Ab Initio Modeling of the Endohedral Reactivity of Polyoxometallates: 1. Host−Guest Interactions in $[RCN\subset(V_{12}O_{32})^{4-}]$ ($R = H, CH_3, C_6H_5$)

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Abstract: The origin of the host−guest interaction energy between R−CN molecules ($R = CH_3, C_6H_5$) and the basket-like cavitand $(V_{12}O_{32})^{4-}$ has been investigated by means of ab initio Hartree−Fock calculations on the model system $[HCN\subset(V_{12}O_{32})^{4-}]$ and on the two observed complexes. The computed stabilization energies range from −12.8 to −14.4 kcal·mol^{-1} for the three considered systems. Decomposition energy analysis shows that most of the stabilization should be attributed to an electrostatic origin, including direct coulombic interaction, polarization of the guest molecule and counter polarization of the vanadate host. The stabilization energy due to orbital interactions and charge transfer is increasing with the acceptor potentialities of the R substituent: $H < CH_3 < C_6H_5$. Mulliken population analysis indicates that two opposite charge flows should be considered for $R \neq H$: (i) a net donation from the cyanide π orbitals to the surrounding V^V d shells and (ii) a back donation from the eight oxygen atoms at the rim of the vanadate basket to the acceptor orbitals of R. Both electrostatic and charge transfer stabilization energies should therefore be attributed to the dual potentialities (acidic/basic; donor/acceptor) of the R−CN molecules duly activated by a convenient positioning with respect to the vanadate sites with opposite properties. The complementarity of the electrostatic properties of the host and guest molecules is evidenced by the computed distributions of the electrostatic potential. The relatively acidic character of the accessible region located inside the vanadate host, as compared to the external, basic side is attributed to the topological features defining *concavity*. A generalization of that correlation between concavity/convexity and acidity/basicity to the class of hollow polyoxometallate clusters could provide a mechanism explaining the stabilization and the self-assembly of "electronically inverse" host−guest systems.

1. Introduction

Supramolecular systems are involved in various domains of chemistry, biochemistry and physics. The specific reactivity of microporous media (zeolites), application of the template effect, biology, photochemistry, tailor-made molecular knots and induced molecule self-organization are some of the most active fields of chemical research involving the concept of molecular symbiosis.[1,2] Apart from systematic studies carried out on zeolites,[3] the ab initio modeling of those systems is less developed, however, and the reasons for that have been clearly pointed out by Cioslowski and Lin:[4] large sizes, low symmetries and molecular flexibility leading to flat potential hypersurfaces plagued with local minima.

Supramolecular systems involving polyoxometallate hosts might in some cases be more amenable to sophisticated calculations: size is large but symmetry is often present; X-ray structural characterization reduces the need for time-consuming geometry optimization of the host molecule or at least provides a good starting point for it; and high oxidation numbers for metal relieves or cancels the problems of nondynamic correlation associated with the localization of d electrons.[5]

Polyoxometallate cavitands, or carcerands display surprising specific properties, that have scarcely been analyzed yet in terms of host−guest electrostatic and/or orbital interactions.[6] For example, most of the encapsulation complexes recently characterized by Müller and colleagues[2,7] and by others[8] are organized around and possibly shaped by a negatively charged guest atom or molecule (halogen, sulfate or carbonate ions, or even polyoxometallate as in the "cluster within cluster" $[V_4O_8\subset V_{30}O_{74}]^{10-}$ system[2,9]), even though the reactivity of

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(1) For recent reviews and highlights, see for instance: (a) Desiraju, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311. (b) Lawrence, D. S.; Jiag, T.; Levett, M. *Chem. Rev.* **1995**, *95*, 2229. (c) Jørgensen, T.; Hansen, T. K.; Becher, J. *Chem. Soc. Rev.* **1994**, *23*, 41. (d) *New J. Chem.* Special Issue on "Topology in Molecular Chemistry", Sauvage, J. P., Ed.; **1993**, *17*, 617−763. (e) Hunter, C. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1079. (f) Grohmann, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2107. (g) Wenz, G. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 803.

(2) Müller, A.; Reuter, H.; Dillinger, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2328.

(3) See, for instance: (a) Greatbanks, S. P.; Sherwood, P.; Hillier, I. H. *J. Phys. Chem.* **1994**, *98*, 8134 and references therein. (b) Allavena, M., Kassab, E., Evleth, E. *J. Mol. Struct.* **1994**, *325*, 85. (c) Pisani, C.; Birkenheuer, U. *Int. J. Quantum Chem., Symp.* **1995**, *29*, 221.

(4) Cioslowski, J.; Lin, Q. *J. Am. Chem. Soc.* **1995**, *117*, 2553.

(5) See, for example (a) Paldus, J. In *SCF, Theory and Applications*; Carbo, R., Klobukowski, K., Eds.; Elsevier: Amsterdam, 1990; pp 1−45 and references therein. (b) Böhm, M. C. *Theor. Chim. Acta* **1981**, *60*, 233; *Chem. Phys. Lett.* **1981**, *81*, 284. (c) Bénard, M. *Chem. Phys. Lett.* **1983**, *96*, 183; *J. Chem. Phys.* **1979**, *71*, 2546.

(6) Müller, A.; Diemann; E., Krickemeyer, E.; Che, S., unpublished. Müller, A.; Sölter, D. unpublished; referred to in ref 2.

(7) (a) Müller, A.; Penk, M.; Rohlfing, R.; Krickemeyer, E.; Döring, J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 926. (b) Müller, A.; Döring, J. *Z. Anorg. Allg. Chem.* **1991**, *595*, 251. (c) Müller, A. *Nature* **1991**, *352*, 115. (d) Pope, M. T. *Nature* **1992**, *355*, 27. (e) Müller, A. *J. Mol. Struct.* **1994**, *325*, 13 and references therein. (f) Müller, A.; Hovemeier, K.; Krickemeyer, E.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 779. (g) Khan, M. I.; Müller, A.; Dillinger, S.; Bögge, H.; Chen, Q.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1780.

(8) (a) Chang, Y. D.; Salta, J.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 325. (b) Yamase, T., Ohtaka, K. *J. Chem. Soc., Dalton Trans.* **1994**, 2599.

(9) (a) Müller, A.; Rohlfing, R.; Krickemeyer, E.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 909. (b) Mitchell, P. C. H. *Nature* **1991**, *348*, 15. (c) Müller, A.; Krickemeyer, E.; Penk, M.; Rohlfing, R.; Armatage, A.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1674. (d) Müller, A.; Rohlfing, R.; Döring, J.; Penk, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 588.

