizes in an orthorhombic structure (space group Immm), consisting of infinite two-dimensional (2D) host layers of the lepidocrocite (γ-FeOOH) type. The substitution of Ni atoms for Ti in the 2D octahedral layers results in negative charges that are compensated by interlayer Cs+ ions. Raman scattering and XPS indicate that local structural perturbations are induced upon exchange of interlayer Cs ions with protons H3O+. Magnetic measurements reveal typical paramagnetism induced by Ni substitution; the effective paramagnetic moment μeff = 1.57(1) μB and Curie–Weiss temperature −2.51(1) K are obtained for HxTi2−x/2Nix/2O4·xH2O. Ni- and Mg-codoped titanates CsxTi2−x/2(NiyMg1−y)x/2O4 (x = 0.7, 0 ≤ y ≤ 1) were also reported. The crystal structure, interlayer chemistry, and magnetic properties of the titanates depend on the Ni substitution levels, indicating opportunities for tuning of the properties by controlling the nature and level of lattice substitutions.

Synthesis and Characterization of Mixed Chalcogen Triangular Complexes with New Mo-3(mu(3)-S)(mu(2)-Se-2)(3)(4+) and M-3(mu(3)-S)mu(2)-Se)(3)(4+) (M = Mo, W) Cluster Cores

In our pursuit of mixed chalcogen-bridged cluster complexes, solids of the compositions Mo3SSe6Br4 and W3SSe6Br4 were prepared using high-temperature synthesis from the elements. Treatment of Mo3SSe6Br4 with Bu4NBr in a vibration mill yielded (Bu4N)(3)([Mo-3(mu3-S)(mu2-Se-2)(3)Br-6]Br) (I). Its all-selenide analogue (Bu4N)(3)([Mo-3(mu3-S)-]
Se)(mu(2)-Se-2)(3)Br--(6)Br} (II) was prepared from Mo3Se7Br4 in a similar way. Both compounds were characterized by IR, Raman, and Se-77 NMR spectroscopy. The structure of 11 was determined by X-ray single-crystal analysis. Compound I is isostructural with II and contains the new Mo-3(mu(3)-S)Se-6(4+) cluster core. By treatment of a 4 M Hpts solution of I with PPh3 followed by cation-exchange chromatography, the new mixed chalcogenido-molybdenum aqua ion, [Mo-3(mu S--(3))(mu(2)-Se)(3)(H2O)(9)](4+), was isolated and characterized using UV-vis spectroscopy and, after derivatization into [Mo-3(mu S--(3))(mu(2)-Se)(3)(acac)(3)(py(3))](+), electrospray ionization mass spectrometry. From HCl solutions of the aqua ion, a supramolecular adduct with cucurbit[6]uril (CB[6]), [{Mo-3(mu(3)-S)(mu(2)-Se)(3)(H2O)(6)Cl-3(2)CB[6]Cl-2 center dot 11H(2)O (III)}, was isolated and its structure determined using X-ray crystallography. W3SSe6Br4 upon reaction with H3PO2 gave a mixture of all of the [W3SxSe4-x(H2O)(9)](4+) species. After repeated chromatography, crystals of [{W-3(mu(3)-S)(mu(2)-Se)(3)(H2O)(7)Cl--(2)}(2)CB[6]Cl-4 center dot 12H(2)O (IV) were crystallized from the fraction rich in [W-3(mu(3)-S)Se-3(H2O)(9)](4+) and structurally characterized.

**Bioinorganic Chemistry Modeled with the TPSSh Density Functional**

In this work, the TPSSh density functional has been benchmarked against a test set of experimental structures and bond energies for 80 transition-metal-containing diatomics. It is found that the TPSSh functional gives structures of the same quality as other commonly used hybrid and nonhybrid functionals such as B3LYP and BP86. TPSSh gives a slope of 0.99 upon linear fitting to experimental bond energies, whereas B3LYP and BP86, representing 20% and 0% exact exchange, respectively, give linear fits with slopes of 0.91 and 1.07. Thus, TPSSh eliminates the large systematic component of the error in other functionals, reducing rms errors from 46-57 to 34 kJ/mol. The nonhybrid version of the functional, TPSS, gives a slope of 1.08, similar to BP86, implying that using 10% exact exchange is the main reason for the success of TPSSh. Typical bioinorganic reactions were then investigated, including spin inversion and electron affinity in iron-sulfur clusters, and breaking or formation of bonds in iron proteins and cobalamins. The results show that differences in reaction energies due to exact exchange can be much larger than the usually cited similar to 20 kJ/mol, sometimes exceeding 100 kJ/mol. The TPSSh functional provides energies approximately halfway between nonhybrids BP86 and TPSS, and 20% exact exchange hybrid B3LYP: Thus, a linear correlation between the amount of exact exchange and the numeric value of the reaction energy is observed in all these cases. For these reasons, TPSSh stands out as a most promising density functional for use and further development within the field of bioinorganic chemistry.
Accurate Computation of Reduction Potentials of 4Fe–4S Clusters Indicates a Carboxylate Shift in Pyrococcus furiosus Ferredoxin

