Shape-selective binding of nitriles to the inorganic cavitand, $V_{12}O_{32}{}^{4-}$

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Abstract

The benzonitrile guest-host complex $[C_6H_5CN \subset (V_{12}O_{24}{}^{4-})]$ has been prepared by thermal dehydration of $H_2V_{10}O_{28}{}^{4-}$ in C_6H_5CN. Single crystal X-ray structural analysis of its solvated tetraphenylphosphonium salt $1/2\{(V_{12}O_{32})[P(C_6H_5)_4]_4 \cdot (C_6H_5CN)_6\}$ [$b = 19.392(9)$, $b = 11.679(4)$, $c = 30.881(15)$, $\beta = 107.78(4)$, P2/c-C_{2h}^4 (No. 13)] revealed the presence of $P(C_6H_5)_4^+$ cations, C_6H_5CN molecules of solvation, and discrete $[C_6H_5CN \subset (V_{12}O_{32}{}^{4-})]$ ions in which an benzonitrile molecule is located in the center of a $V_{12}O_{32}{}^{4-}$ cavitand. The $V_{12}O_{32}{}^{4-}$ ion binds CH_3CN in preference to C_6H_5CN in $C_6H_5NO_2$ with $K_{eq} = 10 \pm 3$ for the equation $CH_3CN + [C_6H_5CN \subset (V_{12}O_{32}{}^{4-})] = C_6H_5CN + [CH_3CN \subset (V_{12}O_{32}{}^{4-})]$. According to computer modeling studies, van der Waals forces can account for the gross structural features of $[CH_3CN \subset (V_{12}O_{32}{}^{4-})]$ and $[C_6H_5CN \subset (V_{12}O_{32}{}^{4-})]$, but metal–ligand interactions are responsible for preventing a close approach of the guest molecules to the interior walls of the host cavity.

Introduction

We recently reported the synthesis and structure of a molecular guest-host complex $[CH_3CN \subset (V_{12}O_{32}{}^{4-})]$, **a**, in which an acetonitrile molecule is suspended in the center of a basket-like $V_{12}O_{32}{}^{4-}$ cage [1]. All the V−N

a
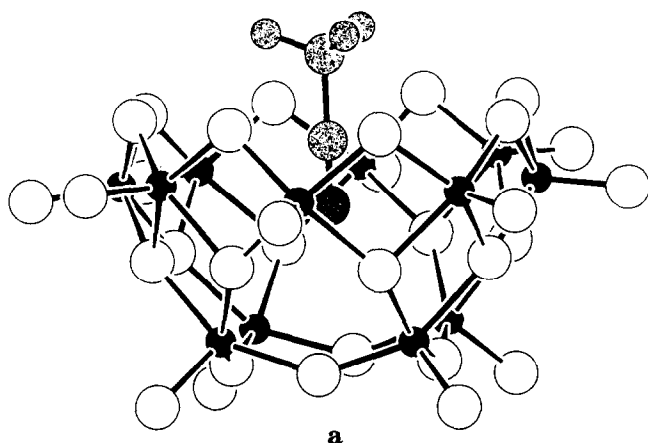
and V—C distances in this structure exceed 3.2 Å, indicating very weak metal–ligand interactions between the host and the guest molecule. Given the weakness of these metal–ligand interactions, it becomes reasonable to view $[CH_3CN \subset (V_{12}O_{32}{}^{4-})]$ as an inorganic analogue of purely organic acetonitrile-cavitand complexes such as the acetonitrile solvate of the tetramethylene-bridged 2-methylresorcinol/acetaldehyde-derived calixarene, **b**, [2, 3]:


