An Interpretation of the Structure of the Inclusion Complexes $[RCN\subset(V_{12}O_{32})^{4-}]$ (R = CH_3, C_6H_5) from Electrostatic Potentials

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Klemperer *et al.* have recently reported the synthesis and the structure of guest–host complexes in which an acetonitrile (**1**) or a benzonitrile (**2**) molecule is located in the center of a $(V_{12}O_{32})^{4-}$ basket-like cavitand.[1] The structure of **1** and space filling cutaway views of **1** and **2** are reproduced with the kind permission of the authors (Figure 1). Some differences were noticed between the structures of **1** and **2**: acetonitrile goes deeper into the basket than benzonitrile by 0.46 Å, but none of the CH_3CN atoms have van der Waals contacts with the cavitand, whereas the two benzonitrile ortho hydrogens are in contact with four oxygen atoms at the rim of the basket.[1c] A molecular modeling approach based upon the minimization of van der Waals interaction energies was not able to reproduce the experimental structures,[1c] thus suggesting that metal–ligand or electrostatic interactions are at work.

Ab initio SCF calculations have been carried out on the cavitand, $(V_{12}O_{32})^{4-}$, idealized to C_{4v} symmetry, and, separately, on the guest molecules CH_3CN and C_6H_5CN.[2] We report the maps of electrostatic potential (ESP) obtained from those calculations. Figure 2 displays the ESP distribution inside the polyvanadate cavity in two planes sharing the symmetry axis of the molecule with a dihedral angle of 45°. Figure 3 displays the ESP generated by the isolated molecules of (a) acetonitrile and (b) benzonitrile. The location of CH_3CN and C_6H_5CN in the Cartesian framework matches the position of those molecules in the respective host–guest complexes.

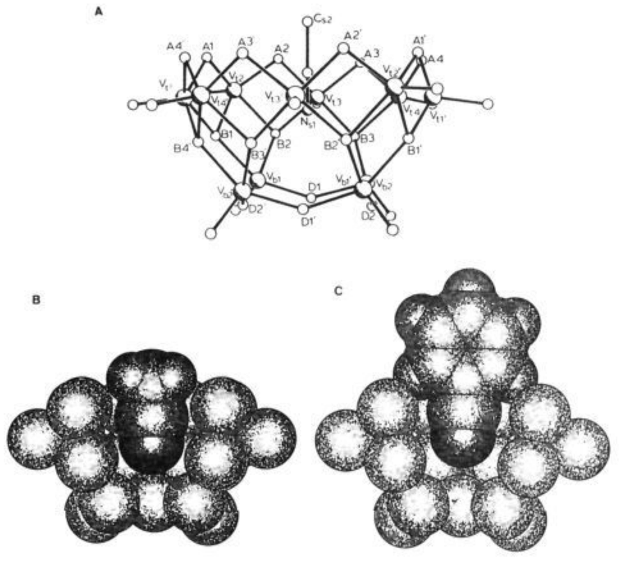

Figure 1. (a) Perspective plot of $[CH_3CN\subset(V_{12}O_{32})^{4-}]$, reprinted from ref 1a with permission. (b and c) Space-filling cutaway view of observed $[M\subset(V_{12}O_{32})^{4-}]$: (b) M = CH_3CN and (c) M = C_6H_5CN. Reproduced from ref 1c with permission.