This work describes the computation and accurate reproduction of subtle shifts in reduction potentials for two mutants of the iron-sulfur protein Pyrococcus furiosus ferredoxin. The computational models involved only first-sphere ligands and differed with respect to one ligand, either acetate (aspartate), thiolate (cysteine), or methoxide (serine). Standard procedures using vacuum optimization gave qualitatively wrong results and errors up to 0.07 V. Using electrostatically screened geometries and large basis sets for expanding the wave functions gave quantitatively correct results, with errors of only 0.03 V. Correspondingly, only this approach predicted a change in the coordination mode of aspartate (i.e., a carboxylate shift) accompanying the reduction of the wild-type cluster, confirming results from synthetic models and explaining why electrostatic screening is necessary. Hence, the carboxylate shift appears to occur in the proteins from which data were collected. The results represent the most accurate predictions of shifts in reduction potentials for modified proteins, the success in part being due to the similar nature of the three amino acid ligands involved. The predicted carboxylate shift is expected to tune aspartate’s degree of electron donation to the cluster's two oxidation states, thus making the reversible redox reaction feasible.

A density functional theory study of the electronic properties of Os(II) and Os(III) complexes immobilized on Au(111)

We present a density functional theory (DFT) study of an osmium polypyridyl complex adsorbed on Au(111). The osmium polypyridyl complex \([\text{Os}(\text{bpy})_2(\text{P0P})\text{Cl}]^{(n+)}\) \([\text{bpy is } 2,2'-\text{bipyridine}, \text{P0P is } 4,4'-\text{bipyridine}, n = 1 \text{ for osmium}(\text{II}), \text{and } n = 2 \text{ for osmium}(\text{III})]\) is bound to the surface through the free nitrogen of the P0P ligand. The calculations illuminate electronic properties relevant to recent comprehensive characterization of this class of osmium complexes by electrochemistry and electrochemical scanning tunneling microscopy. The optimized structures for the compounds are in close agreement with crystallographic structures reported in the literature. Oxidation of the complex has little effect on these structural features, but there is a substantial reordering of the electronic energy levels with corresponding changes in the electron density. Significantly, the highest occupied molecular orbital shifts from the metal center to the P0P ligand. The surface is modeled by a cluster of 28 gold atoms and gives a good description of the effect of immobilization on the electronic properties of the complexes. The results show that the coupling between the immobilized complex and the gold surface involves electronic polarization at the adsorbate/substrate interface rather than the formation of a covalent bond. However, the cluster is too small to fully represent bulk gold with the result that, contrary to what is experimentally observed, the DFT calculation predicts that the gold surface is more easily oxidized than the osmium(II) complex.
Studies directed to understanding the structure of chitosan-metal complexes: Investigations of mono- and disaccharide models with platinum(II) group metals

X-ray and NMR experiments were performed with simple chitosan models based on glucosamine monosaccharides and disaccharides to understand the binding properties and structures of the complexes formed between this polysaccharide and platinum(II) metals. Subjection of the glucosamine derivatives with [PdCl2(PhCN)]2 provided trans-diamine complexes which upon further treatment with excess (NH4)PF6 generated complexes possessing two 5-membered chelate rings involving the C2-amine and the C3-hydroxyl group of the two individual glucosamine units.
Syntheses and X-ray diffraction, photochemical, and optical characterization of Cu2SixSn1-xS3 (0.4 <or = x <or = 0.6) for photovoltaic applications.

The study of the pseudobinary system Cu(2)SnS(3-)Cu(2)SiS(3) shows that a solid solution (Cu(2)Si(x)Sn(1-x)S(3)) exists in the range 0.4 <or = Si/(Sn+Si) <or = 0.6. Based on diffuse reflectance and photoelectrochemical measurements these compounds show potential as absorber materials for photovoltaic devices. The compounds were prepared at 850 degrees C from copper sulfide, silicon, tin, and sulfur and were analyzed with single-crystal (for x approximately 0.40) and powder diffraction techniques. Optical band gaps of 1.25, 1.35, and 1.45 eV were observed for the three compositions x = 0.39, 0.48, and 0.61; cathodic photocurrent occurring is significant.

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Preparation, Properties, and Reactivities of Unprecedented Oxo-Sulfido Nb(IV) Aqua ions and Crystal Structure of (Me2NH2)6[Nb5(μ3-S)2(μ3-O)2(μ2-O)2(NCS)14]∙3.5H2O

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Research output: Contribution to journal › Journal article – Annual report year: 2006 › Research › peer-review

Synthesis and vibrational circular dichroism of enantiopure chiral oxorhenium(V) complexes containing the hydrotris(1-pyrazolyl)borate ligand

The infrared and vibrational circular dichroism (VCD) spectra of six chiral oxorhenium(V) complexes, bearing a hydrotris(1-pyrazolyl)borate (Tp) ligand, have been investigated. These complexes are promising candidates for observation of parity violation (symmetry breaking due to the weak nuclear force). New chiral oxorhenium complexes have been synthesized, namely, [TpReO(μ2-O)(CH3)2CH2O2-O, O)] (4a and 4b) diastereomers and [TpReO(μ2-N(CH3)CH2CH2O-N, O)] (5) and [TpReO(μ2-N( tBu)CH2CH2O-N, O)] (6) enantiomers. All compounds could be obtained in enantiomerically pure form by using either column chromatography or HPLC over chiral columns. VCD spectroscopy of these compounds and of [TpReO(μ2-N(CH3)CH(CH3)CH(Ph)O-N, O)] (2) and [TpReO(μ2-N(CH2)3CHCO2-N, O)] (3) (with chiral bidentate ligands derived, respectively, from ephedrine and proline) were studied. This allowed the absolute configuration determination of all compounds together with their conformational analysis, by comparing calculated and experimental spectra. This is the first VCD study of rhenium complexes which further demonstrates the applicability of VCD spectroscopy in determining the
Synthesis of Thin Cr₃Se₄ Films from Modulated Elemental Reactants via Two Amorphous Intermediates: A Detailed Examination of the Reaction Mechanism

