Organometallic Chemistry and Coordination Compounds

MS07.00.01 HYDROGEN BONDS IN ORGANOMETALLIC CHEMISTRY: DIRECT AND INDIRECT PARTICIPATION OF TRANSITION METAL CENTERS. Lee Brammer, Department of Chemistry, University of Missouri-St. Louis, 8001 Natural Bridge Rd., St. Louis, MO 63121-4499, USA

Hydrogen bonds in which transition metal centers participate directly in either the acceptor (X–H...M, X–H...H–M) or donor (M–H...X, M(H2)...X) role have been the subject of definitive study only in recent years. Such interactions are important in the protonation/ deprotonation reactions of metal centers and metal hydride species. Discussion of such hydrogen bonds will draw examples from both our own work and that of other groups. Structure and bonding aspects of such hydrogen bonds will be presented from an experimental (crystallographic and spectroscopic) and theoretical viewpoint.

It has also begun to be recognized that interligand hydrogen bonding is of great importance in the way many organometallic molecules interact with each other. Some examples of "soft" C–H...X interactions will be discussed with emphasis on X = halogen. The indirect effect on these hydrogen bonds of the transition metal centers to which the ligands are coordinated will be discussed.

MS07.00.02 ELECTRON-DEFORMATION DENSITY INVESTIGATIONS ON ORGANOMETALLIC COMPOUNDS: SUCCESS AND PITFALLS. C. Krüger, K. Angermund, J. Bruckmann, F. Lutz and C. Kopiske, Max-Planck-Institut fur Kohlenforschung D-45470 Mulheim a. d. Ruhr Strukturchemie

The detailed experimental determination of the Electron Deformation Densities of organometallic compounds and their ligands can reveal structural effects which are often overlooked in the course of a normal structural characterization of compounds. These minor effects include:

1. slight disorder problems within ligands,
2. heavy atom disorder,
3. general disorder on a molecular level,
4. co-crystallizing impurities (less than 3%).

Some of these effects, if not taken into account, cause molecular distortions larger than those introduced by erroneous space group assignment, etc.

Structural investigations of several phosphines, Nickel-phosphine as well as zirconium complexes will serve as examples. It is concluded that statistically more than 10% of all structural investigations published so far may suffer in their geometrical data from these effects.

A description of our standard low temperature data collection and data reduction procedure for EDD-measurements will be given. Finally, EDD data obtained by scintillation counter techniques will be compared to CCD counter data using identical crystals as well as data reduction procedures.

MS07.00.03 MOLECULAR MECHANICS FOR ORGANOMETALLIC MOLECULES: PREDICTION AND EXPLANATION. Tatjana V. Timofeeva and Norman L. Allinger, Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov St., 28, 117813, Russia Department of Chemistry, Computational Center for Molecular Structure and Design, University of Georgia, Athens, Georgia 30602-2556, USA

In recent years molecular mechanics (MM) begun to penetrate the wide field of organometallic chemistry. Until recently only few attempts have been made to calculate such molecules. The calculations were hindered by two problems, first, the connectivities (graphs) of these molecules are not compartable with traditional MM software. The second reason is that too many different types of bond angles have to be described for the same atom type. It is well known that that ligands in organometallic molecules have no consistent bond angles to describe their positions in the coordination sphere of the metal atom. So very often the leading role in formation of coordination sphere around metal atom plays ligand-ligand non-bonded interactions. To describe ligand positions two ways could be used: dummy atom technique and quasi non-bonded interactions of molecular fragments. For instance any metallocene molecule could be described as metal atom joint by two bonds to the centers of the Cp-rings (dummy atoms), or like metal atom joint with 10 carbon atoms of Cp-rings by strong potential of non-bonded type (6-exp, 6-12).

Using mentioned approach several series of organometallic molecules have been described in a free state and in crystal. It was shown that for unsubstituted and substututed metallocenes of main II and IVA groups and for lantanides II the conformation of bent sandwich is preferable in free and in solid state. It is due to the interligand attraction when M-ligand distances are long. The bending is bigger when the metal-carbon distances (metal radii) is bigger. Systematical increase of bending in crystal according to our calculations is due to additional M-ligand interaction with the ligands of the neighboring molecules. The same regularity was found for a series of sandwich metallocarboranes of the $[RR'C_2B_4H_2]_2M$ type, where M=Si, Ge, Sn, Pb. Molecules with short M-ligand distances (M=Si, Ge) have parallel, and bent-sandwich conformation for atoms with bigger radii (M=Sn, Pb).

MS07.00.04 STRUCTURES OF SODIUM COMPLEXES OF CITRACONIC ACID. Graciela Díaz de Delgado, Teresa González, and Alexander Briceño V. Laboratorio de Cristalografía, Departamento de Química, Facultad de Ciencias, Universidad de Los Andes, Mérida 5101, Venezuela.

The structures of two sodium complexes of citraconic acid are presented in this paper. Sodium citraconate monohydrate (1) and sodium hydrogen citraconate (2) were obtained by slow evaporation of H_2O/DMSO solutions containing citraconic acid and sodium carbonate in molar ratios of 1:1 and 2:1 respectively. Crystal data for (1): Monoclinic, C2/m, with lattice parameters a=10.967(3), b=6.811(2), c=10.207(3)Å, β=88.23(2)°, Z=4. The refinement on F^2 converged at wR^2=0.1000, R=0.0337, S=1.084 for 862 reflections with I>2(I). Crystal data for (2): Monoclinic, $P2_1/c$, with lattice parameters a=12.003(4), b=5.395(2), c=10.213(4)Å, β=111.12(2)°, Z=4, wR^2=0.1927, R=0.0761, S=1.098 for 953 reflections with I>2(I).

Compound (1) is a coordination polymer where the two sodium atoms display different coordination geometries. One sodium atom is pentacoordinated with Na-O distances in the range 2.278(2)-2.596(2)Å while the other is coordinated to six oxygen atoms with Na-O distances between 2.362(1) and 2.546(1)Å. In compound (2) layers of Na atoms with citraconate moieties above and below the plane stack along the a-axis. The sodium atom is hexacoordinated with Na-O distances of 2.329(2) to 2.596(2)Å.

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