

Theoretical Study of Host • • Guest Interactions in Clathrates with a Cd(CN)₂ Host

Eliseo Ruiz and Santiago Alvarez*

Departament de Química Inorgànica, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain

Received April 28, 1995[®]

The clathrate Cd(CN)₂•CCL₄ is theoretically studied by means of extended Hückel tight-binding (EHTB) band calculations and the corresponding crystal orbital difference (COD and ICOD) curves. The small energy required for partial rotation of the CCL₄ molecules inside the cavities may explain the rotational disorder of the guest molecules found in the experimental structure. The host and guest sublattices interact through the 2a₁, 1t₁, and 2t₂ lone-pair orbitals of Cl and the σ*(Cd–N) and σ*(Cd–C) orbitals of the Cd(CN)₂ framework, with smaller contributions from the π*_{CN} orbitals. Ab initio (HF-MP2) calculations on bimolecular models provide rough estimates of the host • • guest and guest • • guest interaction energies in the Cd(CN)₂•CCL₄ and Cd(CN)₂•CMe₄ clathrates, indicating that all interactions are weakly attractive, with the guest • • guest interactions favoring a structure with all the guest molecules at the same rotation angle relative to the Cd(CN)₂ skeleton.

The Hofmann-type tetragonal host lattice Ni(CN)₄Ni(NH₃)₂ enclathrates mostly aromatic molecules,¹ (dioxane² and 1-hexanol³ are the exceptions). In contrast, the smaller cavities of a Cd(CN)₂ host with the cristobalite structure enclathrate non-aromatic molecules, such as cyclohexane, halogenated derivatives of ethane,⁴ or the series of substituted methanes CX_{4–n}Y_n (X = Cl, Me; n = 0–4).^{5,6} Clathrates with different structures for the Cd(CN)₂ hosts have been obtained by varying the nature of the organic guest molecules.^{7–11}

In previous papers^{12–14} we have studied the host • • guest interactions in the Hofmann clathrates by using extended Hückel tight-binding (EHTB) theory, as well as ab initio MP2 calculations on model bimolecular complexes. Such studies showed that EHTB calculations and the derived *crystal orbital displacement* functions (COD) provide a useful tool for the qualitative study of host • • guest interactions, whereas MP2 calculations provide semiquantitative estimates of the interaction energies, even if the need to use molecular rather than periodical calculations necessarily introduces some error in the results. In essence, it was found that the main stabilizing interactions involve N–H • • C hydrogen bonds between the ammonia groups in the host lattice and the aromatic rings and C–H • • N

hydrogen bonds between the phenylic hydrogen atoms and the nitrogen end of the cyano groups of the host. The Cd(CN)₂ clathrates are different from the Hofmann compounds in three important aspects: (1) The enclathrated molecules are not aromatic, (2) there are no hydrogen atoms in the host lattice to form hydrogen bonds, and (3) the guest molecules are placed between layers and modify the layer stacking pattern of the host lattice in the Hofmann clathrates, but are actually trapped in three-dimensional cavities of a rigid host in the Cd(CN)₂ clathrates.

In the following sections we summarize first the crystal structure of the Cd(CN)₂ host lattice and the orientation of the guest molecules within. Next, the electronic structure of the host lattice is described, and its interaction with the CCL₄ guest molecule is examined using EHTB calculations and COD functions. Finally, semiquantitative estimates of the interaction energies are obtained through ab initio MP2 calculations on model supramolecular complexes of the CCL₄ and CMe₄ clathrates.