The reaction of Cr/Se multilayers when they are annealed occurs in two steps: interdiffusion of the single layers to an amorphous Cr–Se alloy and crystallization of Cr₃Se₄. Both reaction steps were characterized using various techniques. At approximately 300 °C the layers have interdiffused completely to form a homogeneous amorphous Cr–Se alloy. Short-range order in the alloy was probed with X-ray absorption spectroscopy (XAS) and, according to the results of this, is already very similar to Cr₃Se₄, which crystallizes around 500 °C. Crystallization occurs at a well-defined temperature, whereas crystallite growth proceeds in the whole temperature interval above the crystallization temperature and is not finished at 660 °C. The reaction yields a polycrystalline thin film of Cr₃Se₄ in a preferred orientation exhibiting a (00l) texture. In Cr-rich samples amorphous Cr is present as a by-product. A Cr–Se/Se multilayer was observed as an intermediate in the interdiffusion of some Cr-rich samples which is stable between 200 and 250 °C.
An unprecedented tetranuclear niobium aqua ion with a capping μ4-sulfido ligand
A new niobium aqua ion, with an unprecedented metal-metal bonded tetranuclear Nb4(μ4-S)(μ2-O)54+ core, is obtained upon treatment of Zn-reduced ethanolic solutions of NbCl5 with HCl in the presence of a sulfide source. The red aqua ion, obtained upon cation-exchange chromatography, forms readily the thiocyanate complex which have been crystallized as Cs4.67Na1.33[¬Nb4SO5(NCS)10]∙2.33H2O and structurally characterized.

Electrochemical and Spectroscopic Studies of the Chloro and Oxochloro Complex Formation of Nb(V) and Ta(V) in NaCl-AlCl3 Melts

General information
Publication status: Published
Organisations: Department of Chemistry
Contributors: Ooi, B. L., Søtofte, I.
Pages: 480-482
Publication date: 2005
Peer-reviewed: Yes

Publication information
Journal: Inorganic Chemistry
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Issue number: 3
ISSN (Print): 0020-1669
Ratings:
Scopus rating (2005): SJR 2.005 SNIP 1.495
Web of Science (2005): Indexed yes
Original language: English
Source: orbit
Source-ID: 183429
Research output: Contribution to journal › Journal article – Annual report year: 2005 › Research › peer-review
Solid-state photochromic device based on nanocrystalline TiO$_2$ functionalized with electron donor-acceptor species

**General information**

Publication status: Published
Organisations: Risø National Laboratory for Sustainable Energy
Contributors: Biancardo, M., Argazzi, R., Bignozzi, C.
Pages: 9619-9621
Publication date: 2005
Peer-reviewed: Yes

**Publication information**

Journal: Inorganic Chemistry
Volume: 44
ISSN (Print): 0020-1669
Ratings:
Scopus rating (2005): SJR 2.005 SNIP 1.495
Web of Science (2005): Indexed yes
Original language: English
DOIs: 10.1021/ic0514593
Source-ID: 185339
Research output: Contribution to journal → Journal article – Annual report year: 2005 → Research → peer-review

The reaction between ZnO and molten Na$_2$S$_2$O$_7$ or K$_2$S$_2$O$_7$ forming Na$_2$Zn(SO$_4$)$_2$ or K$_2$Zn(SO$_4$)$_2$, studied by Raman spectroscopy and X-ray diffraction

Reactions between solid ZnO and molten Na$_2$S$_2$O$_7$ or K$_2$S$_2$O$_7$ at 500 are shown by Raman spectroscopy to be 1:1 reactions leading to solns. By lowering the temp. of the soln. melts, colorless crystals form. Raman spectra of the crystals are given and tentatively assigned. Crystal structures of the monoclinic salts at room temp. are given. Na$_2$Zn(SO$_4$)$_2$: space group $P2_1/n$ (No. 13), $Z = 8$, $a = 8.648(3)$ Å, $b = 10.323(3)$ Å, $c = 15.103(5)$ Å, $\beta = 90.879(6)$ deg., and $wR^2 = 0.0945$ for 2748 independent reflections. K$_2$Zn(SO$_4$)$_2$: space group $P2_1/n$ (No. 14), $Z = 4$, $a = 5.3582(11)$ Å, $b = 8.7653(18)$ Å, $c = 16.152(3)$ Å, $\beta = 91.78(3)$ deg., and $wR^2 = 0.0758$ for 1930 independent reflections. In both compds., Zn is nearly perfectly trigonally bipyramidal, coordinated to five O atoms, with Zn-O bond lengths ranging from 1.99 to 2.15 Å, equatorial bonds being slightly shorter on the av. The O-Zn-O angles are approx. 90 deg. and 120 deg.. The sulfate groups connect adjacent Zn$^{2+}$ ions, forming complicated three-dimensional networks. All O atoms belong to nearly perfect tetrahedral [SO$_4$]$^{2-}$ groups, bound to Zn. No O atom is terminally bound to Zn; all Zn oxygens are further connected to S atoms (Zn-O-S bridging). In both structures, some O atoms are uniquely bound to certain S atoms. The sulfate group tetrahedra have quite short (1.42-1.45 Å) terminal S-O bonds in comparison to the longer (1.46-1.50 Å) Zn-bridging S-O bonds. The Na$^+$ or K$^+$ ions adopt positions between the ZnO$_5$ hexahedra and the SO$_4$ tetrahedra, completing the three-dimensional network of the M$_2$Zn(SO$_4$)$_2$ structures. Bond distances and angles compare well with literature values. Empirical correlations between S-O bond distances and av. O-S-O bond angles follow a previously found trend.