b
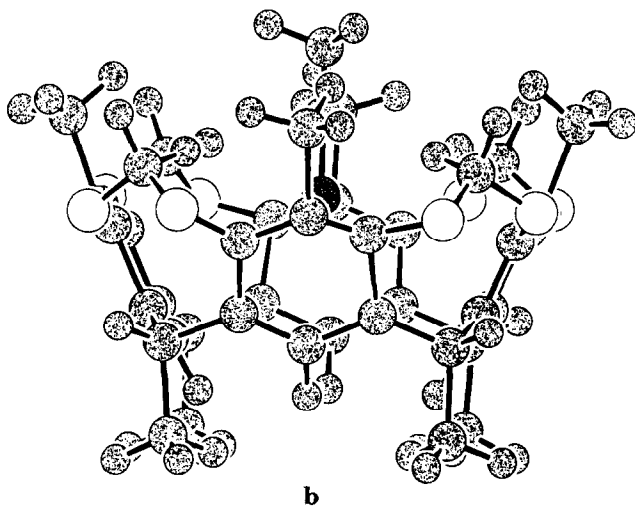
This analogy raises the possibility of shape-selective guest-host binding, a possibility explored in the present communication through the synthesis of the benzonitrile complex $[C_6H_5CN \subset (V_{12}O_{32}{}^{4-})]$. The greater steric bulk of the phenyl group in benzonitrile relative to the methyl group in acetonitrile was expected to restrict access of the nitrile group to the $V_{12}O_{32}{}^{4-}$ cavity. The consequences of this restriction have been examined through single-crystal X-ray diffraction, competitive binding, and van der Waals modeling studies.

Synthesis and structure of $[C_6H_5CN \subset (V_{12}O_{32}{}^{4-})]$

The dodecavanadate inclusion complex $[C_6H_5CN \subset (V_{12}O_{32}{}^{4-})]$ was prepared as a solvated tetraphenylphosphonium (TPP) salt by maintaining a C_6H_5CN solution of $(H_2V_{10}O_{28})$ (TPP)$_4$ at 120 °C for 2-3 minutes. The crude product, obtained by precipitation with diethyl ether after cooling to ambient temperature, was isolated by suction filtration and recrystallized from benzonitrile-toluene. A single crystal X-ray diffraction study of this material revealed the presence of $(C_6H_5)_4{}^+$ cations, isolated C_6H_5CN molecules, and $[C_6H_5CN \subset (V_{12}O_{32}{}^{4-})]$ anions having the structure shown in Fig. 1. Crystallographic data is given in Table 1; atomic coordinates are available as supplementary material (see paragraph at end of paper).

The geometry of the $V_{12}O_{32}{}^{4-}$ framework in $[C_6H_5CN \subset (V_{12}O_{32}{}^{4-})]$ is very similar to the geometry of the corresponding framework in $[CH_3CN \subset (V_{12}O_{32}{}^{4-})]$ (see Fig. 1 caption and [1]). However, the guest-host interactions in the two complexes are quite different, and can be most easily visualized from the cutaway spacefilling representations shown in Figs. 2a and b. The CH_3CN nitrile group is seen to extend much farther into the $V_{12}O_{32}{}^{4-}$ basket than the C_6H_5CN nitrile group: the distance from the nitrile nitrogen to the mean plane of the four 'bottom' vanadium centers V_b, V_{b1}, V_{b2}, $V_{b1'}$ and $V_{b2'}$ in Fig. 1 is 2.22 Å in the CH_3CN adduct and 2.68 Å in the C_6H_5CN adduct; $N–V_b$ distances are 3.263(9) and 3.302(9) Å in the CH_3CN adduct but 3.608(8) and 3.619(8) Å in the C_6H_5CN adduct. In the case of the CH_3CN adduct, none of the CH_3CN atoms have van der Waals contacts with the $V_{12}O_{32}{}^{4-}$ cage. In the C_6H_5CN adduct, the two benzonitrile *ortho* hydrogen atoms are in contact with four of the eight O_A oxygen atoms at the rim of the basket: the $H \cdots O_A$ distances of 2.537 and 2.555 Å correspond to van der Waals contacts between hydrogen atoms and oxygen atoms having 1.4 and 1.2 Å van der Waals radii, respectively [4]. In both structures, however, the guest-host complexes lie on crystallographic C_2 axes, and the nitrile molecules are therefore located on the $V_{12}O_{32}{}^{4-}$ cage axis in each case.
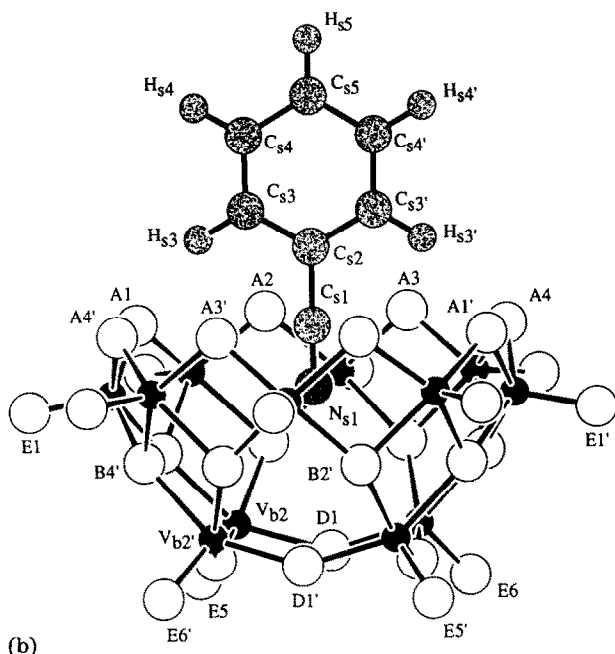

