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An Electrochemically-Controlled Molecular Shuttle. Krzysztof Wozniak¹, Bohdan Korybut-Daszkiewicz², Renata Bilewicz¹, Agnieszka Wieckowska¹, Sławomir Domagała¹, ¹Chemistry Department, Warsaw University, 02-093 Warszawa, ul. Pasteura 1, Poland, ²Institute of Organic Chemistry, Polish Academy of Sciences, 01-224 Warszawa, Kasprzaka 44/52, Poland. E-mail: kwozniak@chem.uw.edu.pl

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In this contribution we will present novel homo- and hetero-[2]catenanes (and bismacrocycles) self-assembled using macrocyclic transition metal complexes and benzo-crown ether as building blocks and discuss interactions between two metal centers via $\pi \dots \pi$ interactions. We will present the first example of heterodinuclear bismacrocyclic transition metal complex exhibiting potential-driven intramolecular motion of the interlocked crown ether unit. To our knowledge, this is the first instance of a transition metal heterodinuclear catenane which reveals translocation of the crown unit back and forth between two different metal centers in response to an external stimulus – an applied potential. By applying appropriate potentials either copper or nickel (or both) are reversibly oxidized to the higher (+3) oxidation state. This favours interaction with the π -electron-rich aromatic system of the crown unit which relocates the crown towards the oxidized metal center. The nickel centers affected by the hydroquinol groups are oxidized more easily than those not surrounded by the crown units. This “frozen” interconversion within the molecule can be better observed at lowered temperature or shorter time scales. The phenomenon of controlled intramolecular motion can potentially be applied in molecular devices.

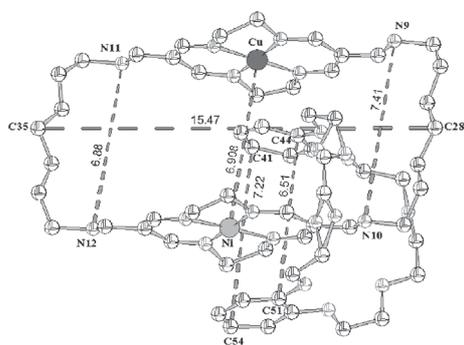


Figure 1. Novel hetero-[2]catenane with hydrogens omitted for clarity.

s2.m10.o1

Charge Density Studies of Some Iron Nitrosyl Complexes. Yu Wang, J. J. Lee and I. J. Hsu, Department of Chemistry, National Taiwan University, Taipei, Taiwan. E-mail: yuwang@xtal.ch.ntu.edu.tw

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Charge density and bond characterization have been investigated on some Iron-nitrosyl complexes in terms of accurate single crystal diffraction at 100K and an open-shell DFT calculation. The iron atom is four- five- and six-coordinated with sulfur and nitrogen atoms in various geometries. The nitrosyl group (NO) could be linear or bent with Fe-N-O close to or deviate from 180 degree. Since these complexes are related to biological activities, this study may shine some light on how it operates via electron density distribution, especially at the iron site and at the NO group. It is known that NO group could be a radical neutral species or NO^+ , a nitrosyl, or NO^- , a nitroxide group. Thus the unpaired electron can be located either at Fe or at the NO group; meanwhile the formal charge of the Fe will be dependent on the charge on the NO group. According to the electron density distribution based on the multipole model and on the DFT calculation, the electronic configuration of iron atom and the charge of NO group can be determined. In addition, the location of the unpaired electron will be confirmed with single crystal EPR and SQUID measurements. The formal charge of Fe will be complemented by the x-ray absorption spectroscopy. Topological analysis on the total electron density will give the bond characterization in terms of topological properties associated with bond critical points. The VSCC of Fe in various coordination geometries, together with the detail descriptions and their correlations to the metal ligand bond will be presented.