**General information**

Publication status: Published
Organisations: Department of Chemistry
Contributors: Berg, R. W., Thorup, N.
Pages: 3485-3493
Publication date: 2005
Peer-reviewed: Yes

**Publication information**

Journal: Inorganic Chemistry
Volume: 44
Issue number: 10
ISSN (Print): 0020-1669
Crystal Structure and Spectroscopic Properties of CsVO2SO4

General information
Publication status: Published
Organisations: Department of Chemistry, Institute of Chemical Engineering and High Temperature Chemical Processes
Contributors: Rasmussen, S. B., Boghosian, S., Nielsen, K., Eriksen, K. M., Fehrmann, R.
Pages: 3697-3701
Publication date: 2004
Peer-reviewed: Yes

Publication information
Journal: Inorganic Chemistry
Volume: 43
Issue number: 12
ISSN (Print): 0020-1669
Ratings:
Scopus rating (2004): SJR 1.644 SNIP 1.382
Web of Science (2004): Indexed yes
Original language: English
Source: orbit
Source-ID: 178202
Research output: Contribution to journal › Journal article – Annual report year: 2004 › Research › peer-review

Ferromagnetic ordering in bis(benzene)chromium(+) bis(4,5-dimethoxybenzene-1,2-dithiolato)nickel(-)

General information
Publication status: Published
Organisations: Solar Energy Programme, Risø National Laboratory for Sustainable Energy
Contributors: Schiodt, N., Sessoli, R., Krebs, F. C.
Pages: 1986-1991
Publication date: 2004
Peer-reviewed: Yes

Publication information
Journal: Inorganic Chemistry
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Ratings:
Scopus rating (2004): SJR 1.644 SNIP 1.382
Web of Science (2004): Indexed yes
Original language: English
DOIs: 10.1021/ic034610m
Source: orbit
Source-ID: 306733
Research output: Contribution to journal › Journal article – Annual report year: 2004 › Research › peer-review

NMR spectroscopic and X-ray crystallographic study of methylcobalt(III) compounds with saturated amine ligands
The C-13 chemical shifts of methylcobalt(III) compounds with saturated amine ligands in cis positions to the methyl group and a monodentate ligand, L = CN-, NH3, NO2, N-3(-), H2O, or OH-, in the trans position are reported. The amine ligands
used, 1,2-ethanedianine (en), 1,3-propanedianine (tn), N,N'-bis(2-aminoethyl)-1,3-propanedianine (2,3.2-tet), N,N'-bis(3-
aminopropyl)-1,2-ethanedianine (3,2,3-tet), and 1,4,8,11-tetraazacyclotetradecane (cyclam), all exert an apparent cis
influence on the 13 C resonance signal of the coordinated methyl group. In the trans-[Co-(en)(2)(CH3)(L)](n+ series the
N-15 resonance frequency of the coordinated en has also been measured. The influence of L on the en N-15 chemical
shifts is reverse the influence on the methyl C-13 chemical shifts except in the case of L = NO2-, which affects a further
deshielding of the amine nitrogen nucleus. The methyl (1)J(CH) coupling constants in the trans-[Co(en)(2)(CH3)(L)](n+)
series range from 128.09 Hz (L = CN-) to 134.11 Hz (L = H2O). The crystal structures of trans-[Co(en)(2)(CH3)(ClZnCl3)],
trans-[Co(3,2,3-tet)(CH3)(N-3)]ClO4, trans, trans-[[CH3(en)(2)CO(CN)Co(en)(2)(CH3)][PF6](3)(CH3CN), and cis-
[Co(en)(2)(CH3)(NH3)]ZnCl4 were determined from low-temperature X-ray diffraction data.