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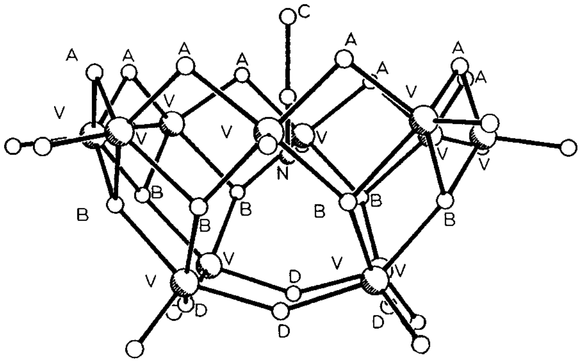

Figure 1. Perspective plot of $CH_3CN\subset(V_{12}O_{32})^{4-}$ (Reprinted from ref 11a with permission).

parent molecules is mainly oriented toward the fixation of *cationic* species.[10] This suggests that the reactivity of polyoxometallate cages could be different *inside* and *outside* the cavity. We intend to address those problems in a series of forthcoming studies. Our first report will be devoted to the inclusion complexes $[RCN\subset(V_{12}O_{32})^{4-}]$ ($R = CH_3, C_6H_5$) (Figure 1) that have been synthesized and structurally characterized by Klemperer *et al.*[11] In a preliminary study on those complexes, based on ab initio computed electrostatic potentials (ESP), it has been shown that the electric field induced in the inner part of the vanadate host perfectly fits the dipole of the guest nitrile molecules.[12] In the present work, the qualitative investigation based on ESP is extended in space in order to compare the internal to the external parts of the cavitand and try to characterize the conditions for a specific endohedral reactivity for polyoxometallates. Furthermore, the host−guest interaction energy has been computed for the $[HCN\subset(V_{12}O_{32})^{4-}]$ model as a function of the displacement of the guest molecule inside and outside the cage. The energy profile obtained with this model has been completed by single point calculations carried out on the real complexes $[CH_3CN\subset(V_{12}O_{32})^{4-}]$ and $[C_6H_5CN\subset(V_{12}O_{32})^{4-}]$.

2. Details of the Calculation

Ab initio SCF calculations have been carried out on the supersystems $[RCN\subset(V_{12}O_{32})^{4-}]$ ($R = H, CH_3, C_6H_5$) and on the separate host and guest molecules by means of the ASTERIX program system[13] adapted to core potential evaluation.[14] Similar calculations have also been carried out for hypothetic systems involving the same polyoxovanadate host and linear guest molecules with zero dipole moment (N_2, C_2H_2). The experimental structure reported by Day and colleagues for $[CH_3CN(V_{12}O_{32})]C_6H_5P]_4{\cdot}3CH_3CN{\cdot}4H_2O$[11a] was used to define the geometry of the host molecule. A slight modeling of the structure was however necessary to take advantage of the C_{4v} point group symmetry. This symmetry was retained for calculations on complexes involving linear guest molecules but was reduced to C_{2v} for $[C_6H_5CN\subset(V_{12}O_{32})^{4-}]$ and to C_s for $[CH_3CN\subset(V_{12}O_{32})^{4-}]$. Standard geometrical parameters taken from experiment were adopted for the guest molecules, and no further geometry optimization of either component of the supersystem was attempted.

The Ar core potential proposed by Hurley *et al.*[15] has been used for vanadium, and the five valence electrons were described by 4s, 2p, 6d basis sets contracted into 2s, 1p, 2d,[16] with d functions reduced to five components. The electron core potentials (ECP) of Pacios and Christiansen[17] were 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: $\zeta_s = 0.120\,568$; $\zeta_p = 0.092\,431$).[16] The choice of ECP to describe the atomic inner shells of $(V_{12}O_{32})^{4-}$ was made in order to avoid the important basis set superposition error (BSSE) generally associated with a poor (i.e., minimal) all-electron description of the atomic cores. A double-ζ description of the cores could be afforded however for the C and N atoms of the guest molecules, which have been described by means of the 10s, 6p basis sets of Huzinaga,[18] 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[18] contracted into triple-ζ was used for hydrogen. The energy of HCN located inside the vanadate cavity, at 0.65 Å below the position determined for the energy minimum has been computed by the counterpoise method[19] with the ghost orbitals of $V_{12}O_{32}$. It was found to be $-92.856\,303$ hartrees, instead of $-92.855\,362$ hartrees for HCN alone ($\Delta E = -0.6$ kcal·mol^{-1}). Unfortunately, the energy of $(V_{12}O_{32})^{4-}$ with the ghost orbitals of HCN could not be obtained due to an erratic behaviour related to the nodal structure of the ECP. It should be remembered however that BSSE exclusively affects the charge transfer part of the host−guest interaction energy[20] which represents no more than 20% of the total interaction energy for $[HCN\subset(V_{12}O_{32})^{4-}]$ at equilibrium (Table 1).

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.[5] Moreover, comparative studies carried out on smaller molecules suggest that correlation does not induce drastic modifications of the ESP distribution.[21] The most important source of error that should be attributed to the lack of electron correlation is the neglect of the dispersion energy. Dispersion forces are known to become important in case of noncovalent close contacts such as the hydrogen bonds, and their neglect in the present study might yield a significant underestimate of the interaction energy for $[C_6H_5CN\subset(V_{12}O_{32})^{4-}]$, for which O···H close contacts have been evidenced between host and guest.[11c]

The calculation and the decomposition of the $HCN/(V_{12}O_{32})^{4-}$ interaction energy reported in Table 1 have been carried out without introducing counterions. Calculations on selected points of the potential energy curve were also carried out in the presence of point charges whose position was deduced from that of the $(PC_6H_5)^+$ counterions in the crystal. The total energy of the $HCN\subset(V_{12}O_{32})$ complex was consistently shifted down by ~0.421 hartree, and a slight increase (+2.2 kcal·mol^{-1}) of the stabilization energy was obtained without any significant

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[10] See, for example, refs 3−18: Day, V. W.; Klemperer, W. G.; Maltbie, D. J. *J. Am. Chem. Soc.* **1987**, *109*, 2991.

[11] (a) Day, V. W.; Klemperer, W. G.; Yaghi, O. M. *J. Am. Chem. Soc.* **1989**, *111*, 5959. (b) Klemperer, W. G.; Marquart, T. A.; Yaghi, O. M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 49. (c) Klemperer, W. G.; Marquart, T. A.; Yaghi, O. M. *Mater. Chem. Phys.* **1991**, *29*, 97.

[12] Rohmer, M.-M.; Bénard, M. *J. Am. Chem. Soc.* **1994**, *116*, 6959.

[13] (a) Ernenwein, R.; Rohmer, M.-M.; Bénard, M. *Comput. Phys. Commun.* **1990**, *58*, 305. (b) Rohmer, M.-M.; Demuynck, J.; Bénard, M.; Wiest, R.; Bachmann, C.; Henriet, C.; Ernenwein, R. *Comput. Phys. Commun.* **1990**, *60*, 127. (c) Rohmer, M.-M., Ernenwein, R.; Ulmschneider, M.; Wiest, R.; Bénard, M. *Int. J. Quantum Chem.* **1991**, *40*, 723.

