

s9.m1.o3 **The Attractive H \cdots H Interaction: A New Type of Hydrogen Bond.** T.F. Koetzle, *Chemistry Department, Brookhaven National Laboratory, P.O. Box 5000, Upton, NY 11973-5000 USA.*

Keywords: hydrogen bonding, neutron diffraction, dihydrogen bond.

A new type of hydrogen-bonding interaction has recently been recognized that utilizes the σ -bonding electron pair E-H as the acceptor where E stands for a main-group element such as boron, or for a transition metal. Neutron diffraction studies and quantum-mechanical calculations have indicated that these interactions are significantly attractive, with energies comparable to those of conventional hydrogen bonds that utilize lone-pair electrons for acceptors. The H \cdots H contacts involved may be as much as 0.5 Å shorter than the conventional van der Waals distance of 2.4 Å, so that the term 'dihydrogen bond' has been used to denote this type of interaction.

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s9.m1.o4 **Interanionic O-H \cdots O Interactions: the Charge Density Point of View** P. Macchi,^{a,b} B.B. Iversen,^b A. Sironi,^a B.C. Chakoumakos,^c F.K. Larsen^b a) *Dipartimento di Chimica Strutturale e Stereochimica Inorganica, Via Venezian 21, 20133 Milano, Italy;* b) *Department of Chemistry, University of Aarhus, DK-8000 Aarhus C Denmark;* c) *Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA*

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Inter-anion δ^- O-H \cdots O δ^- interactions in the solid state have been the subject of a recent scientific discussion. Because of the electrostatic repulsion between two anions, Braga and coworkers suggested that these H \cdots O 'contacts' should be regarded as *pseudo-hydrogen bonds*, in spite of very short H \cdots O distances [1]. In their understanding, the conformation adopted by two anions minimizes the repulsion but does not produce a chemical bond, and the stability of the crystal structure is due only to cation-anion attractions (*tugboat effect*). However, using the structure correlation method and experimental solid state observations, Steiner did not find reasons for considering these interactions significantly different from other O-H \cdots O hydrogen bonds.[2]

We have determined, from X-ray and neutron experiments, the experimental electron density distribution of KHC₂O₄, the most addressed example of δ^- O-H \cdots O δ^- interactions discussed so far. Many reasons lead us to consider the δ^- O-H \cdots O δ^- a normal hydrogen bond: a) geometrical features (like the elongation of O-H in the solid state) are hardly explainable otherwise (as also suggested by Steiner [2]); b) the electrostatic potential of the molecule in the crystal is substantially different (at H site) from that in the isolated molecule [1] and does not reveal H \cdots O repulsion; c) the topological analysis of the charge density speaks for a strong (and partially covalent) hydrogen bond.

According to our results, the polarization of the charge density occurring in the solid state is so large that a gas-phase calculation on the isolated anion is not a suitable method for predictive purposes [1]. In addition, a definition of the chemical bond based on global energy contribution can not be used for accounting local parameters (such as interatomic distances).

[1] a) D. Braga, F. Grepioni, J.J. Novoa, *Chem. Commun.*, **1998**, 1959; b) J.J. Novoa, I. Nobeli, F. Grepioni, D. Braga, *New J. Chem.*, **2000**, 24, 5.
[2] T. Steiner, *Chem. Commun.*, **1999**, 2229.