

Bonding in an Unusual Nickel Carbide

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The bonding in an unusual nickel carbide polymer network synthesized by Musanke and Jeitschko is analyzed using qualitative, band-structure calculations in the framework of extended Hückel tight-binding theory. The carbide features infinite, one-dimensional, vertex-sharing chains of Ni squares. Each square is centered by a carbon and flanked by C₂ units.

In this electron-rich polymer, the Ni atoms act as electron acceptors through their s and p orbitals. The orbital interaction schemes reveal that there is little Ni-Ni bonding and essentially no Ni to C₂ back-donation. Molecular orbital interaction diagrams of some molecular models are used to describe the bonding in ${}^1_{\infty}[\text{Ni}_3\text{C}_5]^{8-}$.

We also discuss the stability of the planar building block of the polymer, (CNi₄)⁴⁻ (which resembles planar CH₄) with respect to a “tetrahedral” alternative and we do so for the extended ${}^1_{\infty}[\text{Ni}_3\text{C}]^{4-}$ and ${}^1_{\infty}[\text{Ni}_3\text{C}_5]^{8-}$ chains. In each model case the tetrahedral alternative is favored, and there is no sign of stabilization of a crucial CL₄ orbital. Such stabilization is partially achieved through bonding to two Ca axial to the C in the center of the Ni₄ ring, but it takes the entire inter-chain calcium network to effect the observed stabilization.

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