**General information**
Publication status: Published
Organisations: Department of Chemistry, Roskilde University
Contributors: Kofod, P., Harris, P.
Pages: 2680-2688
Publication date: 2004
Peer-reviewed: Yes

**Publication information**
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Ratings:
Scopus rating (2004): SJR 1.644 SNIP 1.382
Web of Science (2004): Indexed yes
Original language: English
Source-ID: 154473
Research output: Contribution to journal › Journal article – Annual report year: 2004 › Research › peer-review

Red and yellow dichroistic crystals of a vanadium(V) compound, potassium (mu-oxo, di-mu-sulfato)bis(oxodisulfato-
vanadate), K-8(VO)(2)O(SO4)(6), have been obtained from the ternary catalytic model melt system K2S2O7-K2SO4-
V2O5. By slow cooling of the melt from 420 to 355 degreesC, crystal growth occurred, using solid V2O5 crystals present
in the melt as nucleation promoter. The compound crystallizes in the monoclinic space group P2(1) with a = 13.60(9)
Angstrom, b = 13.93(9) Angstrom, c = 14.05(9) Angstrom, beta = 90.286(10) degrees, and Z = 2. It contains two VO6
octahedra linked together by a mu-oxo and two mu-sulfato bridges. Furthermore, each octahedron has two monodentate
sulfate ligands, making the dimeric entity coordinatively saturated. IR spectroscopy shows bands arising from V=O-V and
V=O stretches as well as splitting of sulfate bands due to the different degrees of freedom present for different
conformations of sulfate ligands. The coordination of vanadium in K8(VO)20(SO4)6 is discussed in relation to the reaction
mechanism Of SO2 oxidation catalysis.

**Crystal Structure and Spectroscopic Characterization of K8(VO)2O(SO4)6**:  

**General information**
Publication status: Published
Organisations: Department of Chemistry
Contributors: Rasmussen, S. B., Rasmussen, R. C., Fehrmann, R., Nielsen, K.
Pages: 7123-7128
Publication date: 2003
Peer-reviewed: Yes

**Publication information**
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Ratings:
Scopus rating (2003): SJR 1.484 SNIP 1.412
Web of Science (2003): Indexed yes
Original language: English
Source-ID: 39002
Research output: Contribution to journal › Journal article – Annual report year: 2003 › Research › peer-review
Isolation and Molecular Structure of Hexacyanoruthenate(III)
The [Ru(CN)(6)](3-) ion is synthesized in aqueous solution and isolated as [Ph(4)AS](3)[Ru(CN)(6)].2H(2)O (1). Compound 1 crystallizes as orange needles in the monoclinic space group P2(1)/n with cell parameters a = 11.346(2) Ångstrom, b = 23.107(5) Ångstrom, c = 25.015(5) Ångstrom, beta = 99.55(3) degrees, V = 6467.1(22) Ångstrom(3), Z = 4. The octahedral anion has Ru-C bond lengths in the range 2.023(6)-2.066(6) Ångstrom. DFT calculations reproduce experimental geometries for [M(CN)(6)](3-) (M = Fe, Ru) equally well and yield significantly higher spin densities on the cyanide ligands in [M(CN)(6)](3-) (M = Ru, Os) than in [Fe(CN)(6)](3-).

General information
Publication status: Published
Organisations: Department of Chemistry
Contributors: Bendix, J., Steenberg, P., Setøfte, I.
Pages: 4510-4512
Publication date: 2003
Peer-reviewed: Yes

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Original language: English
Source: orbit
Source-ID: 36075
Research output: Contribution to journal > Journal article – Annual report year: 2003 > Research > peer-review

Spectroscopic and Thermal Investigations of the Fluoroaluminate Complex Formation in NaF-KF and LiF-NaF-KF Eutectics

General information
Publication status: Published
Organisations: Department of Chemistry, Centre National de la Recherche Scientifique
Contributors: Barner, J. H. V., Bessada, C., Berg, R. W.
Pages: 1901-1907
Publication date: 2003
Peer-reviewed: Yes

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Journal: Inorganic Chemistry
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Web of Science (2003): Indexed yes
Original language: English
Source: orbit
Source-ID: 28465
Research output: Contribution to journal > Journal article – Annual report year: 2003 > Research > peer-review

Crystal structure and spectroscopic properties of Na2K6(VO)(2)(SO4)(7)
Red-brown crystals of a new mixed alkali oxo sulfato vanadium(V) compound Na2K6(VO)(2)(SO4)(7), suitable for X-ray determination, have been obtained from the catalytically important binary molten salt system M2S2O7-V2O5 (M = 80% K and 20% Na). By slow cooling of a mixture with the mole fraction X-V2O5 = 0.24 from 325 degreesC, i.e., just below the liquidus temperature, to the solidus temperature of around 300 degreesC, a dark reddish amorphous phase was obtained containing crystals of the earlier described V(V)-V(IV) mixed valence compound K-6(VO)(4)(SO4)(8) and Na2K6-(VO)(2)(SO4)(7) described here. This compound crystallizes in the tetragonal space group P4(3)2(1)2 (No. 96) with a = 9.540(3) Ångstrom, c = 29.551(5) Ångstrom at 20 degreesC and Z = 4. It contains a distorted VO6 octahedron with a short V-O bond of 1.552(6) Ångstrom, a long one of 2.276(5) Ångstrom trans to this, and four equatorial V-O bonds in the range 1.881(6)-1.960(6) Å. The deformation of the VO6 octahedron is less pronounced compared to that of the known oxo sulfato V(V) compounds. Each VO3+ group is coordinated to five sulfate groups of which two are unidentately coordinated and three are bidentate bridging to neighboring VO3+ groups. The length of the S-O bonds in the S-O-V bridges of the two
unidentately coordinated sulfato groups are 1.551(6) Angstrom and 1.568(6) Angstrom, respectively, which are unusually long compared to our earlier measurements of sulfate groups in other V(111), V(IV), and V(V) compounds.