[14] Leininger, T.; Jeung, G.-H., unpublished.

[15] Hurley, M. M.; Pacios, L. F.; Christiansen, P. A.; Ross, R. B.; Ermler, W. C. *J. Chem. Phys.* **1986**, *84*, 6840.

[16] Jeung, G.-H., unpublished.

[17] Pacios, L. F.; Christiansen, P. A. *J. Chem. Phys.* **1985**, *82*, 2664.

[18] (a) Huzinaga, S. *Approximate Atomic Functions*; Technical Report, University of Alberta, Canada, 1971. (b) Huzinaga, S.; McWilliams, D.; Domsky, B. *J. Chem. Phys.* **1971**, *54*, 2283.

[19] Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

[20] Bauschlicher, Jr.; C. W., Bagus, P. S. *J. Chem. Phys.* **1984**, *81*, 5889.

[21] Luque, F. J.; Orozco, M.; Illas, F.; Rubio, J. *J. Am. Chem. Soc.* **1991**, *113*, 5203.

Table 1. Stabilization Energies (ΔE, kcal·mol^{-1}) Computed for Several Guest Molecules in the Cavity or in the Vicinity of the $(V_{12}O_{32})^{4-}$ Host (See Also Figure 5)

	ΔE						
guest	total	electrostatic[a]	P_{guest}[a]	P_{host}[a]	CT[a]	position of N[b] (Å)	Θ[c]
HCN	−12.8	−5.3	−2.7	−2.2	−2.6	+0.65[d]	0.
HCN	−15.0[e]					+0.65	0.
HCN	+5.9	+7.6				+3.18	0.
HCN		+1.1				+3.18	79.[f]
HCN	+9.1	+10.1				+6.35	0.
HCN	−13.1	−11.3				+6.35	180.
CH_3CN	−14.4	−3.7	−2.5	−3.55	−4.65	0.[g]	0.
CH_3CN	−16.7	−12.7				+5.93	180.
C_6H_5CN	−14.1	+1.8	−6.7	−3.9	−5.3	+0.48[g]	0.
C_6H_5CN	−16.1	−2.0				+0.75	0.
C_6H_5CN	−16.2					+0.82[d]	0.
C_6H_5CN	−15.6	−3.2				+1.01	0.
C_6H_5CN	−15.1	−3.5				+8.14	180.
N_2	−2.9	+1.6				0.	
N_2	−5.0	−1.9				+0.63	
C_2H_2	+10.6	+14.9				+0.63	

[a] Host−guest electrostatic interaction energy, obtained from the energy of the first SCF iteration on the supersystem; P_{guest}: polarization energy of the guest molecule; P_{host}: counter polarization of $(V_{12}O_{32})^{4-}$; CT: orbital interaction and charge transfer energies. [b] Defined with respect to the observed position of N along the symmetry axis in CH_3CN. The axis is oriented toward the top of the cavity. [c] Θ = 0: the CN group is collinear to the symmetry axis in the position observed for CH_3CN and C_6H_5CN in the inclusion complex (Figure 1); Θ = 180: the CN group is still collinear to the symmetry axis, but the guest molecule occupies an "upside down" position with the nitrile group outside the cavity. [d] Computed equilibrium position of the guest molecule, with respect to the observed position of CH_3CN. [e] Assuming the presence of four positive charges arranged around $(V_{12}O_{32})^{4-}$ according to the positions of the counterions. [f] Optimized value of Θ. The corresponding electrostatic energy (+1.1 kcal·mol^{-1}) is the highest value obtained along the HCN inversion process, suggesting that HCN can enter the cavity without activation barrier. [g] Experimentally observed position of the guest molecule.

change of the equilibrium position. As expected from previous investigations by Weber et al.[22] the ESP distribution in the vicinity of $(V_{12}O_{32})^{4-}$ reacted to the presence of counterions by a practically uniform shift to higher potentials.

Calculations carried out on such large systems cannot pretend to quantitative accuracy. Some sources of systematic errors (basis set truncation, BSSE, neglect of electron correlation and dispersion effects, neglect of geometrical optimization and reorganization of the host molecule) have been reviewed in this section. We are confident however that the order of magnitude of the host−guest interaction energies, the trends disclosed by energy decomposition analysis and the distribution of electrostatic potentials are basically reliable and will provide guidelines for future investigations on similar complexes.

3. Inside and Outside: Influence of Topological Factors on the ESP Distribution

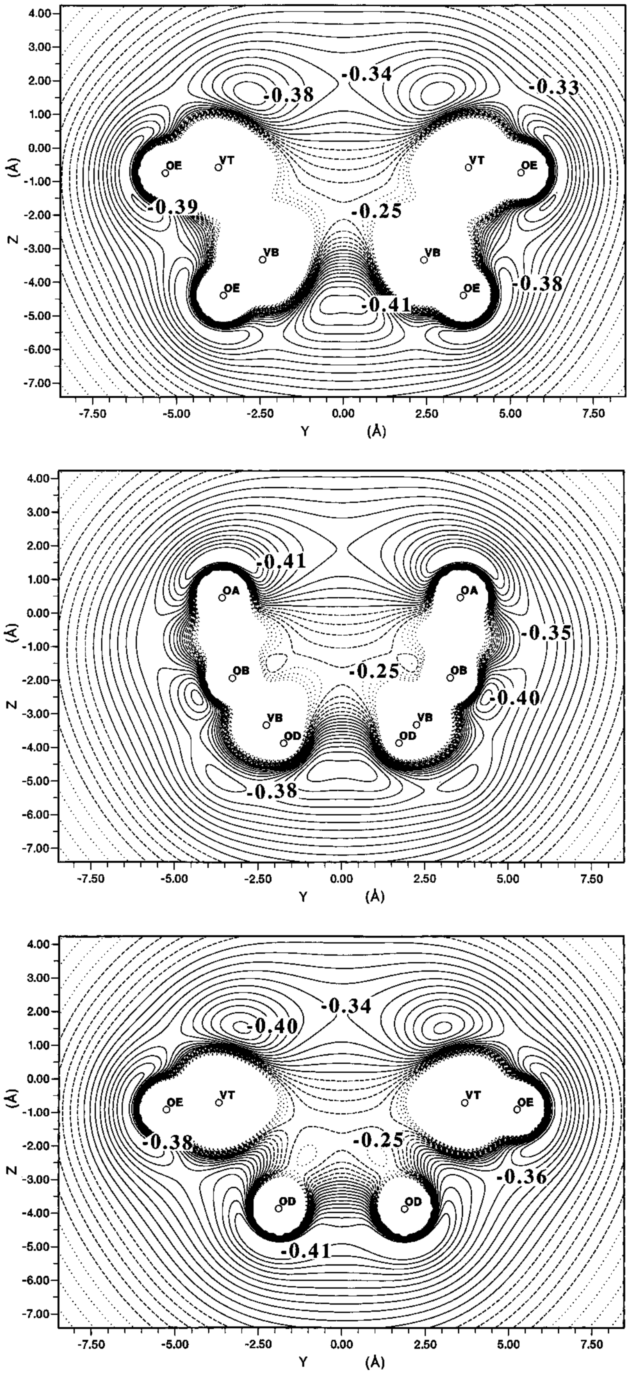

Figure 2. Maps of the electrostatic potential (ESP) distribution generated by $(V_{12}O_{32})^{4-}$ in three planes respectively containing (a) two V_B and two O_E atoms, (b) two O_A atoms (rotated by 21.6° with respect to (a)), (c) two O_D, two V_T and two O_E atoms (rotated by 45° with respect to (a)). Contour interval: 0.01 hartree (first dotted line: −0.21 hartree; first broken line: −0.25 hartree; first solid line: −0.30 hartree; last solid line: −0.41 hartree). Distances in Å.

