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New World for Acetylcholine Determination in Brain Microdialysis

All success in neuroscience has come from developing new measurement tools and applying them to important problems. Micro-electrodes, EEG, fMRI, cell culture and LC/EC for neurotransmitters are just a few of

these. Acetylcholinesterase inhibition-free microdialysis in awake animals now opens the door for the study of acetylcholine *in vivo* under realistic physiological conditions. This method is essential to promote our understanding of the role of acetylcholine in learning and memory as well as the action of psychotropic drugs. Now it is time to move up to the next generation method.

References

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In the EC Literature

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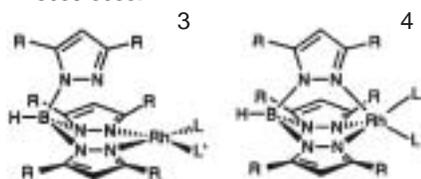
Single-Molecule Magnets: Two-Electron Reduced Version of a Mn₁₂ Complex and Environmental Influences on the Magnetization of (PPh₄)₂[Mn₁₂O₁₂(O₂CCHCl₂)₁₆(H₂O)₄]

M. Soler, W. Wernsdorfer, K.A. Abboud, J.C. Huffman, E.R. Davidson, D.N. Hendrickson, and G. Christou, *J. Am. Chem. Soc.* 125 (2003) 3576-3588.

The family of Mn₁₂ clusters [Mn₁₂O₁₂(O₂CCX₃)₁₆(H₂O)₄] is of great interest, due to their ability to act as single-molecule magnets. In this study, the synthesis and characterization of [Mn₁₂O₁₂(O₂CCHCl₂)₁₆(H₂O)₄] **2** and related anions was discussed. The cyclic voltammogram of **2** (recorded using a CV-50W) showed three reversible reductions, two of which were accessible using iodide as a reducing agent. Therefore, both the monoanion and dianion could be synthesized and characterized, in contrast to [Mn₁₂O₁₂(O₂CMe)₁₆(H₂O)₄], for which only the monoanion has been characterized. The positive shift of redox potentials was consistent with the electron-withdrawing properties of the chloride-substituted carboxylate ligand.

Reversible Sequence of Intramolecular Associative and Dissociative Electron-Transfer Reactions in Hydrotris (Pyrazolylborate) Complexes of Rhodium

W.E. Geiger, N.C. Ohrenberg, B. Yeomans, N.G. Connelly, D.J.H. Emslie, *J. Am. Chem. Soc.* 125 (2003) 8680-8688.

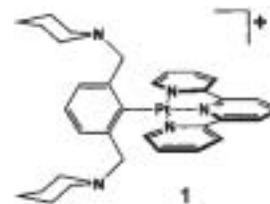


The one-electron oxidation of [RhLL'(2-Tp^{Me2})] **3** (Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate) leads to a change in the bonding mode of the Tp^{Me2} ligand from ² to ³ **4**. The mechanism of this oxidation was investigated for various L and L' by cyclic voltammetry. For L = CO and L' = P(OPh)₃ or PPh₃, oxidation was quasi-reversible. However, for L = CO, L' = PCy₃ and L = L' = PPh₃, the mechanism was consistent with a chemical reaction following the electron transfer reaction, and electrochemical activity was modeled using a square scheme. Quantitative values for the redox potentials and rate constants of the electron transfer reactions and chemical reactions were obtained using both homogeneous redox catalysis (which involves the addition of a mediator) and simulation using DigiSim.

DigiSim is a registered trademark of Bioanalytical Systems, Inc

An Outer-Sphere Two-Electron Platinum Reagent

H. Jude, A.K. Bauer, and William B. Connick, *J. Am. Chem. Soc.* 125 (2003) 3446-3447.



Although platinum(II) complexes can be oxidized to the platinum(IV) oxidation state, such processes are typically irreversible due to the large structural reorganization required for interconversion of the square-planar platinum(II) and the octahedral platinum(IV). This article discusses the characterization by cyclic voltammetry using CV-50W of a platinum(II) complex **1** that displays two reversible one-electron reductions and a reversible two-electron oxidation. The unusual oxidative behavior of **1** was attributed to the constrained meridional coordination of the terpyridine ligand and availability of the tertiary amine lone pairs on the other ligand for coordination to the platinum(IV) center. The latter requirement was demonstrated by the irreversible oxidative behavior of the related complex in which these lone pairs are protonated.

Gold Electrodes Wired for Coupling with the Deeply Buried Active Site of *Arthrobacter globiformis* Amine Oxidase

C.R. Hess, G.A. Juda, D.M. Dooley, R.N. Amil, M.G. Hill, J.R. Winkler, and H.B. Gray, *J. Am. Chem. Soc.* 125 (2003) 7156-7157.

The active site in many enzymes is buried deep within the protein, which often prevents facile direct electron transfer between electrochemically active sites and electrode surfaces. In this study, the electronic coupling between the active site of an amine oxidase and the surface of a gold electrode was enhanced by binding an electron-conducting oligomer in the substrate channel. The functional groups at the ends of this oligomer were diethylamine (for binding to the active site) and a thiol (for adsorption to the surface of the gold electrode). Characterization of this system by cyclic voltammetry using a CV-50W showed a reversible reduction at -140 mV (vs. SCE in phosphate buffer, pH 7), which was attributed to the quinone active site. In contrast, neither the unmodified amine oxidase nor gold electrodes derivatized by the conducting polymer alone showed any electrochemical activity at this potential.

Electron Transfer Reactions of Redox Cofactors in Spinach Photosystem I Reaction Center Protein in Lipid Films on Electrodes

B. Munge, S.K. Das, R. Ilagan, Z. Pendon, J. Yang, H.A. Frank, and J.F. Rusling, *J. Am. Chem. Soc.* 125 (2003) 12457-12463.

One method that has become popular for the electrochemical studies of proteins is thin layer voltammetry, in which proteins are entrapped in monolayers or multilayers on the electrode surface. In this study, spinach Photosystem I reaction center (a protein-cofactor complex involved in photosynthesis) was trapped in lipid films on pyrolytic graphite electrodes, and its redox properties were characterized by cyclic voltammetry and square wave voltammetry using a BASi 100B/W. Two well defined redox processes were observed, which were assigned to the phyloquinone and iron-sulfur cluster cofactors by comparison with systems selectively depleted of these components. The detection of these particular cofactors was attributed to their proximity to the protein surface, other cofactors being more deeply buried within the complex.

Role of Electron-Transfer Processes in Reactions of Diarylcarbenium Ions and Related Quinone Methides with Nucleophiles

A.R. Ofial, K. Ohkubo, S. Fukuzumi, R. Lucius, and H. Mayr, *J. Am. Chem. Soc.* 125 (2003) 10906-10912.

Although second-harmonic alternating current voltammetry (SHACV) is not a widely used technique, it can be useful for measuring the redox potentials of species for which the electron transfer reaction is followed by a rapid chemical reaction. In this article, the SHACV technique on the BASi 100B/W was used to measure the redox potentials of a series of diarylcarbenium ions and structurally related quinone methides. The redox potentials obtained in this way showed linear correlation with empirical electrophilicity parameters and were used to investigate the reactivity of these molecules with nucleophiles.