conference abstracts

s2.m1.p5 **Experimental Charge Density of a Trinuclear Mixed-Valence Iron Compound**. J. Overgaard[a], B.B. Iversen[a], F.K. Larsen[a], S.P. Palii[b], G.A. Timco[b], G. Wu[c]. *Department of Chemistry, University of Aarhus, DK-8000 Aarhus C;[b] Institute of Chemistry, Academy of Sciences of the Republic of Moldova, Chisinau, MD-2028, Moldova;[c] National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY 11973, New York.*
Keywords: charge spin densities.

Both Mössbauer spectroscopy and X-ray crystallographic studies of the compound, $[Fe_2^{III}Fe^{II}(\mu^3-O)(O_2CC(CH_3)_3)_6(NC_5H_5)_3]$, have recently been carried out at various temperatures[1,2]. The X-ray study revealed that a temperature dependent electron transfer takes place between only two of the three Fe-atoms at temperatures higher than 35 K. Below this temperature the valence of all three Fe-atoms is trapped. The space group is unaffected by the valence trapping proces, thus the asymmetric unit, which consists of one complete molecule, is the same at all temperatures. Determination of the accurate electron density at 28 K enables us to investigate the molecule in its valence trapped configuration and to speculate on the electronic reasons for the different temperature dependence of the structurally identical Fe^{III}-atoms.

An extensive dataset was collected at the National Synchrotron Light Source with the crystal cooled to 28 K and using synchrotron radiation of wavelength 0.643 Å and a Bruker SMART CCD. A total of 130460 reflections integrated and averaged to 32582 unique reflections with an internal agreement of 3.4 %. Additional low-order data, collected at a conventional source at a similar temperature, were included in the final refinements. The data were fitted to a multipolar model using the XD program package resulting in R(F)=4.0%.

Details of the refinement, which is non-standard due to the acentric space group and the large number of atoms, will be presented to emphasize the reliability of the obtained model. The results of a topological analysis will be given to illustrate the electronic features, in particular in the region of the temperature dependent bonds. Furthermore, derived d-orbital populations for the metals from the refined population parameters give some implications for the mechanism of electron transfer in mixed valence compounds.

[1] R. Wu et al "Electron Localization and Delocalization in Mixed-Valence Transition Metal Clusters: Structural and Spectroscopic Studies of Oxo-Centered Trinuclear Complexes $[Fe_3O(OOCCMe_3)_6(py)_3]^{+/0}$ and $[Mn_3O(OOCCMe_3)_6(py)_3]+/0$", *Inorg. Chem.* (1998), 37: 1913-1921.
[2] C. Wilson et al "Multi-temperature Crystallographic Studies of Mixed-Valence Polynuclear Complexes. Valence Trapping Process in the Trinuclear Oxo-bridged Iron Compound, $[Fe_3O(O_2CC(CH_3)_3)_6(NC_5H_5)_3]$", *submitted to JACS.*

s2.m1.p6 **Topological Analysis of Experimental Charge Densities of Organometallic Carbene Complexes**. M.A. Tafipolsky, W. Scherer, K. Öfele, F.J. Kohl, *Anorganisch-chemisches Institut, Technische Universität München, Lichtenbergstraße 4, D-85747, Garching, Germany.*
Keywords: X-ray diffraction; topological analysis; charge density.

Organometallic carbene complexes play an increasingly important role as key intermediates in homogeneous catalysis such as in olefin metathesis, Fischer-Tropsch synthesis, olefin and alkyne polymerization and cyclopropanation[1]. As a recent development, *N*-heterocyclic carbenes are used to complement and extend the capabilities of the ubiquitous phosphane ligands[2]. We have addressed the question on the σ-donor/π-acceptor capabilities of a carbene ligand by analyzing directly the topology of the electron charge density[3] of the Cr=C(carbene) bond and could show that the topological parameters are a more sensitive probe of the nature of the carbene bonding in comparison with the carbonyl stretching frequencies.

The topology of the experimental (single-crystal high-resolution X-ray diffraction) and/or the theoretical (at the BPW91/DZVP2 level) electron charge density distributions of a series of pentacarbonyl chromium carbene complexes of the formula L-$Cr(CO)_5$ (where L denotes *N,N'*-dimethylpyrazolyl-3-ylidene **1**, *N,N'*-dimethylimidazolin-2-ylidene **2** and 2,3-diphenylcyclopropenylidene **3**) has been analyzed.

Compounds **1** and **2** are known to display an unexpected stability which gave rise for speculations on the aromatic character of the cyclic carbenes and inhibited π-acceptor capabilities. Our topological studies, however, give *direct* insight into the nature of the metal-carbene bonding in **1-3**. The shorter experimental Cr=C(carbene) bond (2.044 *vs* 2.132 Å) and the larger experimental bond ellipticity (0.15 *vs* 0.01) in **3** compared to **1** were found. We attribute this fact to a more pronounced π-acceptor capability of the cyclopropenylidene ligand in **3**.

We have shown that the topological approach can be successfully used to access the question on the degree of electron charge delocalization in the *N*-heterocyclic carbene ligands of **1** and **2**. We found that such a delocalization is much more pronounced in the complex **2** compared to that in **1**. It remains to be seen whether these small differences in the degree of cyclic electron delocalization as observed in the carbene ligands in **1** and **2** might play a significant role in catalysis, even when the σ donor and π acceptor capabilities of both carbene ligands seem to be rather similar.

[1] Herrmann W. A., Köcher C. "N-Heterocyclic Carbenes.", *Angew. Chem., Int. Ed. Engl.,* (1997), 36: 2162 - 2187.
[2] Herrmann W. A., Köcher C., Gooßen L. J., Artus G. R. "Heterocyclic Carbenes: A High-Yielding Synthesis of Novel, Functionalized N-Heterocyclic Carbenes in Liquid Ammonia.", *Chem. Eur. J.,* (1996), 2: 1627 - 1636.
[3] Bader R. F. W. "Atoms in Molecules: A Quantum Theory.", International Series of Monographs on Chemistry, Vol. 22, Oxford University Press, Oxford, U.K., 1990.