Our preliminary study had revealed that the inner part of the hollow $(V_{12}O_{32})^{4-}$ vanadate was characterized by surprisingly high electrostatic potentials, as compared to the ESP values obtained at the entrance and at the bottom of the cavity. The dipolar field evidenced along the symmetry axis of the vanadate host was shown to be complementary to the dipole specific to the guest nitrile molecules. It was then proposed that the stabilization of the inclusion complex was an effect of this dipole−dipole interaction, the orbital interactions and charge transfer effects being assumed negligible.[12] A more global display of the ESP distribution of $(V_{12}O_{32})^{4-}$ showing both the inner and the outer sides of the dodecavanadate (Figure 2) immediately suggests that the external part of the open cage (including the "rim" composed of eight oxygen atoms) is consistently and considerably more nucleophilic than the cavity. Figure 2 shows that $(V_{12}O_{32})^{4-}$ is surrounded by an envelope of low potentials whose highest value never exceeds −0.33 e Å^{-1}. In contrast to that, the ESP value in the accessible part of the cavity reaches −0.25 e Å^{-1} (Figure 2). Several ESP minima can be detected on the outer side of $(V_{12}O_{32})^{4-}$ and analyzed in

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(22) Weber, J.; Roch, M.; Williams, A. F. *Chem. Phys. Lett.* **1986**, *123*, 246.

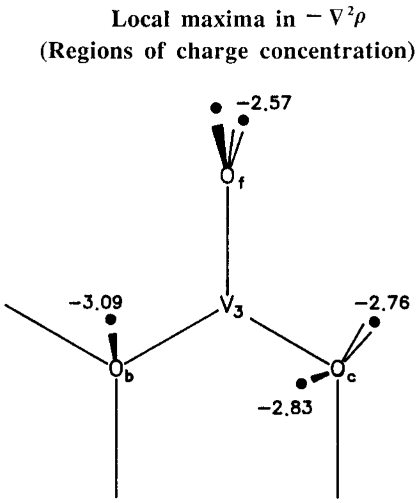

Figure 3. Characterization of the (3, −3) critical points of the Laplacian of ρ, with the values of $\nabla^2\rho$, in the vicinity of three distinct oxygen sites in $(V_{10}O_{28})^{6-}$.[23]

relation with previous studies on the ESP and electron density distribution of polyoxometallates and other transition metal complexes.

Terminal, doubly bridging (O_A, O_D) and triply bridging (O_B) oxygens (Figure 1) are characterized by more or less extended regions of low potentials opposite to the direction(s) of the oxygen−vanadium bond(s). Let us consider first the case of the doubly bridging oxygens. The nucleophilic regions associated with O_A and O_D sites tend to develop in the plane perpendicular to the one containing the O−V bonds. A similar pattern had been noticed around the doubly bridged sites of the $(V_{10}O_{28})^{6-}$ ion and could be correlated with the presence of twin local maxima in the opposite Laplacian distribution of the electron density.[23] Those (3, −3) critical points are interpreted in terms of local charge concentrations.[24] The doubly bridging oxygen atoms in a polyoxovanadate molecule have their surrounding organized in an approximate tetrahedral arrangement: two directions are pointing toward the bonding metal atoms and the two remaining ones toward the charge concentrations. Note that those charge concentrations appear in the nonbonding regions in agreement with the pattern of the Laplacian distribution in ionic bonds.[25] The orientation of the charge concentrations, and that of the associated bow of low potentials, is therefore conditioned by the position of the vanadium atoms: the nucleophilic area of each doubly bridging oxygen is deduced from the V−V line by a S_2 symmetry operation with respect to the oxygen atom.

The same tetrahedral organization of space is found around triply bridging oxygen atoms, but three directions out of four are now occupied by the tripod of vanadium neighbors. The last direction—and that direction only—is pointing toward a region of low potentials (Figure 2) that has been connected in the case of $(V_{10}O_{28})^{6-}$ to an important charge concentration. The nucleophilic region is therefore opposite with respect to oxygen to the tripod of metal atoms. Figure 3 summarizes the positions of the critical points of charge concentration obtained in the case of $(V_{10}O_{28})^{6-}$ for oxygen atoms in terminal, doubly bridging, and triply bridging positions.

Let us assume now that the polyhedron made of all metal atoms with all doubly- and triply-bridging oxygens is a *convex* polyhedron. This hypothesis is sufficient for assigning to the polyhedron an *inside* and an *outside*. All lines joining two atoms of the convex polyhedron that are not nearest neighbors, and more specifically any couple of metal atoms, are *inside*. The nucleophilic region of a doubly bridging oxygen, connecting the directions of a tetrahedron centered on oxygen and opposite to a V−V line, is clearly *outside*. The direction of the ESP minimum associated with a triply bridging oxygen, which is perpendicular to the plane containing three V−V lines, and opposite to that plane with respect to the oxygen atom, is also pointing *outside*. The terminal oxygens are themselves outside the convex polyhedron and their nucleophilic region, opposite to the V−O bond, is still repelled further. This could be summarized as follows: in a polyhedral structure made of metal atoms and bridging oxygens, *convexity favors basicity*. Two consequences can be deduced more specifically regarding hollow cages and inclusion complexes:

(1) The inner part of spherical or convex polyoxometallates is expected to be a region of charge depletion, where an electrophilic character can develop in relation with relatively high values of the electrostatic potential. This electrophilic character could explain the stabilization of negatively charged atoms or guest molecules inside the cage. The central oxygen atom in Lindqvist ions $(M_6O_{19})^{n-}$, retaining a high negative charge and loosely attached to the metal framework, could itself be considered as a guest anion in a cage molecule. Same is true for some standard or capped Keggin polyanions like the recently characterized $[PMo^{V}{}_6Mo^{VI}{}_6O_{40}(V^{IV}O)_2]^{5-}$ [26] that can be considered as a $(PO_4)^{3-}$ anion encapsulated in a convex $[V_2Mo_{12}O_{38}]^{2-}$ cage structure.