**General information**
Publication status: Published
Organisations: Department of Chemistry, University of Patras, Foundation for Research and Technology-Hellas
Contributors: Karydis, D., Boghosian, S., Nielsen, K., Eriksen, K. M., Fehrmann, R.
Pages: 2417-2421
Publication date: 2002
Peer-reviewed: Yes

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Ratings:
Scopus rating (2002): SJR 1.615 SNIP 1.385
Web of Science (2002): Indexed yes
Original language: English
Source: orbit
Source-ID: 42874
Research output: Contribution to journal › Journal article – Annual report year: 2002 › Research › peer-review

**Cobalt(III) complexes of [3(5)]adamanzane, 1,5,9,13-tetraazabicyclo[7.7.3]nonadecane. Report of an inert, chelate hydrogen carbonate ion**

Three cobalt(III) complexes of themacrocyclic tetraamine [3(5)]adamanzane (1,5,9,13-tetraazabicyclo[7.7.3]-nonadecane) were isolated as salts. The X-ray crystal structures were solved for the compounds [Co([3(5)]adz)-(CO3)AsF6 (1b), [Co([3(5)]adz)(HCO3)]znBr(4).H2O (2a), and [Co([35]adz)(SO4)]AsF6.H2O (3a). The coordination geometry around the cobalt(III) ion is a distorted octahedron with the inorganic ligands at cis-positions. Complex 2 is the second example of a cobalt(III) complex for which the X-ray structure shows a chelate binding mode of the hydrogen carbonate entity. The pK(a) value of the [Co([3(5)]adz)(HCO3)](2+) ion (2) was determined spectrophotometrically to be 0.27 (25 degreesC, I = 5.0 M). The protonation appears to occur at the noncoordinated carbonyl oxygen atom of the carbonate group, with hydrogen bonding to the crystal water molecule. Evidence is presented for this oxygen-atom as the site of protonation in solution as well. In 5.0 M CF3SO3H a slow reaction of the carbonate complex, quantitatively yielding the [Co([3(5)]adz)(H2O)(2)](3+) ion, was observed. k(obs) 7.9(1) x 10(-6) s(-1) at 25 degreesC.

**General information**
Publication status: Published
Organisations: Department of Chemistry
Contributors: Broge, L., Søtofte, I., Olsen, C. E., Springborg, J.
Pages: 3124-3129
Publication date: 2001
Peer-reviewed: Yes

**Publication information**
Journal: Inorganic Chemistry
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Ratings:
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Web of Science (2001): Indexed yes
Original language: English
Source: orbit
Source-ID: 46338
Research output: Contribution to journal › Journal article – Annual report year: 2001 › Research › peer-review

**Cobalt(II), nickel(II), copper(II), and zinc(II) complexes with [3(5)]adamanzane, 1,5,9,13-tetraazabicyclo[7.7.3]nonadecane and [2.3](2)(2)(1)]adamanzane, 1,5,9,12-tetraazabicyclo[7.5.2]hexadecane**

Isolation of the free bicyclic tetraamine, [3(5)]adamanzane .H2O (1,5,9,13-tetraazabicyclo[7.7.3]-nonadecane .H2O), is reported along with the synthesis and characterization of a copper(II) complex of the smaller macrocycle [(2.3)(2)(2)(1)]-adamanzane (1,5,9,12-tetraazabicyclo[7.5.2]hexadecane) and of three cobalt(II), four nickel(II), one copper(II), and two zinc(II) complexes with [3(5)]adamanzane. For nine of these compounds (2-8, 10b, and 12) the single-crystal X-ray structures were determined. The coordination geometry around the metal ion is square pyramidal in
[Cu((2.3)(2.1)adz)Br]ClO4 (2) and trigonal bipyramidal in the isostructural structures [Cu((3.5)adz)Br]Br (3), [Ni-(3.5)adz]Cl (5), [Ni((3.5)adz)Br]Br (6), and [Co((3.5)adz)Cl]Cl (8). In [Ni((3.5)adz)(NO3)]NO3 (4) and [Ni((3.5)-adz)]ClO4]ClO4 (7) the coordination geometry around nickel(II) is a distorted octahedron with the inorganic ligands at cis positions. The coordination polyhedron around the metal ion in [Co((3.5)adz)][ZnCl4] (10b) and [Zn((3.5)adz)][ZnCl4] (12) is a slightly distorted tetrahedron. Anation equilibrium constants were determined spectrophotometrically for complexes 2-6 at 25 and 40 degreesC and fall in the region 2-10 M(-1) for the halide complexes and 30-65 M(-1) for the nickel(II) nitrate complex (4). Rate constants for the dissociation of the macrocyclic ligand from the metal ions in 5 M HCl were determined for complexes 2, 3, 5, 8, 10, and 12. The reaction rates vary from half-lives at 40 degreesC of 14 min for the dissociation of the Zn((3.5)adz)(2+) complex (12) to 14-15 months for the Ni((3.5)adz)Cl+ ion (5).