(a)
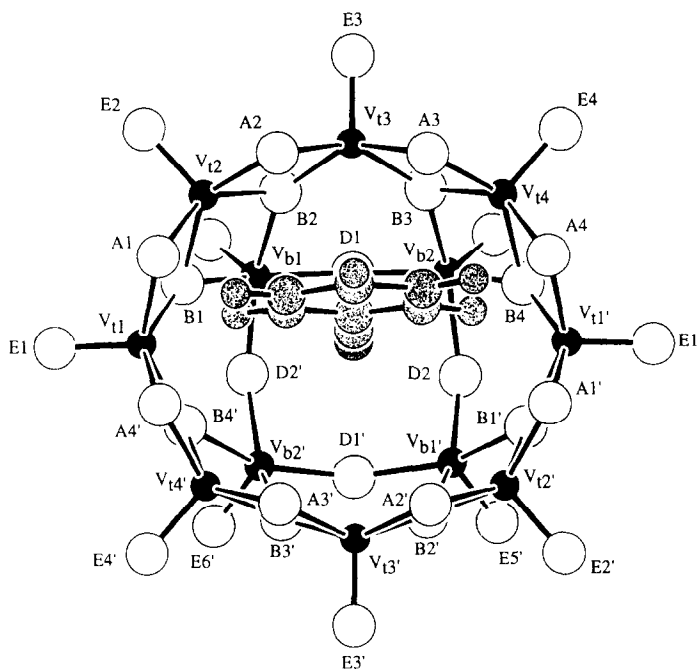
Fig. 1.

Fig. 1. Computer generated view of the $[C_6H_5CN \subset (V_{12}O_{32}{}^{4-})]$ anion viewed (a) nearly along and (b) approximately perpendicular to the crystallographic C_2 axis passing through the benzonitrile guest molecule. Vanadium atoms are represented by filled spheres; oxygen atoms are represented by open spheres; and carbon, hydrogen, and nitrogen atoms in the benzonitrile molecule are represented by shaded spheres. Vanadium atoms at the top and bottom of the $V_{12}O_{32}{}^{4-}$ cavitand are labeled V_t and V_b, respectively. Oxygen atoms which bridge two V_t atoms are labeled A, oxygens which bridge two V_t and one V_b atoms are labeled B, and oxygens which bridge two V_b atoms are labeled D. Terminal oxygen atoms are labeled E. Atoms with primed labels are related to atoms with unprimed labels are related by a crystallographic C_2 axis. Vanadium–oxygen bond distances range between 1.586(7) and 1.601(7) Å for O_E oxygens, 1.769(7) and 1.842(8) Å for O_A and O_D oxygens, and 1.885(7) and 1.970(7) Å for O_B oxygens.