(2) The suggestion that the acidic/basic character of a metal oxide surface is governed by the topological concept of convexity/concavity provides a rationale to the observed encapsulation of basic precursors. A flexible oxometallate fragment will react to the approach of a negatively charged precursor by bending into a concave/acidic surface. The tailor-shaped self assembly of a polyoxometallate host around the precursor would therefore result from a straightforward polarization mechanism.

One should not forget however that those "electronically inverse hosts" that are formed by using the template function of an anionic guest still represent an exception. Most discrete host−guest systems based upon a polyoxometallate "open" or "closed" structure encapsulate cationic species and are referred to as "electronically normal" according to Müller's classification.[2] It should be noticed that all those structures, either closed like $[Mo^{VI}O_3)_4Mo^{V}{}_{12}O_{28}(OH)_{12}]^{8-}$,[27] or open like the cryptand $[As_4W_{40}O_{140}]^{28-}$ [28] or the host−guest system $[NaP_5W_{30}O_{110}]^{14-}$ [29] are nonconvex polyhedra in which some bridging oxygens are oriented toward the cavity with respect to their nearest metal neighbors. Some cases are less trivial, such as polyoxometallate hosts that encapsulate strongly polar guest systems. As noticed by Müller, those structures are coupling electronically normal

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(23) Kempf, J.-Y.; Rohmer, M.-M.; Poblet, J.-M.; Bo, C.; Bénard, M. *J. Am. Chem. Soc.* **1992**, *114*, 1136.

(24) Bader, R. F. W. *Atoms in Molecules, A Quantum Theory*; Clarendon Press: Oxford, 1994.

(25) (a) Bader, R. F. W.; Henneker, W. H. *J. Am. Chem. Soc.* **1965**, *87*, 3063. (b) Bader, R. F. W.; Preston, H. J. T. *Int. J. Quantum Chem.* **1969**, *3*, 327. (c) Bader, R. F. W.; MacDougall, P. J.; Lau, C. D. H. *J. Am. Chem. Soc.* **1984**, *106*, 1594. (d) MacDougall, P. J.; Schrobilgen, G. J.; Bader, R. F. W. *Inorg. Chem.* **1989**, *28*, 763.

(26) Chen, Q., Hill, C. L. *Inorg. Chem.* **1996**, *35*, 2403.

(27) (a) Khan, M. I.; Müller, A.; Dillinger, S.; Bögge, H.; Chen, Q.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1780. (b) Khan, M. I.; Chen, Q.; Salta, J.; O'Connor, C. J.; Zubieta, J. *Inorg. Chem.* **1996**, *35*, 1880.

(28) (a) Robert, F.; Leyrie, M.; Hervé, G.; Tézé, A.; Jeannin, Y. *Inorg. Chem.* **1980**, *19*, 1746. (b) Leyrie, M.; Thouvenot, R.; Tézé, A.; Hervé, G. *New J. Chem.* **1992**, *16*, 475.

(29) (a) Alizadeh, M. H.; Harmalker, S. P.; Jeannin, Y.; Martin-Frère, J.; Pope, M. T. *J. Am. Chem. Soc.* **1985**, *107*, 2662. (b) Creaser, I.; Heckel, M. C.; Neitz, J. R.; Pope, M. T. *Inorg. Chem.* **1993**, *32*, 1573.

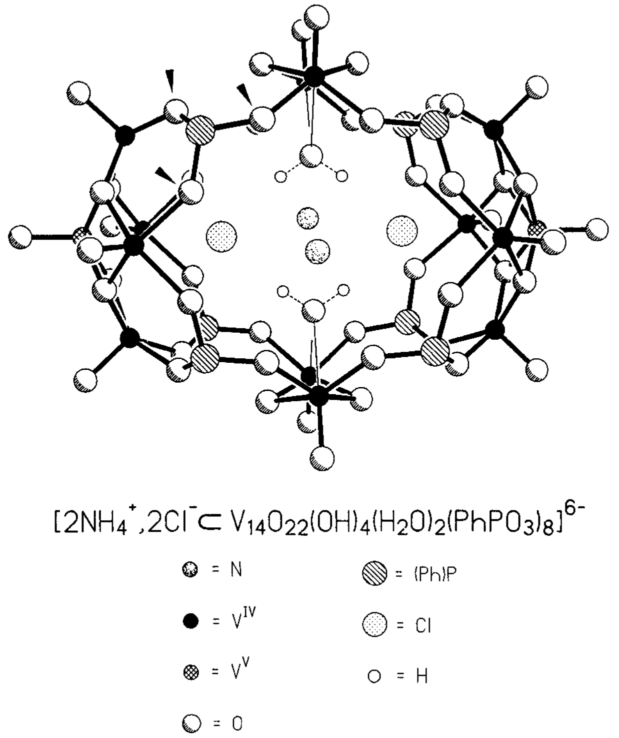

Figure 4. An example of encapsulation complex coupling electronically normal and inverse subhosts: $(2NH_4^+,2Cl^-)\subset[V_{14}O_{22}(OH)_4(H_2O)_2(PhPO_3)_8]^{6-}\cdot 5H_2O\cdot 4DMF$ (DMF = dimethylformamide).[2,30] Reproduced from those references with permission.

and inverse subhosts[2] and the topology of the cage molecule appears to conform *locally* to the polarity of the closest fragment of the guest system. A typical example of such an *electronically bifunctional* host system[2] is provided by the inclusion complex $(2NH_4^+,2Cl^-)\subset[V_{14}O_{22}(OH)_4(H_2O)_2(PhPO_3)_8]^{6-}\cdot 5H_2O\cdot 4DMF$ (DMF = dimethylformamide) (Figure 4).[2,30] The nucleophilic parts of the guest system, namely the chlorine atoms, are encapsulated each in a fully convex hemispherical cavity ("coronand"). Those convex half-shells were shown to be topologically similar to those forming the "electronically inverse" host $[H_4V^{IV}{}_{18}O_{42}]^{8-}$ structured around a halogen anion template.[2,7a,30] In the complex of Figure 4, the two coronands are linked together by four V^{IV} centers that break the convexity of the host cage with eight doubly bridging oxygens having their nucleophilic sides oriented toward the guest cations. The complex seems to be further stabilized by the presence of two water molecules inside the cavity.[30]

Another example of a polar guest molecule is provided by the $[V_4O_4](O_{term})_4$ cluster encapsulated itself in a polyoxovanadate cage.[2,9] An electrostatic potential analysis should be necessary to document in this case the electronic complementarity of the host and guest structures. Finally, the $[N_3^-\subset(H_2V_{18}O_{44})^{4-}]$ complex[9c,31] assumed by Müller to behave as an electronically inverse system[2] because of the negative charge of the guest molecule should rather be considered as a host structure adapted to a strongly polar guest. The HOMO of N_3^- is a nonbonding orbital localized on the terminal nitrogen atoms.[32] In the first approximation, the terminal nitrogens therefore share a (2−) charge whereas the central atom should be attributed a positive charge. The electrophilic character of the central N atom is evidenced in the host−guest complex by the inside bending of the four oxygen bridges surrounding that nitrogen.

