

TOPOLOGICAL ANALYSIS AND BOND CHARACTERIZATION OF KNiF₃ AND K₂NiF₄Y. Wang¹ L. Chen¹ H. S. Sheu² I. J. Hsu¹ J. J. Lee¹¹National Taiwan University Department of Chemistry #1, Sect. 4 Roosevelt Road TAIPEI 106 TAIWAN ²SRRC, Hsin-Chu, Taiwan

The well-known perovskite and the K₂NiF₄ type structures are very important structure types in minerals and in high temperature superconductors, the bond characterization of these two solid are thus investigated. The Ni center is coordinated in an octahedral fashion in both structures, though its site symmetry is *m3m* and *4/mmm* respectively. The bondings of Ni-F and K-F are characterized in terms of topological analyses of electron densities of both crystals. Electron density is derived both from single crystal diffraction and from solid-state calculation. Detail comparison between experiment and theory will be given. Additional electron density maps are obtained from powder diffraction data processed with maximum entropy method. Band structure calculation leads to a clear picture of a covalent character of Ni-F and an ionic character of K-F. The σ donor and π donor of F atom of Ni-F bond are demonstrated in the density of states to be bonded with *d*(eg) and *d*(t_{2g}) orbitals of Ni respectively. The crystal field splitting, 10 Dq, is 1.2 and 1.4 eV for KNiF₃ and K₂NiF₄ respectively, which is in good agreement with that derived from the x-ray absorption experiment. The difference in Ni center between these two structures can only be detected by detail examination of the band structure and of the atomic graph where significant differences are located between Ni-F bonds along c-axis and a-axis in K₂NiF₄. The effect of second nearest neighbor on a chemical bond is thus realized.

Keywords: CHARGE DENSITY; BANDSTRUCTURE; TOPOLOGICAL ANALYSIS**ELECTRON DENSITY DISTRIBUTIONS OF HYPERVALENT BONDS IN PENTACOORDINATE BORON AND CARBON COMPOUNDS**D. Hashizume¹ M. Harakawa¹ M. Yasui¹ F. Iwasaki¹ Y. Yamamoto² K. Akiba³¹The University of Electro-Communications Department of Applied Physics and Chemistry 1-5-1, Chofugaoka, Chofu TOKYO 182-8585 JAPAN²Graduate School of Science, Hiroshima University ³Advanced Research Center for Science and Engineering, Waseda University

There is no transition state as famous as those of bimolecular nucleophilic substitution reactions especially for carbon atom. Hypervalent compounds have been postulated as the transition state since the central atom on the reaction should expand the valence shell. Recently, pentacoordinated hypervalent boron and carbon compounds were synthesized. The structures are trigonal bipyramidal likewise to the proposed structure of the transition state. To clarify the properties of the hypervalent bonds, the electron density distribution studies were carried out. The diffraction data of boron compound were collected in the laboratory, while those of the carbon compound were collected utilizing the synchrotron radiations at SPring-8 BL04B2 beam line. Each data set was collected by the IP Weissenberg cameras by an oscillation method. The electron density distribution analyses were carried out by a multipole expansion method. On the deformation maps, the dative characters of the hypervalent bonds were clearly observed in each compound. The lone pair electrons on the ligand oxygen atoms were directed to the electron deficient 2p orbital on the boron or carbon atom. Topological analyses were performed to characterized the properties of the bonds quantitatively. The bond paths were clearly observed along the hypervalent bonds. The small positive Laplacian ρ and small ρ values at the bond critical points indicate the electrostatic characters of these bonds. In the boron compounds, the large bond ellipticity values may imply the electron donation from the 2p orbitals of the sp² hybridized ligand oxygen atoms to boron atom.

Keywords: HYPERVALENT COMPOUND, CHARGE DENSITY, TOPOLOGICAL ANALYSIS**CHARGE DENSITY DISTRIBUTION IN 2-METHYL-1,3-CYCLOPENTANEDIONE**T. Borowiak¹ M. Kubicki¹ G. Dutkiewicz¹ C. Jelsch² C. Lecomte²¹Adam Mickiewicz University Faculty of Chemistry Ul.Grunwaldzka 6 POZNAN 60-780 POLAND ²Laboratoire de Cristallographie et Modelisation des Materiaux Mineraux et Biologiques. CNRS UMR 7036. Universite H. Poincare, BP 239, 54506 Vandoeuvre-les-Nancy cedex. France

The charge density distribution in 2-methyl-1,3-cyclopentanedione (enol form) has been determined by means of high-resolution X-ray diffraction at 110K. The five-membered ring is perfectly planar, as the molecule lies at the crystallographic plane of symmetry in the space group *C2/m*. The positions of hydrogen atoms are also consistent with the *m*-symmetry, and there are no signs of disorder of the methyl group, that was observed in the room temperature study [1]. The Hansen-Coppens multipole model was used to describe the electron density, the molecular symmetry highly reduced the number of non-zero multipoles. The deformation density distribution clearly shows differences between formally double and single bonds, but the analysis of the respective values confirms the significant resonance within the fragment O=C-C=C-OH. These conclusions are also supported by topological analysis of charge density distribution. The values of ρ at bond critical points in the conjugated fragment O=C-C=C-O are: 2.85, 2.04, 2.32 and 2.29e⁻³, respectively, and corresponding Laplacian values are: -29.1, -17.5, -22.4 and -20.1e⁻⁵. The bond critical point was also found for strong intermolecular O-H...O hydrogen bond (H...O distance of 1.632(7) Å); the corresponding ρ value is very high, 0.43 e⁻³, and the positive Laplacian value (4.50 e⁻⁵) suggests mainly 'closed-shell' kind of interaction, that is typical for hydrogen bonds.

References

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Keywords: CHARGE DENSITY TOPOLOGICAL ANALYSIS HYDROGEN BONDS**THE ELECTRON DENSITY DISTRIBUTION IN PARAMAGNETIC AND ANTIFERROMAGNETIC MnO: A γ -RAY DIFFRACTION STUDY**

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Highly accurate single-crystal structure factors, up to $\sin\theta/\lambda = 1.6 \text{ \AA}^{-1}$, have been measured from MnO at 295 K (100% data completeness) and in the antiferromagnetic state at 15 K (86% data completeness) using 316.5 keV γ radiation. Moderate uniaxial pressure was applied in the low-temperature phase to force a single-T-domain sample. A detailed description of the electron-density distribution is presented. The occupancies of the 3d shell are computed from multipole refinement parameters, showing significant differences between the two magnetic phases. The total number of d electrons is found to be 4.74(2), i.e. considerably smaller than the formal value of 5. It can be compared straightforwardly with the magnetic moment as obtained from neutron diffraction and taking into account the zero-point spin deviation: 4.72(4) μ_B . The close agreement between the γ ray and neutron result supports the reliability of the multipole partitioning leading to physically meaningful atomic charges. A careful analysis of electronic properties in the inter-nuclear regions reveals the Mn-O interaction to be purely ionic.

Keywords: MNO, γ RAY DIFFRACTION, CHARGE DENSITY