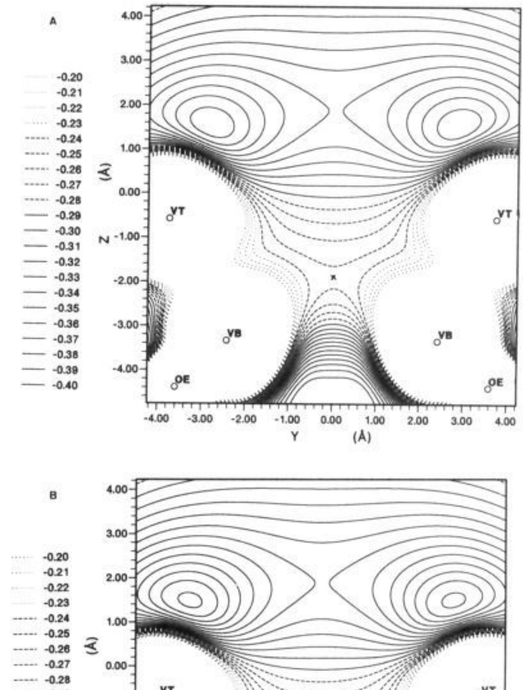

Figure 2. Maps of the electrostatic potential (ESP) distribution generated by $(V_{12}O_{32})^{4-}$ in the planes containing the symmetry axis and (a) two V_b sites and (b) two O_D sites. X represents the saddle point. Contour interval: 0.01 hartree, distances in Å.

The topology of the ESP distribution inside the cavitand as illustrated in Figure 2 is characterized by three distinct regions from the top to the bottom of the basket. At about 1 Å above the circle of eight oxygen atoms (A sites, Figure 1) defining the rim of the basket, we find a nucleophilic region associated with low potentials. This region appears in both planes of Figure 2 as twin minima at –0.38 (Figure 2a) and –0.40 hartree (Figure 2b). From those minima, the ESP value steadily increases inside the cavity until reaching a saddle point located on the symmetry axis, at 1.45 Å above the four bottom vanadium centers V_b. The region with relatively high potential (–0.24 to –0.25 hartree)[9] extending ~0.7 Å around the saddle point can be considered as an "electrophilic plateau". Beyond this plateau, a sharp decrease

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(2) Ab initio SCF calculations have been carried out on $(V_{12}O_{32})^{4-}$, CH_3-CN and C_6H_5CN by means of the ASTERIX program system,[3] adapted to core potential evaluation.[4] The Ar core potential proposed by Hurley *et al.*[5] has been used for vanadium, and the five valence electrons were described by a 4s, 2p, 6d basis set contracted into 2s, 1p, 3d.[6] The core potential of Pacios and Christiansen[7] was used for the 1s core of oxygen, and the valence shell was described by a 5s, 5p set contracted into 3s, 3p (most diffuse exponents: $\zeta_s = 0.120568$; $\zeta_p = 0.092431$).[6] All electron calculations have been carried out on CH_3CN and C_6H_5CN. The 10s, 6p basis sets of Huzinaga[8] were used for C and N atoms. They were contracted into 5s, 4p for the atoms of the nitrile group and into 4s, 2p for the carbons of the methyl and phenyl substituents. A 6s basis set[8] contracted into triple-ζ was used for hydrogen. No specific treatment has been carried out to account for electron correlation. Since vanadium in the host molecule is formally d^0, electron delocalization due to symmetry constraints is not expected to alter the quality of the SCF wave function. Moreover, comparative studies carried out on smaller molecules suggest that correlation does not induce drastic modifications of the ESP distribution (see: Luque, F. J.; Orozco, M.; Illas, F.; Rubio, J. *J. Am. Chem. Soc.* **1991**, *113*, 5203).