The origin of the host−guest stabilization in electronically inverse host−guest systems has however remained elusive up to now. Extended Hückel calculations carried out on the model cluster ion $[V_{18}O_{42}(Cl)]^{13-}$ show that the resulting electrostatic energy is positive, unless attractive interactions with the cationic lattice are accounted for.[6] In order to supplement with quantitative information our qualitative model based upon electrostatic potential, we have carried out a calculation and an analysis of the host−guest interaction energy in $RCN\subset(V_{12}O_{32})^{4-}$.

4. Host−Guest Interactions in $RCN\subset(V_{12}O_{32})^{4-}$

The HCN molecule is characterized by a dipole moment in the gas phase (2.98D) somewhat smaller than that of acetonitrile (3.92D) and benzonitrile (4.18D). The polarity is quite similar, however, with negative Mulliken charges on nitrogen (−0.16e for HCN, −0.15e for acetonitrile, −0.10e for benzonitrile) and on the cyanide carbon (−0.15e, −0.06e, and −0.22e, respectively) and the positive counterpart on H, CH_3 or C_6H_5. HCN has however the advantage of being linear and respectful of the host C_{4v} symmetry as long as its move is restricted to a linear displacement along the symmetry axis. The $HCN\subset(V_{12}O_{32})^{4-}$ system has therefore been considered as a model for studying the host−guest interaction in the inclusion systems characterized by Klemperer *et al.*[11] The interaction energies are plotted in Figure 5 as a function of the displacement of HCN inside and outside the host cavity. This displacement is defined by plotting on the horizontal axis the position of the nitrogen atom with respect to an origin corresponding to the projection on the symmetry axis of the four O_D bridging oxygens (Figure 1). In Table 1, the position taken for the nitrogen atom has been defined with respect to the observed position of N in $CH_3CN\subset(V_{12}O_{32})^{4-}$. This table displays the total host−guest interaction energies computed for selected positions of HCN and of the following guest systems: CH_3CN, C_6H_5CN, N_2, and C_2H_2. Most computed points correspond to $\Theta = 0$ which means that the HCN molecule remains collinear with the symmetry axis. For some calculations, HCN was allowed to deviate from that axis, except for the nitrogen atom. Θ represents the angle between the symmetry axis of the host and the linear HCN. A Θ value of 180° means that HCN is again collinear with the symmetry axis but upside down.

The solid line in Figure 5 corresponds to the total interaction energy defined as

$$\Delta E = E_{\text{supersystem}} - E_{\text{host}} - E_{\text{guest}}$$

where the energy of the supersystem and those of the fragments are obtained after convergence of the SCF process. The energy E_0 of the supersystem obtained at the *first iteration step* from the Schmidt orthonormalized starting vectors of the separated fragments has been given a physical meaning for weakly interacting systems: it defines the *Coulombic part* of the interaction energy,[33] represented on Figure 5 as a broken line

$$\Delta E_{\text{Coulombic}} = E_{0(\text{supersystem})} - E_{\text{host}} - E_{\text{guest}}$$

At the equilibrium position, the electrostatic attraction corresponds to 5.3 kcal·mol^{-1} out of a total interaction energy of 12.8 kcal·mol^{-1}. Note however that $\Delta E_{\text{Coulombic}}$ includes the Pauli exchange term, a repulsive contribution that may become

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[30] Müller, A.; Hovemeier, K.; Rohlfing, R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1192.

[31] Müller, A.; Diemann, E.; Krickemeier, E.; Che, S. *Naturwissenschaften* **1993**, *80*, 77.

[32] Eberson, L.; Gonzalez-Luque, R.; Lorentzon, J.; Merchan, M.; Roos, B. O. *J. Am. Chem. Soc.* **1993**, *115*, 2898.

[33] Kollman, P. A.; Allen, L. C. *Theor. Chim. Acta* **1970**, *18*, 399.

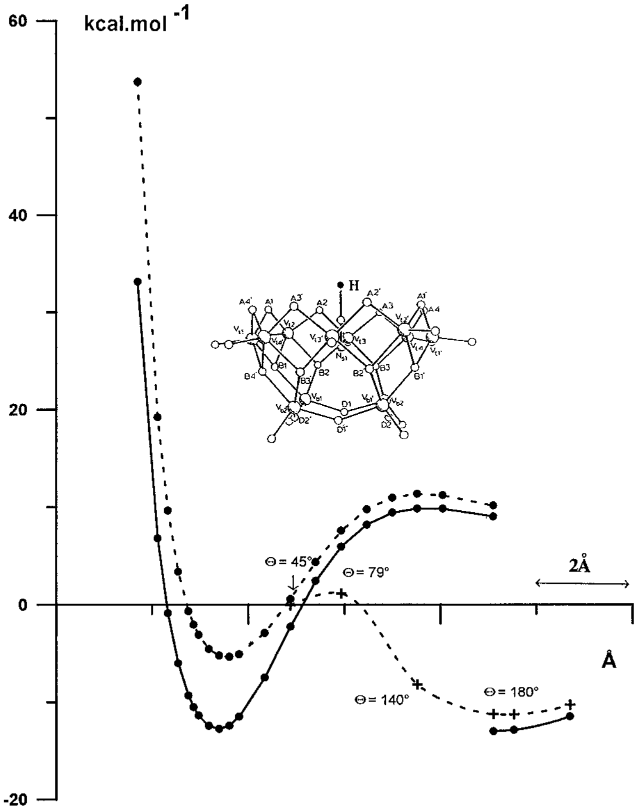

Figure 5. Total (solid line) and Coulombic (dotted line) host-guest interaction energies (kcal·mol^{-1}) computed for HCN$\subset$(V$_{12}$O$_{32}$)$^{4-}$ as a function of the position of N on the symmetry axis. The origin of the distances corresponds to the projection of the O$_D$ oxygens on that axis. After the bifurcation point, the dotted line with crosses corresponds to the Coulombic interaction energy for $\Theta \neq 0$ (Θ = angle between the linear HCN and the symmetry axis). The total interaction energy has been plotted again for $\Theta = 180°$ (HCN upside down).

important and even predominant when stronger atom−atom interactions like hydrogen bonds are present.

