TOPOLOGY AND BASICITY IN POLYOXOVANADATES: AB INITIO STUDY OF THE CAGED MOLECULES $[V_{18}O_{42}]^{12-}$ AND $[V_7O_{12}(O_3PH)_6]^-$

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Ab initio Hartree-Fock calculations have been carried out on the octadecavanadate ion $[V_{18}O_{42}]^{12-}$ (**1**), on its protonated derivative $[H_4V_{18}O_{42}]^{8-}$ (**2**), and on the vanadophosphate cluster $[V_7O_{12}(O_3PH)_6]^-$ (**3**), taken as a model for $[V_7O_{12}(O_3PR)_6]^-$ (**3**$'$). The spheroidal clusters (**2**) and (**3**$'$) have been recently characterized as "electronically inverse hosts" in the encapsulation complexes $Cs_9[X@H_4V_{18}O_{42}]\cdot 12H_2O$ (X = Br, I) and $(Ph_4P)_2[Cl@V_7O_{12}(O_3PPh)_6]$. An estimate of the electrostatic potential distribution including the contribution of the lattice potential yields highly positive values of the potential inside the host cavities for (**2**) and (**3**). Those values are larger than the electrostatic potential computed at a vacant chloride site of the CsCl crystal, thus explaining the thermodynamic stability of the encapsulated anions.