Molecular Modeling of Bifunctional Chelate Peptide Conjugates. 1. Copper and Indium Parameters for the AMBER Force Field

In this work we describe the development of parameters for In(III) and Cu(II) for the AMBER force field as found in the modeling package MacroModel. These parameters were developed using automated procedures from a combination of crystallographic structures and ab initio calculations. The new parameters were added in the form of AMBER substructures containing specific metal-ligand parameters to the existing force field. These new parameters have produced results in good agreement with experiment without requiring additional changes to the existing AMBER parameters. These parameters were then utilized to examine the conformational effects caused by the conjugation of InDTPA (DTPA = diethylenetriaminepentaacetic acid) and CuDOTA (DOTA 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid) to the cyclic octapeptide octreotide.
Raman Study of the Hexafluoroaluminate Ion in Solid and Molten FLINAK

Publication status: Published
Organisations: Department of Chemistry
Contributors: Brooker, M. H., Berg, R. W., Barner, J. H. V., Bjerrum, N.
Pages: 3682-3689
Publication date: 2000
Peer-reviewed: Yes

Structural and quantum chemical study of Bi5(3+) and isoelectronic main-group metal clusters. The crystal structure of pentabismuth(3+)-tetrachlorogallate(III) refined from X-ray powder diffraction data and synthetic attempts on its antimony analogue.

Publication status: Published
Organisations: Department of Chemistry, Lund University
Contributors: Ulvenlund, S., Ståhl, K., Bengtsson-Kloo, L.
Pages: 223-230
Publication date: 1996
Peer-reviewed: Yes

Preparation and electronic structure of substituted aromatic dithiolene complexes of gold (III)

Publication status: Published
Organisations: Risø National Laboratory for Sustainable Energy
Contributors: Schiødt, N., Sommer-Larsen, P., Bjørnholm, T., Nielsen, M., Larsen, J., Bechgaard, K.
Pages: 3688-3694
Publication date: 1995
Peer-reviewed: Yes
General information
Publication status: Published
Organisations: Risø National Laboratory for Sustainable Energy
Contributors: Løgager, T., Holcman, J., Sehested, K., Pedersen, T.
Pages: 3523-3529
Publication date: 1992
Peer-reviewed: Yes

Conductivity, Thermal Analysis, and Phase Diagram of the System Cs2S2O7-V2O5. Spectroscopic Characterization of the Compound, Cs4(VO2)2(SO4)2S2O7

General information
Publication status: Published
Organisations: Department of Chemistry, Energy and Materials
Contributors: Folkmann, G., Hatem, G., Fehrmann, R., Gaune-Escard, M., Bjerrum, N.
Pages: 961-964
Publication date: 1991
Peer-reviewed: Yes

Laser flash photolysis and pulse radiolysis of aqueous solutions of the fluoroxysulfate ion SO4F-

General information
Publication status: Published
Organisations: Risø National Laboratory for Sustainable Energy
Contributors: Klæning, U., Sehested, K., Appelman, E.
Pages: 3582-3584
Publication date: 1991
Peer-reviewed: Yes

Vibrational Spectra of Nb(V) Fluoro and Oxofluoro Complexes Formed in Alkali-Metal Fluoride Melts

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry
Contributors: Barner, J. H. V., Christensen, E., Bjerrum, N., Gilbert, B.
Pages: 561-566
Publication date: 1991
Peer-reviewed: Yes
Crystal Structure and Vibrational Spectra of Na2VO(SO4)2

General information
Publication status: Published
Organisations: Department of Chemistry, Energy and Materials
Contributors: Fehrmann, R., Boghosian, S., Papatheodorou, G., Nielsen, K., Berg, R. W., Bjerrum, N.
Pages: 3294-3298
Publication date: 1990
Peer-reviewed: Yes

Arsenic(IV). A Pulse-Radiolysis Study

General information
Publication status: Published
Organisations: Risø National Laboratory for Sustainable Energy
Contributors: Klanning, U., Bielski, B., Sehested, K.
Pages: 2717-2724
Publication date: 1989
Peer-reviewed: Yes

Crystal Structure and Infrared and Raman Spectra of K4(VO)3(SO4)5

General information
Publication status: Published
Organisations: Department of Chemistry, Energy and Materials
Contributors: Fehrmann, R., Boghosian, S., Papatheodorou, G., Nielsen, K., Berg, R. W., Bjerrum, N.
Pages: 1847-1853
Publication date: 1989
Peer-reviewed: Yes
Complex Formation in Pyrosulfate Melts. 2. Calorimetric Investigations of the System V2O5-K2S2O7, V2O5 . K2S2O7-K2SO4, V2O5 . 2K2S2O7-K2SO4, and V2O5 . 3K2S2O7-K2SO4 at 430°C

Crystal Structure and Infrared and Raman Spectra of KV(SO4)2

Chloro Complexes in Molten Salts, 10. Potentiometric and Spectrophotometric Study of the System KCl-AlCl3-CuCl at 300°C

Cryoscopy in the KCl-AlCl3 System. High-Precision Phase Diagram Near Equimolar Composition, with Comments on Oxide Contaminations and Effective Chloride Concentrations in Tetrachloroaluminate Melts
Magnetic Dimer Excitations in Cs3Cr2Cl9 Studied by Neutron Scattering

The energy dispersion of the singlet-triplet dimer excitation in Cs3Cr2Cl9 has been studied by inelastic neutron scattering (INS) at temperatures down to 1.3 K. The results can be accounted for by using a completely isotropic Heisenberg Hamiltonian in the random phase approximation (RPA). Only nearest-neighbor interactions need to be considered. From the excellent fit, three exchange parameters were obtained: J = -1.75 meV (intradimer), J = -0.032 meV (interdimer, intrasublattice) and J = -0.031 meV (interdimer, intersublattice). These values indicate that Cs3Cr2Cl9 is far from ordering magnetically. The systematic variation of the exchange parameters on substitution of Cl by Br and I is discussed.