A further step in the analysis of the interaction energy was reached by computing the polarization energy P_{guest} of HCN in the field of the host molecule and the counter-polarization energy P_{host} of the vanadate cage due to the presence of HCN. The energy decomposition analysis proposed by Bagus *et al.* (Constrained Space Orbital Variation, CSOV),[34] explicitely provides those quantities and appears from this point of view particularly suited to the analysis of *electrostatic* interactions between molecular fragments. Other energy decomposition methods such as the EDA method proposed by Morokuma and Kitaura[35] are more oriented toward the analysis of the charge transfer part of the interaction which is sometimes important but never dominant in the systems considered in the present study. Within the CSOV framework, the polarization energies of the guest and host fragments are obtained in that order by optimizing (i) the wave function of HCN in the supersystem while freezing the orbitals of the isolated host, and then (ii) the wave function of (V$_{12}$O$_{32}$)$^{4-}$, still considered as part of the supersystem, but without further relaxing the orbitals of HCN. The sum of polarization energies $P_{\text{guest}} + P_{\text{host}}$ was computed to be 4.9 kcal·mol^{-1} for HCN$\subset$(V$_{12}$O$_{32}$)$^{4-}$ (Table 1). When the host−guest electrostatic attraction and the polarization contributions are considered altogether, it appears that 80% of the host−guest stabilization energy should be attributed an electrostatic origin. The remaining 20% (2.6 kcal·mol^{-1}) mainly result from weak orbital interactions leading to a global charge transfer of ∼0.1e from HCN to the vanadate molecule. It should be finally noticed that the introduction of positive charges modeling the counterions has a weak but nonnegligible influence on the total stabilization energy, increased from 12.8 to 15.0 kcal·mol^{-1} (Table 1). In case of a near balance between attractive and repulsive interactions in the isolated host−guest system, the influence of crystal packing could condition the stability of the system, as already suggested by Müller and colleagues.[2,6]

The position of the nitrogen atom of HCN at equilibrium is up by 0.63 Å with respect to the position of N in the observed structure of CH$_3$CN$\subset$(V$_{12}$O$_{32}$)$^{4-}$. Hydrogen is then located almost exactly at the position of minimal electrostatic energy characterized at the entrance of the cavity (Figure 2). The stabilization energy rapidly decreases when hydrogen departs from that position. If HCN is constrained to leave the cage along the symmetry axis, the interaction becomes repulsive at +1.7 Å with respect to the equilibrium position, and the repulsion increases beyond this point up to 9.9 kcal·mol^{-1} and then slowly diminishes as the nitrile group moves away from the low potential region (Figure 5). It should be noticed that the electrostatic part of the host−guest interaction energy (dotted curve) becomes largely dominant in the repulsive section of the curve. The effect of allowing the linear HCN guest molecule to deviate from the symmetry axis has been considered. The nitrogen atom was constrained to remain on the symmetry axis, and the Coulombic interaction energy was optimized as a function of the tilt angle Θ. A bifurcation point occurs on the electrostatic interaction curve at 1.4 Å above the equilibrium position computed for HCN (+2.05 Å with respect to the origin, Figure 5). Beyond that point, Θ becomes different from zero and rapidly increases to 79° (+3.18 Å) which corresponds for HCN to a near-horizontal position above the rim of the vanadate cage, with an electrostatic interaction energy close to zero. When the nitrogen atom moves further away along the symmetry axis, Θ keeps on increasing until HCN is completely turned upside down ($\Theta = 180°$ and HCN outside the cage). A second minimum of the host−guest stabilization energy is obtained for that position ($\Delta E = 13.1$ kcal·mol^{-1}). Although the encapsulation complex and what could be called an "external adduct" display equivalent stabilization energies, the latter one has not been characterized experimentally, probably due to the looser packing of the external adduct and to the repulsive interactions that are expected to develop between the negatively charged cyano group and the nearest vanadate neighbors. The dispersion forces, not accounted for at the present level of calculation, are also expected to further stabilize the most densely packed conformation.[36] At variance from the energy minimum characteristic of the inclusion process, the external adduct is almost exclusively stabilized through Coulombic interaction (86% of the stabilization energy). Accounting for the constraint that keeps the nitrogen atom on the symmetry axis, the path linking both energy minima corresponds to an inversion of the HCN position along that axis. This inversion is achieved with a relatively small variation of the position of H (+1.3 Å), which stays during the whole process in the region of low potential topping the entrance of the vanadate cavity. It can be reasonably

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(34) Bagus, P. S.; Hermann, K.; Bauschlicher, C. W., Jr. *J. Chem. Phys.* **1984**, *80*, 4378; **1984**, *81*, 1966.

(35) (a) Morokuma, K.; Kitaura, K. In *Chemical Applications of Atomic and Molecular Electrostatic Potentials*; Politzer, P., Truhlar, D. G., Eds.; Plenum, New York, 1981. (b) Kitaura, K.; Sakaki, S.; Morokuma, K. *Inorg. Chem.* **1981**, *20*, 2292.

(36) (a) Mahanty, J.; Ninham, B. W. *Dispersion Forces*; Academic Press: London, 1976. (b) Isrealachvili, J. *Intermolecular and Surface Forces*, 2nd ed.; Academic Press: London, 1991.

inferred that the stabilization of the external adduct exclusively involves the electrophilic part of the H−CN (or R−CN) molecule.

The host−guest stabilization energy was computed for the real systems $CH_3CN\subset(V_{12}O_{32})^{4-}$ and $C_6H_5CN\subset(V_{12}O_{32})^{4-}$ assuming first for those encapsulation complexes the experimentally determined geometry[11] (Table 1). The order of magnitude of the total stabilization energy computed for those complexes is similar to that obtained for the model system $HCN\subset(V_{12}O_{32})^{4-}$: respectively 14.4 $kcal{\cdot}mol^{-1}$ ($R = CH_3$) and 14.1 $kcal{\cdot}mol^{-1}$ ($R = C_6H_5$) compared to 12.8 $kcal{\cdot}mol^{-1}$ ($R = H$). A marked decrease of the Coulombic interaction is noticed for CH_3CN and especially for C_6H_5CN, for which the electrostatic interaction term becomes repulsive ($\Delta E_{Coulombic} = +1.8$ $kcal{\cdot}mol^{-1}$) at the experimental geometry. This decrease of $\Delta E_{Coulombic}$ is compensated in part by a rise of the polarization energies P_{host}, and, for $C_6H_5CN\subset(V_{12}O_{32})^{4-}$, P_{guest}, so that the part of the electrostatic stabilization including polarization effects remains high (69% for CH_3CN, and 62% for C_6H_5CN). For C_6H_5CN, the interpretation of the energy decomposition analysis might be biased because of the predominant influence of the Pauli repulsion term in the calculation of $\Delta E_{Coulombic}$. Additional calculations carried out on $C_6H_5CN\subset(V_{12}O_{32})^{4-}$ at different positions of the guest molecule in the cavity show that $\Delta E_{Coulombic}$ becomes attractive when diminishing the Pauli repulsion through an increase of the O···H distances (Table 1). Note however that the so-obtained coulombic attraction is rapidly offset by an overall decrease of the other sources of stabilization. Eventually, the computed equilibrium position of the $C_6H_5CN\subset(V_{12}O_{32})^{4-}$ system is obtained after an upward shift of 0.34 Å of the guest molecule with respect to its observed position. The total stabilization energy associated with that position is 16.2 $kcal{\cdot}mol^{-1}$ (Table 1).