Competitive binding studies

The binding selectivity of the $V_{12}O_{32}{}^{4-}$ cavitand could be probed at 8 °C by ^1H NMR spectroscopy in $C_6D_5NO_2$ solution by adding different amounts of p-toluonitrile to $[CH_3CN \subset (V_{12}O_{32}{}^{4-})](TBA)_4$, $TBA^+ = (n\text{-}C_4H_9)_4N^+$. With the $V_{12}O_{32}{}^{4-}$ concentration fixed at 1.3×10^{-2} M and the total $CH_3C_6H_4CN$ concentration ranging from 5.0×10^{-3} to 2.7×10^{-2} M, it was possible to obtain well-resolved methyl group resonances for free CH_3CN, free $CH_3C_6H_4CN$, bound CH_3CN, and bound C_6H_5CN. The equilibrium constant for eqn. (1) could therefore be calculated using integrated NMR intensities.

$$[CH_3C_6H_4CN \subset (V_{12}O_{32}{}^{4-})] + CH_3CN =$$

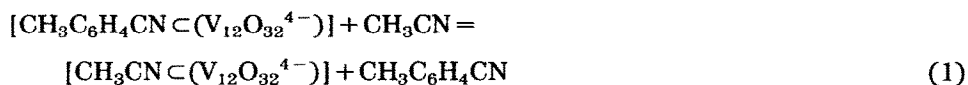$$[CH_3CN \subset (V_{12}O_{32}{}^{4-})] + CH_3C_6H_4CN \tag{1}$$

TABLE 1

Crystallographic data for $(V_{12}O_{32})[P(C_6H_5)_4]_4(C_6H_5CN)_6$

formula	$\frac{1}{2}\{(V_{12}O_{32})[P(C_6H_5)_4]_4 \cdot (C_6H_5CN)_6\}$
formula weight	1549.80
space group	$P2/c\text{-}C_{2h}^4$ (No. 13)
cell constants	
a, Å	19.392(9)
b, Å	11.679(4)
c, Å	30.881(15)
α, deg	90.00
β, deg	107.78(4)
γ, deg	90.00
V, Å^3	6660(8)
Z	4
ρcalcd, g cm^{-3}	1.546
temp, °C	-75
μ, cm^{-1}	8.97
radiation	Mo(K$\bar{\alpha}$)
$R(F_0)$	0.060
$R_w(F_0)$	0.060

By averaging five different values calculated over the concentration range just given, a value of $K_{eq} = 10 \pm 3$ was obtained.

Van der Waals forces in $V_{12}O_{32}{}^{4-}$ host-guest complexes

If one assumes that the binding preference of $V_{12}O_{32}{}^{4-}$ for CH_3CN relative to p-$CH_3C_6H_4CN$ arises from enthalpic considerations, this preference can clearly be related to the smaller size of the CH_3CN guest molecule relative to the $CH_3C_6H_4CN$ guest molecule which allows deeper penetration into the $V_{12}O_{32}{}^{4-}$ binding cavity (see Figs. 2a and b). This relationship between structure and stability in turn raises the more fundamental question of which types of interatomic forces determine the structure and stability of the $V_{12}O_{32}{}^{4-}$ adducts in question. Are van der Waals forces solely responsible for guest–host interactions as in analogous organic cavitand complexes [2, 3], or do metal–ligand interactions, either covalent or electrostatic, also play a role? This question may be approached using a molecular modeling approach that predicts the geometry of host–guest complexes by minimizing van der Waals interaction energies. Any discrepancy between calculated and observed geometries might then be attributed to metal–ligand interactions.

