

ON THE IONIC VS NEUTRAL NATURE OF METAL GUESTS IN THE THERMOELECTRIC CLATHRATE MATERIALSC. Gatti¹ L. Bertini¹ B.B. Iversen² N.P. Blake³¹cnr-Istm, Istituto Di Scienze E Tecnologie Molecolari, Via C. Golgi 19, 20133 Milano, Italy ²department of Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark ³department of Chemistry and Biochemistry, University of California, Santa Barbara, Ca 93106, Usa

Type I inorganic clathrates constitute some of the most promising non-optimized structures discovered in the search for improved thermoelectric materials (TMs). The extent of charge transfer (CT) from the guest metal atoms to the semiconductor framework and the detailed nature of the host-guest interactions are both supposed to affect significantly each one of the three material properties "Seebeck coefficient, thermal and electrical conductivity" determining the figure of merit of TMs. Based on the distinction between charge donation "the flowing of electrons from the valence band of the guest sub-lattice to the conduction band of the framework sub-lattice" and charge transfer, the spatial displacement of electrons from the region of the metal guests sub-lattice to the region of the semiconductor frame, it was in the past concluded that the guest atoms are charge donors, but not ionic in these TMs. By using an *ab-initio* density functional approach and an atomic space partitioning based on quantum mechanics rather than on purely geometrical considerations, we show that the guest atoms (Sr, Ba) are indeed mostly ionic, regardless of the kind of cage they occupy. The insensitivity of CT to the cage size is confirmed by Diffraction Anomalous Fine Structure (DAFS) results across the Sr K edge. The significant displacement of the guest atom from the center of the 24-atom cage is found to be driven by the formation of strong frame-guest interactions also in the larger cage, a mechanism which eventually leads to similar CTs in the two kind of cages. The interplay between CT and thermo-power is investigated by using a one-electron transport model for the Seebeck coefficient evaluation and a number of model clathrates with varied CT, as induced by compression or expansion of the lattice.

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CHARGE DENSITY AND TOPOLOGICAL PROPERTIES OF LARGER MOLECULES OF BIOLOGICAL INTEREST

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Recent experimental developments in X-ray crystallography, especially the introduction of area detectors, has made it possible to collect high resolution data sets in a reasonable time [1] so that charge density studies on larger molecules become feasible. We measured high order diffraction data of up to several hundred thousand reflections on a few biologically active compounds (e. g. penicillin derivatives, strychnine, and the hexapeptide [(Ala)-(Pro)-~]). Data collection was made with synchrotron and conventional MoK α radiation and the advantages/disadvantages of synchrotron versus conventional radiation in combination with CCD area detection will be discussed. In one case (the hexapeptide) a direct comparison of a synchrotron and a MoK α data set can be made. The conclusion is that charge density studies on molecules of more than hundred atoms can be performed in a reasonable time, provided that area detection is applied.

References

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Keywords: CHARGE DENSITY SYNCHROTRON RADIATION HIGH RESOLUTION DIFFRACTION**CHARGE DENSITY DISTRIBUTION AND X-RAY ABSORPTION SPECTROSCOPY OF IRON-NITRO THIOLATE COMPLEXES**I. Hsu¹ C. Hsieh³ C. Chen³ W. Liaw³ Y. Wang^{1,2}¹Department of Chemistry, National Taiwan University No.1, Sec.4, Roosevelt Rd. TAIPEI 106 TAIWAN ²Instrumental Center, National Taiwan University, Taipei, Taiwan ³Department of Chemistry, National Changhua University of Education, Changhua, Taiwan

The biomimic of the degradation of iron-sulfur protein are investigated through tri-, di-, and mono- nuclear iron-NO-sulfur complexes. The coordination sphere of Fe in the trinuclear complex and in the mononuclear one can be described as a tetragonal pyramidal Fe(NO)S₄ core. The dinuclear one consists of one tetrahedral Fe(NO)₂S₂ core and one trigonal bipyramidal Fe(NO)S₄ core. Electron density distributions of these complexes are studied in terms of multipole model based on the X-ray diffraction data and of the molecular orbital calculation. Topological properties associated with the bond critical points (BCP), Laplacian of the electron density as well as electron density at the BCP of each chemical bond will be presented. The comparison between experiment and theory will be made. The intra-molecular chemical bond as well as the binding among iron core in trinuclear and dinuclear complexes will be discussed. Whether there is any binding interaction between two Fe atoms with short Fe-Fe distance of 2.5772(3) Å in trinuclear and of 2.6625(2) Å in dinuclear complex, are good examples of metal-metal interaction. Since NO group could be a NO⁺¹ or radical NO or NO⁻¹, the oxidation state and the net atomic charges of the Fe atoms becomes very interesting and important for their magnetic behavior. The magnetic interaction among Fe atoms will also be discussed by the SQUID and EPR results. The charge density investigation complimented by the Fe L and K -edge X-ray absorption spectroscopy may lead to the understanding of the mechanism of the degradation of iron-sulfur protein.

Keywords: X-RAY CHARGE DENSITY

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DECONVOLUTION OF THERMAL MOTION IN CRYSTALLINE NAPHTHALENE

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Highly redundant X-ray diffraction data of crystalline naphthalene were measured at 100 K, 135 K, 170 K and 205 K using a Nonius KappaCCD. Refinements were carried out using generalized X-ray structure factors (gsf's, multipole expansion) [1]. If the electron density is described solely by the gsf's and the thermal motion by the anisotropic displacement parameters the multipole terms should be temperature independent. This was achieved with a model that employed isotropic polarized hydrogen atoms and multipoles for carbon up to the octapole level. The study made use of 2 different crystals, 4 temperatures and several refinement models. Persistently one of the C-H bonds adopted a length that was 0.05 Å shorter than the other C-H bonds. This short C-H bond appears to be related to a short (2.7 Å) intermolecular CH/ π -interaction.

The different intra- and intermolecular interactions were characterized through a topological analysis of the experimental charge density [2]. These results have been compared to equivalent analysis of the theoretical charge densities of the isolated molecule and of the crystal.

References

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