Crystal Structure of the Cd(CN)₂CX₄ Clathrates

The Cd(CN)₂•CX₄ clathrates crystallize in the cubic system, space group *Fd3m* (No. 227). In these clathrates, the Cd(CN)₂ sublattice presents a structure analogous to that of SiO₂ in cristobalite,¹⁵ with the Cd²⁺ ions tetrahedrally coordinated by four cyano groups. The cyano groups act as bridges between neighboring Cd atoms, in the same way that the O-vertices in cristobalite are shared between neighboring Si atoms, and the result is a three-dimensional network (Figure 1) with cavities delimited by adamantanoid Cd₁₀(μ-CN)₁₂ units (1) where the guest molecules are enclathrated. There are eight Cd atoms per unit cell and eight cavities per unit cell, resulting in the overall stoichiometry Cd(CN)₂•guest. The formal substitution of the oxygen atoms in SiO₂ for the longer CN groups in Cd(CN)₂ gives place to larger cavities (Cd–Cd = 5.5 Å, compared to Si–Si = 3.3 Å). It is interesting to note that Cd(CN)₂ itself crystallizes in the cuprite structure, which is formed by two interpenetrating cristobalite networks. The only compounds known to have such an interpenetrated structure are Cu₂O, Ag₂O, Zn(CN)₂, and Cd(CN)₂, although Proserpio, Hoffmann, and

[®] Abstract published in *Advance ACS Abstracts*, October 1, 1995.

- (1) Iwamoto, T. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., Mac Nicol, D. D., Eds.; Academic Press: London, 1984; Vol. 1, pp 29–57.
- (2) Kendi, E.; Ulku, D. Z. *Kristallogr.* **1976**, *144*, 91–96.
- (3) Hasegawa, T.; Iwamoto, T. *J. Inclusion Phenom.* **1988**, *6*, 143.
- (4) Kitazawa, T.; Nishikiori, S.; Kuroda, R.; Iwamoto, T. *Chem. Lett.* **1988**, 1729–1732.
- (5) Kitazawa, T.; Nishikiori, S.; Yamagishi, A.; Kuroda, R.; Iwamoto, T. *J. Chem. Soc., Chem. Commun.* **1992**, 413–415.
- (6) Kitazawa, T.; Nishikiori, S.-I.; Kuroda, R.; Iwamoto, T. *J. Chem. Soc., Dalton Trans.* **1994**, 1029.
- (7) Kim, J.; Whang, D.; Koh, Y.-S.; Kim, K. *J. Chem. Soc., Chem. Commun.* **1994**, 637.
- (8) Kim, J.; Whang, D.; Lee, J. I.; Kim, K. *J. Chem. Soc., Chem. Commun.* **1993**, 1400.
- (9) Abrahams, B. F.; Hoskins, B. F.; Robson, R. *J. Chem. Soc., Chem. Commun.* **1990**, 60.
- (10) Abrahams, B. F.; Hoskins, B. F.; Liu, J.; Robson, R. *J. Am. Chem. Soc.* **1991**, *113*, 3045.
- (11) Nishikiori, S.; Ratcliffe, C. I.; Ripmeester, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 8590.
- (12) Ruiz, E.; Alvarez, S.; Hoffmann, R.; Bernstein, J. *J. Am. Chem. Soc.* **1994**, *116*, 8207.
- (13) Ruiz, E.; Alvarez, S. *Inorg. Chem.* **1995**, *34*, 3260.
- (14) Ruiz, E.; Novoa, J. J.; Alvarez, S. *J. Phys. Chem.* **1995**, *99*, 2296.

(15) Wells, A. F. *Structural Inorganic Chemistry*, 5th. ed.; Clarendon Press: Oxford, U.K., 1984.

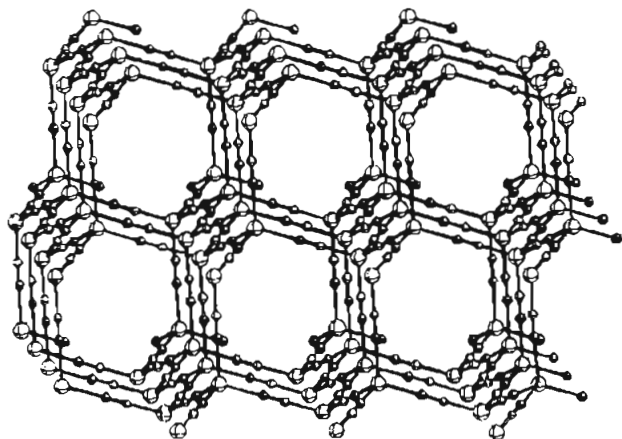
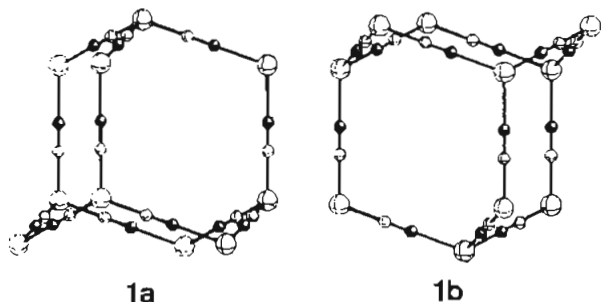