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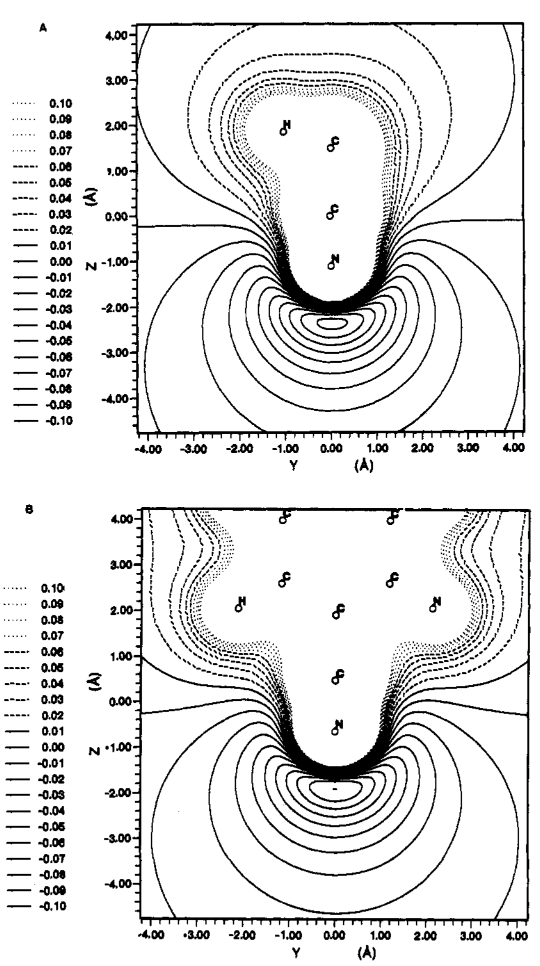

Figure 3. Maps of the ESP distribution generated by the host molecules: (a) CH_3CN (plane containing one CH bond) and (b) C_6H_5CN (plane containing the phenyl cycle). Contour interval: 0.01 hartree, distances in Å.

of the ESP values is noticed, again leading to deep minima (<-0.40 hartree) associated with the D oxygen sites. The ESP distribution in the guest molecules, assumed isolated (Figure 3), is characterized by a minimum located on the symmetry axis, at 1.32 Å below the nitrogen atom.

The comparison between, or, still better, the superimposition of the ESP distributions in the host and guest molecules may help understanding the structure of the inclusion complexes. It appears from Figures 2 and 3 that the stabilization of the R–CN molecules in the host cavity is the consequence of two favorable electrostatic interactions: (i) the attraction between the hydrogens of the R substituent and some of the O_A sites of the host molecule and (ii) *the interaction between the nitrile nitrogen acting as a nucleophile and the electrophilic region characterized inside the basket-like vanadate by a saddle-point of the ESP distribution.* The present investigation, based upon the ESP distributions, is not sufficient to determine which interaction is most important in terms of stabilization energy.

Figures 2 and 3b show that the benzonitrile molecule is perfectly suited for both interactions: the two *ortho* hydrogen atoms have van der Waals interactions with four of the eight O_A atoms[1c] and the ESP minimum in front of the nitrogen atom *almost exactly coincides*, within 0.1 Å, with the saddle point of Figure 2. The orientation of the benzonitrile molecule in the plane containing two O_D atoms (Figure 2b) rather than two V_b atoms (Figure 2a) is in agreement with the electrostatic potential above the rim of the basket being more attractive in the plane of Figure 2b. At variance from C_6H_5CN, the geometry of acetonitrile is not optimal for both interactions. Achieving a van der Waals contact between the hydrogens of CH_3CN and the O_A sites requires the guest molecule to sink very deep into the basket. According to the simulation carried out by Klemperer et al.,[1c] the nitrile nitrogen would be located in such a case at 1.68 Å only from the $(V_b)_4$ plane of the host framework. The ESP minimum associated with the N atom would then coincide with a region of the host molecule where the ESP is rapidly decreasing, beyond the electrophilic plateau (1.10 Å below the saddle point). In order to avoid this unfavorable region while retaining most of the $O_A \cdots H$ attraction, CH_3CN adopts the intermediate "hanging" position characterized experimentally. In that position, the ESP minimum associated with nitrogen is located at 0.55 Å below the saddle-point, that is, close to the edge of the electrophilic plateau (Figures 2 and 3). It is expected that the guest molecule will retain in that position a large part of the attractive electrostatic interaction involving the nitrile group.

Further calculations are being carried out on those inclusion molecules, and on the model complex with HCN as guest molecule in order to estimate the order of magnitude of the interaction energy, and the energy profile according to the position of the guest molecule in the cavitand.

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(9) The ESP distribution is uniformly shifted to negative energies because the cavitand has been considered as an isolated anion with charge 4−.