2,9-Di(2'-pyridyl)-1,10-phenanthroline: A Tetradentate Ligand for Ru(II)

R. Zong and R.P. Thummel, J. Am. Chem. Soc. 126 (2004) 10800.



Polypyridine complexes of Ru(II) have been very widely studied. Quaterpyridine typically acts as a bridging ligand between two Ru(II). This article discusses a new quaterpyridine ligand with a more rigid structure that prevents adoption of the helical geometry required for bridging. It was shown (by X-ray crystallography) that Ru(II) complexes of this ligand have an octahedral geometry, with the quaterpyridine ligand acting as a planar tetradentate ligand. Various 4-substituted pyridine ligands were used for the axial ligands. It was shown by cyclic voltammetry using a BASi epsilonTM electrochemical analyzer that the complexes showed one metal-based oxidation and two ligand-based reductions. The potential of the metal-based oxidation was significantly affected by the electron-donating or withdrawing properties of the axial ligands (e.g., an electrondonating ligand decreases the oxidation potential), whereas these properties had a much smaller effect on the reductions.

Binding and Electrochemical Recognition of Barbiturate and Urea Derviatives by a Regioisomeric Series of Hydrogen-Bonding Ferrocene Receptors

J. Westwood, S.J. Coles, S.R. Collinson, G. Gasser, S.J. Green, M.B. Hursthouse, M.E. Light, and James H.R. Tucker, Organomet. 23 (2004) 946.



This article examined the interaction of a series of ferrocenecontaining amidopyridyl receptors (2 and 3) with some urea and barbiturate derivatives through hydrogen bonding. The magnitude of the interaction was determined by proton NMR titration and cyclic voltammetry using a BASi100B/W (as indicated by a negative shift in the redox potential of the ferrocene moiety relative to the uncomplexed receptor). As expected, the degree of interaction varied both with the type of sites available for hydrogen bonding and the relative orientation of these sites.

Electronic Properties of Mononuclear, Dinuclear, and Polynuclear Cobaltacarboranes: Electrochemical and Spectroelectrochemical Studies

F.F. de Biani, M. Corsini, P. Zanello, H. Yao, M.E. Bluhm, and R.N. Grimes, J. Am. Chem. Soc. 126 (2004) 11360

The redox properties of molecules containing multiple redox centers is highly dependent on the degree of interaction among these centers. In this article, cyclic voltammetry using a BASi 100B/W was used to characterize the redox properties of a wide range of cobaltacarboranes containing one to six metal centers. These molecules were classified according to the Robin-Day scheme (Class I = localized, Class II = partially delocalized, or Class III = fully delocalized) through measurement of the separation of the redox processes in the cyclic voltammograms (increasing delocalization increasing this separation). It was found that the extent of delocalization was strongly influenced by the nature of the linking unit and the presence of substituents on the carborane cages. Extended Hückel molecular orbital calculations were also used to provide additional insight into the electronic structures of selected molecules.

Mixed Valence Isomers

J.C. Salsman, C.P. Kubiak, and T. Ito, J. Am. Chem. Soc. 127 (2005) 2382.



If a molecule has two redox centers, then the redox properties of the molecule depend on the degree of interaction between these two centers. If there is partial delocalization between the centers, then it is sometimes possible to isolate the product of the first oxidation or reduction reaction (often referred to as a mixed valence complex). Although there are two alternate charge distributions (depending on which redox center the charge is associated with), these are degenerate if the redox centers are identical. However, if the centers are not identical, then the two possible isomers are not degenerate, and may be identified. In this article, two triruthenium clusters were coupled using a methyl pyrazine bridging ligand, and asymmetry was introduced by a) the methyl group on the pyrazine ligand and b) an isotopically-labeled CO ligand (4 and 5). Cyclic voltammetry (using a CV-50W) showed the two expected reductions, separated by 340 mV, indicative of strong coupling. The isomers were also characterized by infrared spectroelectrochemistry. There were two carbonyl bands for both the neutral isomers and the fully reduced dianionic isomers, due to the isotope substitution, whereas there were four carbonyl bands for the mixed valence complex, due to the presence of both mixed valence isomers.

Multielectron Redox Chemistry of Iron Porphyrinogens

J. Bachmann and D.G. Nocera, J. Am. Chem. Soc. 127 (2005) 4730.

Porphyrinogens are macrocyclic tetrapyrrole molecules that can be converted to porphyrins through meso substituent oxidative elimination. In this study, a series of redox-related iron porphyrinogens was synthesized and their redox properties were investigated by cyclic voltammetry, differential pulse voltammetry and chronocoulometry using a CV-50W. It was found that the iron(III) complex [LFe(III)]⁻ undergoes a one-electron metal-based reduction of iron(III) to iron(II) to generate [LFe(II)]²⁻, and a four-electron oxidation of the porphyrinogen ring to generate $[L^{\Delta\Delta}Fe(II)]^{2+}$, although it should be noted that one of these electron is intercepted for reduction of iron(III) to iron(II), resulting in a net threeelectron oxidation. The reduced and oxidized molecules were synthesized using appropriate chemical redox reagents, and were characterized by X-ray crystallography and molecular orbital calculations, as well EPR, magnetic and Mössbauer measurements.



In the Literature

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Using Mass Spectrometry for Drug Metabolism Studies edited by Walter A. Korfmacher 370 pp, with illus, \$159.95, ISBN 0-8493-1963-3 Boca Raton, FL, CRC Press, 2005.