NbAlCl8. A Molecular Dinuclear Complex in the Solid, Melt and Vapor Phase. Synthesis, Crystal Structure and Raman Spectra

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry
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Publication date: 1984
Peer-reviewed: Yes

Publication information
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Volume: 23
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Original language: English
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Source-ID: 248674
Phase Diagram of the NaCl-AlCl₃ System Near Equimolar Composition, with Determination of the Cryoscopic Constant, the Enthalpy of Melting and Oxid Contaimination

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry
Contributors: Berg, R. W., Hjuler, H. A., Bjerrum, N.
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Raman Spectroscopic and Spectrophotometric Study of the System K₂S₂O₇-KHSO₄ in the Temperature Range 200-450°C

General information
Publication status: Published
Organisations: Department of Chemistry, Energy and Materials
Contributors: Fehrmann, R., Hansen, N. H., Bjerrum, N.
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Chloro Complexes in Molten Salts. 9. Potentiometric and Vapor Pressure Study of the System NaCl-AlCl₃ in the Temperature Range 175-300°C

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Characterization of Tantalum Pentachloride Containing Melts by Raman Spectroscopy

Chloro Complexes in Molten Salts. 6. Potentiometric and Vapor Pressure Study of the System KCl-AlCl₃ in the Temperature Range 275-350 °C

Chloro Complexes in Molten Salts. 5. Potentiometric and Spectrophotometric Study of Chloro Complexes Formed in KCl-AlCl₃-FeCl₃ at 300°C
Lower Oxidation States of Sulfur. 1. Spectrophotometric Study of the Sulfur-Chlorine System in Molten NaCl-AlCl₃ (37-63 mol %) at 150°C

General information
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Organisations: Department of Chemistry, Energy and Materials, Microstructures and Interfaces, Fuel Cells and Solid State Chemistry Division, Risø National Laboratory for Sustainable Energy
Contributors: Fehrmann, R., Bjerrum, N., Poulsen, F. W.
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Lower Oxidation States of Selenium. 2. Potentiometric Study Involving Tetravalent Selenium, Tetraselenium(2+), Octaselenium(2+), and Three Other Low Oxidation States of Selenium in Chloroaluminate Melts

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Organisations: Department of Chemistry, Energy and Materials
Contributors: Fehrmann, R., Bjerrum, N.
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Lower Oxidation States of Tellurium. 4. Tetratellurium(2+) Hexatellurium(2+), and Octatellurium(2+) in Chloroaluminate Melts

General information
Publication status: Published
Organisations: Department of Chemistry, Energy and Materials
Contributors: Fehrmann, R., Bjerrum, N., Andreasen, H. A.
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Publication information
Journal: Inorganic Chemistry
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Research output: Contribution to journal > Journal article – Annual report year: 1976 > Research > peer-review
Chloro Complexes in Molten Salts. IV. A Potentiometric and Spectrophotometric Study of the System KCl-FeCl₃ in the Temperature Range 275-350°C

General information
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Organisations: Energy and Materials, Department of Chemistry
Contributors: Andreasen, H. A., Bjerrum, N.
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Chloro Complexes in Molten Salts. III. Raman Study of the Chloro Complexes Formed in the Molten KCl-AlCl₃-TeCl₄ System

General information
Publication status: Published
Organisations: Microstructures and Interfaces, Fuel Cells and Solid State Chemistry Division, Risø National Laboratory for Sustainable Energy, Energy and Materials, Department of Chemistry, Department of Mechanical Engineering
Contributors: Poulsen, F. W., Bjerrum, N., Nielsen, O. F.
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Lower Oxidation States of Selenium. I. Spectrophotometric Study of the Selenium-Selenium Tetrachloride System in Molten NaCl-AlCl₃ Eutectic Mixture at 150°C

General information
Publication status: Published
Organisations: Department of Chemistry, Energy and Materials
Contributors: Fehrmann, R., Bjerrum, N., Andreasen, H. A.
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Publication date: 1975
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Chloro Complexes in Molten Salts. II. Potentiometric and Spectrophotometric Study of Chloro Complexes in KCl-AlCl3-TeCl4 at 300°C

General information
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Organisations: Energy and Materials, Department of Chemistry
Contributors: Barner, J. H. V., Bjerrum, N., Kiens, K.
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Publication date: 1974
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Potentiometric Study of the Systems KCl-AlCl3 and KCl-AlCl3-ZnCl2 at 300°C, Performed with a Chlorine-Chloride Electrode

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Organisations: Energy and Materials, Department of Chemistry
Contributors: Barner, J. H. V., Bjerrum, N.
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Lower Oxidation States of Tellurium. III. Ditellurium(2+) in Chloroaluminate Melts

General information
Publication status: Published
Organisations: Department of Chemistry
Contributors: Bjerrum, N.
Pages: 2648-2652
Publication date: 1972
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