The stabilization attributable to orbital interactions and charge transfers between the host and guest systems increases from HCN ($\Delta E_{CT} = -2.6$ $kcal{\cdot}mol^{-1}$) to CH_3CN ($\Delta E_{CT} = -4.65$ $kcal{\cdot}mol^{-1}$) and then to C_6H_5CN ($\Delta E_{CT} = -5.3$ $kcal{\cdot}mol^{-1}$ at the observed geometry) (Table 1). This trend is not easy to explain if the discussion is restricted to the global charge transfer between the vanadate molecule and the host fragment. This global transfer is oriented from the R−CN adduct to the host molecule for the three considered complexes, but the amount of transferred charge decreases from 0.10e for HCN to 0.08e for CH_3CN and to 0.02e for C_6H_5CN. A closer examination of the Mulliken charges of R, C and N obtained for the guest molecules successively assumed i) isolated, then ii) polarized, and eventually iii) undergoing charge transfer (Table 2) suggests that for $R \neq H$ the global charge transfer results from two opposite effects. On the one hand, we have a net donation from the cyanide π orbitals to the vanadium atoms, and on the other hand a back donation from the eight oxygen atoms at the top of the vanadate host to the acceptor orbitals of R. That back donation to R cannot exist for HCN due to the lack of an acceptor orbital. In fact, the positive charge of hydrogen increases by 0.04e and so does the positive charge of the cyanide carbon, by 0.08e. The CH_3 substituent has one σ and two π orbitals available for back donation.[37] At variance from HCN, the net charge of R in CH_3CN *decreases* from +0.29e in the polarized fragment to +0.22 in the final wave function including charge transfer. On the opposite way, the nitrile group is involved in donation and back donation interactions resulting in a net donation of 0.15e (Table 2). The rise of the charge transfer energy can be attributed to the addition of those two stabilizing interactions. In $C_6H_5CN\subset(V_{12}O_{32})^{4-}$, the net transfers host → C_6H_5 and CN → host are almost balanced at 0.16−0.18e (Table 2) resulting in a charge transfer energy of 5.3 $kcal{\cdot}mol^{-1}$. Once again, the possibility of obtaining those opposite charge transfer interactions is a consequence of the dual potentialities—donor and acceptor—of CH_3CN and C_6H_5CN, duly activated by a convenient positioning with respect to the acceptor sites (inside) and to the donor sites (outside) of the vanadate host.

Table 2. Mulliken Net Charges (e) Obtained for R, C, and N in $R\text{-}CN\subset(V_{12}O_{32})^{4-}$ at the Following Stages of the Calculation: (i) Isolated Fragments, (ii) Polarized Fragments (Excluding Charge Transfer),[a] (iii) Final SCF Calculation of the Inclusion Complex

	R	isolated	polarized	inclusion	CT[b]
	H				
H		+0.31	+0.31	+0.35	+0.04
C		−0.15	+0.03	+0.11	
					+0.07
N		−0.16	−0.34	−0.35	
	CH_3				
CH_3		+0.21	+0.29	+0.22	−0.07
C		−0.06	0.00	+0.21	
					+0.15
N		−0.15	−0.29	−0.35	
	C_6H_5				
C_6H_5		+0.32	+0.38	+0.22	−0.16
C		−0.22	−0.14	+0.04	
					+0.175
N		−0.10	−0.23	−0.24	

[a] Obtained from the CSOV energy decomposition analysis.[34] [b] Charge transfers from RCN to $(V_{12}O_{32})^{4-}$ (plus sign) and from $(V_{12}O_{32})^{4-}$ to RCN (minus sign) obtained as the difference between the Mulliken populations of R and CN in the final calculation and in the polarized fragments.

As for HCN, the existence of a second minimum characteristic of an external adduct has been evidenced from the calculations. Single point calculations have been carried out to consider the possibility of obtaining stabilizing interaction energies for external conformations of $CH_3CN,(V_{12}O_{32})^{4-}$ and $C_6H_5CN,(V_{12}O_{32})^{4-}$. It was assumed that the guest molecule had been extracted from the cavity and rotated by 180°, changing neither the position of the hydrogen tripod for CH_3CN nor that of the CH···O interactions for C_6H_5CN, with respect to the X-ray determined geometry of the inclusion complexes. As for HCN, stabilization energies slightly larger than those associated with the inclusion complex were obtained from those calculations (Table 1).

Finally, linear molecules with no permanent dipole, such as N_2 and C_2H_2, have been tested on the computer as guest molecules. At the most favorable position (+0.63 Å with respect to the position of N in $CH_3CN\subset(V_{12}O_{32})^{4-}$), N_2 is stabilized by no more than 5 $kcal{\cdot}mol^{-1}$. Acetylene displays a repulsive interaction with the vanadate host. This repulsion exceeds 10 $kcal{\cdot}mol^{-1}$ when carbon occupies the same position as nitrogen in $HCN\subset(V_{12}O_{32})^{4-}$ at equilibrium (Table 1).

5. Summary and Conclusions

An analysis of the ab initio SCF interaction energies computed for the model system $HCN\subset(V_{12}O_{32})^{4-}$ ($\Delta E = -12.8$ $kcal{\cdot}mol^{-1}$) and for the real inclusion complex $CH_3CN\subset(V_{12}O_{32})^{4-}$ ($\Delta E = -14.4$ $kcal{\cdot}mol^{-1}$) show that the host−guest electrostatic interaction and the polarization energies of both fragments play a major role in the stabilization of those complexes. The behavior of $C_6H_5CN\subset(V_{12}O_{32})^{4-}$ ($\Delta E = -14.1$ $kcal{\cdot}mol^{-1}$) does not seem to be basically different, but the decomposition of the host−guest interaction energy appears more difficult to interpret because of the important Pauli repulsion, included in $\Delta E_{Coulombic}$. The importance of electrostatic interactions, and

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(37) Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985.

also the opposite charge transfers evidenced (i) from the cyanide carbon to the host metal backbone and (ii) from the host upper “rim” of eight oxygens to the R substituent suggest that the stabilization of the inclusion complexes is conditioned by the important dipole moment of the considered R−CN systems and by the opposite dipolar field generated inside the cavity of the isolated host. Linear molecules with no permanent dipole were shown to display only weakly attractive (for N_2) or repulsive (for C_2H_2) interactions. Those results confirm that polarizability and accessibility are not the only prerequisites ensuring a sufficient stability for a guest molecule in the vanadate cavity. Since that stability is conditioned in a large part by electrostatic factors, we expect the supramolecular chemistry of vanadate cages to be governed by a key and lock model based upon the electrostatic potential distribution of the host and guest molecules. The local features of the potential distributions in vanadates—and more generally in polyoxometallates—could be correlated with topological criteria such as concavity/convexity≡acidity/basicity, thus providing clues to interpret “at first sight” the origin of the host−guest stabilization in *electronically normal* or in *electronically inverse* supramolecular complexes.

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