I have known Walter Korfmacher for quite some time and have admired his frequent papers from the Schering-Plough Research Institute (SPRI), which often introduce new concepts. This is an edited work with every chapter but one having authors from the industrial world where high throughput, automation and a wide range of structures are most common. I find the practical hints with real world "war stories" to be most useful. As we all know, the appropriate technologies are rarely affordable in academic circumstances.

The focus here is definitely on drug metabolism, both *in vitro* and *in vivo*. This is not a pharmacology or pharmacodynamics book, and there is not much here for the clinical trials environment. Bioanalytical chemistry requires great attention to balancing speed, accuracy, cost and documented validation with the nature of the decisions to be

made. Walter envisions four levels as follows:

- I. Screening (two-point standard curve)
- II. Lead optimization (multipoint standard curve, but no QC)
- III. Lead qualification (multipoint standard curve plus QC)
- IV. Development (GLP rules, full QA)

I would like to have seen a little more attention paid to sample acquisition and preparation, both of which often have more impact than the end game of mass spectrometry. That said, there is a lot of meat here, the examples are excellent and the material is very up-to-date. (*Peter T. Kissinger*)

Drug Discovery for Nervous System Diseases by Franz F. Hefti 319 pp, with illus, paper, \$89.95, ISBN 0-471-46563-1 Hoboken, NJ, John Wiley & Sons, Inc., 2005.

I was delighted to find this book written by a BASi customer of 25 years ago, Franz Hefti, who has extensive experience with neuropharmacology. I enjoyed reading it while riding on my exercise bike. I peddled faster, recognizing that exercise is proven therapy for the brain.

This is not a book about laboratory techniques; it is a neuropharmacology book organized primarily around clinical need with chapters on schizophrenia, depression, anxiety disorders, Alzheimer's disease, Parkinson's disease, ischemic stroke, spinal cord injury, sleep disorders, epilepsy, pain and more. There are five introductory chapters that set the stage, with useful figures, references and a good index. This is a book of capsules, not a thorough review. It would make an excellent augmentation to a seminar course and is handy for old-timers who need a quick refresher on current therapy for neurological disorders. (*Peter T. Kissinger*)

The Last Valley:

Dien Bien Phu and the French Defeat in Vietnam by Martin Windrow, 733 pp, \$30.00, ISBN 0-306-81386-6 Cambridge, MA, Da Capo Press, 2004.

When science and business go badly for me, I sometimes retreat with history books to appreciate how much worse life can really be. This is a long book, suited only to those of us who are fascinated by military history. It covers the post-World War II situation in Southeast Asia quite well. As the Cold War began and European colonialism started to wane, there was much confusion politically, culturally and militarily. Many disruptive changes were occurring worldwide on a scale that is guite familiar today. The late 1940s to the mid-1950s frame this book. Europe and Japan were struggling to recover from WWII, Korea was in flames, and China disengaged from the world. Their attempt to re-establish control over Vietnam during 1945 to 1954 is an event from which France has not yet fully recovered, and it led to the continuing involvement of the USA beginning in 1945, an event from which we have not yet truly recovered either. Interestingly, we loaned aircraft to our French colleagues as their fate degraded. I recently read that the U.S. and Vietnam (Hanoi) are having discussions about a tighter military alliance to protect our mutual interests in the South China Sea. Sixty years can include a lot of hardship and sorrow in a very small country. Not only is this book fascinating, but Vietnamese food is fabulous. (Peter T. Kissinger)

Once Upon a Town: The Miracle of the North Platte Canteen, by Bob Green, 264 pp, \$13.95, ISBN: 006008197X, New York, NY, HarperCollins, 2002.

From December 1941 until April 1945, from 5:00 a.m. until after midnight every day, the citizens of North Platte, Nebraska and the surrounding communities did an astonishing thing. They created a canteen in their railroad depot, where volunteers greeted military men on their way to and from World War II with food, smiles, gratitude and a taste of home. Volunteers met every troop train – as many as 35 a day – and for 10 or 20 minutes while the trains were being refueled with coal and water, the men enjoyed free food and perhaps even a dance with one of the local gals. During the short life of the North Platte Canteen, more than six million American soldiers were greeted, fed and entertained.

Once Upon a Town is a tribute to the men, women and girls who made sure that every G.I. was warmly welcomed, thanked for their service, and found tables filled with food, magazines, fruit, cigarettes, cakes and pies, candy, milk and coffee. Don't forget this took place during a time when gas, rubber, sugar, coffee and meat were all rationed, and folks had to save their ration stamps to make sure the canteen had plenty of everything. The book is a moving memoir of a time fast fading from memory, a time when folks banded together to do whatever large or small thing they could to help win the war. People from farms and more than 125 small towns throughout western Nebraska and eastern Colorado took their turn providing food and greeting the troops. A friend who is a native of Nebraska tells me that his father, who was in high school at the time, used to play the piano at the Canteen to provide music for listening and dancing.

This is a quick, enjoyable read that will take you to another time and give you a perspective on the human side of WW II. Based on interviews with people now in their 70s and 80s, along with archival research, the author gives us a poignant account of life on the homefront and of the modest and generous people who made an extraordinary contribution to the war effort. Although the Canteen remains a vivid memory for those who were there, the Union Pacific tore down the depot in the early 1970s, and the veterans and citizens who experienced the Canteen are leaving us, one by one, every day. Thankfully, Bob Green has given us this book so they will never be forgotten. I highly recommend it! (*Alice Schwind*, *BASi*)