Energy minimization calculations were performed using CHEM-X software on a VAX 11/780 computer. Guest–host interaction energies were calculated using those Lennard-Jones potentials for $H-O$, $C-O$, and $N-O$ interactions that have been proven effective in zeolite guest–host calculations [5, 6]. The geometries of the guest molecules were fixed at their experimental geometries,
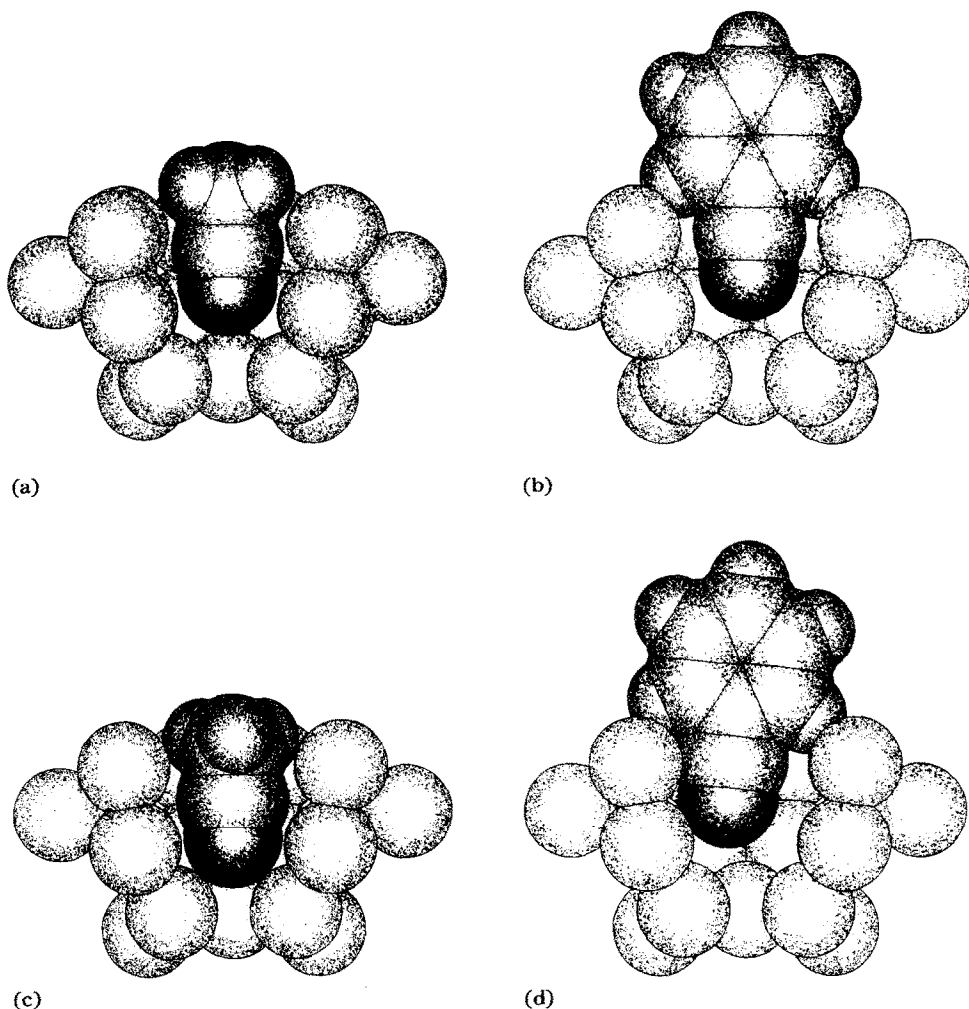
(a)

(b)

(c)

(d)

Fig. 2. Space-filling cutaway views of observed and calculated $[M \subset (V_{12}O_{32}{}^{4-})]$ structures, $M = CH_3CN$ and C_6H_5CN. Experimentally-determined structures are shown in (a) and (b). The structures in (c) and (d) show the guest molecules at their calculated vand er Waals minima in C_{4v-} symmetrized cavitands. All atoms are represented by spheres having van der Waals radii (C, 1.7 Å; H, 1.2 Å; O, 1.4 Å; and N, 1.5 Å [4]).

