

s2.m1.p19 Charge density and electrostatic potentials in $\text{Na}_{10}(\text{N}_3 \text{ @ } \text{H}_3\text{V}_{18}\text{O}_{44})$: a joint X-ray diffraction and ab initio-MO study. M.-M. Rohmer,[#] M. Bénard,[#] V. Pichon[§], ([#]) *Laboratoire de Chimie Quantique, UMR 7551, CNRS and Université Louis Pasteur, Strasbourg, France;* ([§]) *LCM³B, Université Henri Poincaré-Nancy-1, Vandoeuvre-lès-Nancy, France.*

Keywords: charge spin densities.

Theoretical studies carried out in the recent years on encapsulation complexes involving polyoxometalate hosts have emphasized the correlation between the topology of the host cage and the Lewis acido-basic character of the encapsulated species.^{1,2} Concave (i. e. spheroidal, or ellipsoidal) host cages confine inside their walls a portion of space which can be termed electrophilic when compared to the *external* surrounding of the cluster. The possibility to form under hydrothermal conditions such regions of space susceptible to shelter basic moieties explains the synthesis of the so-called *electronically inverse* host-guest systems. In these self-assembly systems, a negatively charged guest acts as a template to the construction of a metal oxide host cage, *itself negatively charged*, adapted to the structure of the guest anion, but inescapably concave. The electrostatic stability of the complex, either in solution or in the crystal, is ensured by the peripheral counter-ions.

The complex $[\text{N}_3 \text{ @ } \text{H}_3\text{V}_{18}\text{O}_{44}]^{10-}$, encapsulating an azide anion, has been synthesized in Achim Müller's group. The structure of a similar complex, with a different distribution of the V^{IV} and V^{V} atoms, had been reported previously.³ Preliminary ab initio calculations have provided some information about problems left unsolved by the initial X-ray structure determination:

- i) the host vanadate cage is a mixed-valence complex, with 14 V^{IV} and 4 V^{V} sites. The V^{V} sites have been located.
- ii) It has been assumed from charge counting considerations that three protons are present in the structure. The location most probable for two of these protons has been deduced from a calculated distribution of electrostatic potentials, accounting for the presence of counter-ions and crystal water molecules. Possible locations for the last proton have been suggested.

We finally present maps of the electron density and of the electrostatic potential for the host cage alone and for the host-guest system, to be compared with the distribution of those observables obtained from high-accuracy X-ray diffraction experiments. The role of the metal core electrons in the density accumulation observed in the vicinity of the vanadium nuclei is clearly demonstrated.

s2.m1.p20 Diffraction Studies of the Experimental Charge Density in 1,2-dihydro-1-methyl-2-nitriminopyridine at 90 K. J. Zaleski. *Institute of Chemistry, University of Opole, 45-052 Opole, Oleska 48, Poland.*

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Crystal and molecular structure together with a charge density distribution of a potentially nonlinear optical material 1,2-dihydro-1-methyl-2-nitrimino-pyridine was studied at 90 K. The crystal is non-centrosymmetric space group $\text{Pna}2_1$ ($a=7.753(2)$, $b=13.829(3)$, $c=6.070(1)\text{Å}$ $Z=4$). The pyridine ring is planar, the N(1) nitrogen atom remains sp^2 hybridised. The NNO_2 group is twisted 26° along C-N bond and 15° along N-N bond. The crystal structure indicates the close intermolecular distances between the oxygen atom O(9) of the nitro group pushed out of the pyridine plane and three hydrogen atoms H(6) and H(4) of the pyridine ring and H(11) of the methyl group. The twist of the nitro group responsible for the noncentrosymmetry of this crystal is therefore caused by a steric hindrance and/or weak C-H...O hydrogen bonds.

Multipole refinement of the X-ray data (up to $\sin\theta/\lambda=1.0$) was done with XD package. Least squares refinement of 279 variables led to $R(F)=0.0230$, $R_w(F)=0.0187$, $R(F^2)=0.0273$, $R_w(F^2)=0.0312$ with a goodness of fit $S=2.54$ for the 4827 reflections.

An analysis of the deformation density and Laplacian of the charge density proves useful for revealing weak hydrogen bonding effects. Bader topological theory was applied to the electron density distribution. We have analysed the topological properties of C-H...O intermolecular critical points. Results so obtained with be compared with those calculated by the ab initio methods.

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