but $V_{12}O_{32}{}^{4-}$ geometries were idealized to C_{4v} symmetry. To insure that symmetrization of the $V_{12}O_{32}{}^{4-}$ framework did not influence results, the geometry of $[CH_3CN \subset (V_{12}O_{32}{}^{4-})]$ was optimized using both the idealized C_{4v}-$V_{12}O_{32}{}^{4-}$ and the observed C_2-$V_{12}O_{32}{}^{4-}$ frameworks. The results of the two calculations did not differ significantly. Optimized geometries of $[CH_3CN \subset (V_{12}O_{32}{}^{4-})]$ and $[C_6H_5CN \subset (V_{12}O_{32}{}^{4-})]$ were obtained by starting from the experimentally observed guest molecule location within the C_{4v}-symmetrized $(V_{12}O_{32}{}^{4-})$ cavitand and allowing the rigid guest molecule to relax to a local energy minimum. The results of these calculations are shown

in Figs. 2c and d, where differences between the calculated and observed structures are apparent by comparison with Figs. 2a and b, respectively.

In the calculated geometry of Fig. 2c, the CH_3CN molecule lies along the $V_{12}O_{32}{}^{4-}$ cage axis, but has penetrated further into the cage than is observed experimentally. The calculated distance from the nitrile nitrogen to the $(V_b)_4$ plane at the bottom of the host framework is 1.68 Å, and the average $N-V_b$ distance is 2.94 Å; the corresponding distances in the observed structure are 2.22 and 3.28 Å, respectively (see above). The calculated position of the guest molecule along the axis of the host molecule is seen to be determined by van der Waals contacts: only four are observed, all between the nitrile nitrogen atom and the four doubly-bridging O_D oxygen atoms at the bottom of the $V_{12}O_{32}{}^{4-}$ cavity. The 2.91 Å calculated $N\cdots O$ contact matches the sum of nitrogen and oxygen van der Waals radii [4], 1.5 and 1.4 Å, respectively, whereas the corresponding 3.34 Å average $N\cdots O$ distance in the observed structure far exceeds that sum. Clearly, forces other than van der Waals forces are responsible for suspension of the CH_3CN molecule above the bottom of the $V_{12}O_{32}{}^{4-}$ cavity, presumably vanadium–nitrile metal–ligand interactions.

The calculated $[C_6H_5CN \subset (V_{12}O_{32}{}^{4-})]$ structure shown in Fig. 2d resembles the experimentally-determined structure of Fig. 2b in that short $H\cdots O_t$ contacts at 2.49 and 2.52 Å prevent the guest molecule from penetrating deeply into the $V_{12}O_{32}{}^{4-}$ cavity. It differs from the experimental structure, however, in that the nitrile group is markedly displaced from the central axis of the cavitand. Observation of off-center displacement in the C_6H_5CN adduct (Fig. 2d) but not in the CH_3CN adduct (Fig. 2c) can be explained using classical arguments [7]: given that van der Waals forces have a short range, a guest molecule will tend to lie on the host molecular axis as long as it can still be in close proximity to all the surrounding host cavity surface atoms. Such a situation arises in Fig. 1c when the guest molecule enters deeply into the binding cavity. When steric factors prevent deep penetration as in Fig. 2d, the short range character of van der Waals forces dictates a lower energy when the guest molecule is displaced off-axis and thus close to at least some host cavity surface atoms, given that it cannot be close to any of them when it remains on-axis. The fact that the C_6H_5CN molecule remains on the host molecular axis in the experimental structure implies that some other, longer range forces are operating. As in the case of the CH_3CN complex, vanadium–nitrile metal–ligand interactions are likely candidates.

Conclusion

The gross structural features of the $[CH_3CN \subset (V_{12}O_{32}{}^{4-})]$ and $[C_6H_5CN \subset (V_{12}O_{32}{}^{4-})]$ guest-host relationship can be explained by van der Waals attractions and repulsions, but metal–ligand interactions play a key role in preventing a close approach of the guest molecules to the interior walls of the host cavity.

Acknowledgements

Supplementary material available

Atomic coordinates have been deposited at the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

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