Figure 1. Structure of the $\text{Cd}(\text{CN})_2$ host lattice. Large white spheres represent Cd atoms, small white spheres C atoms, and black spheres N atoms.

Preuss¹⁶ proposed it for the so far hypothetical compounds $\text{BeF}_2 \cdot \text{SiO}_2$ and $\text{BeF}_2 \cdot \text{GeO}_2$, predicted to be very hard materials.

It has not been possible to distinguish the C and N atoms of the CN groups from the X-ray diffraction spectra. Consistently, the ^{113}Cd NMR spectra of $\text{Cd}(\text{CN})_2$ and its cyclohexane clathrate^{17,18} show five different signals, assigned to the five different environments expected for a random distribution of the N- and C- ends of the cyano groups linked to the Cd atoms, CdN_4 , CdN_3C , CdN_2C_2 , CdNC_3 , and CdC_4 , indicating the existence of static disorder in the NMR time scale. For the present work we consider a simple, ordered structure, in which only two types of Cd atoms (large spheres in Figure 1) exist, differing in whether they are surrounded by four N atoms (white small spheres in Figure 1) or by four C atoms (black small spheres in Figure 1). Experimentally, such an ordered structure has been found for the anionic lattices $[\text{CuM}(\text{CN})_4]^-$ ($M = \text{Zn}, \text{Cd}$), in which the Cu atoms are coordinated by the carbon and M is coordinated by the nitrogen atoms of the cyanides.^{6,19} The hypothetical ordered structure of $\text{Cd}(\text{CN})_2$ is convenient for calculations because of its well-defined periodicity and relatively small unit cell. Notice that one of the trigonal symmetry axes of the tetrahedron is aligned with the crystallographic c axis. In the CdN_4 tetrahedra, the corresponding trigonal face is the base of the tetrahedron (i.e., it is parallel to the ab plane), whereas the CdC_4 tetrahedra are upside down.

There are two types of adamantanoid units: those in which the Cd atom sitting at the local C_3 symmetry axis forms a CdC_4 tetrahedron (we call these C-cavities, **1a**) and those in which a



CdN_4 unit is located at the symmetry axis (N-cavities, **1b**). All

(16) Proserpio, D.; Hoffmann, R.; Preuss, P. *J. Am. Chem. Soc.* **1994**, *116*, 9634.

(17) Nishikiori, S.; Ratcliffe, C. I.; Ripmeester, J. A. *Can. J. Chem.* **1990**, *68*, 2270.

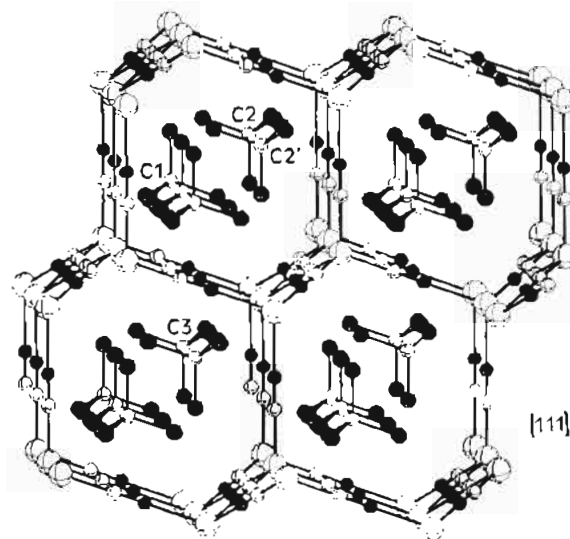
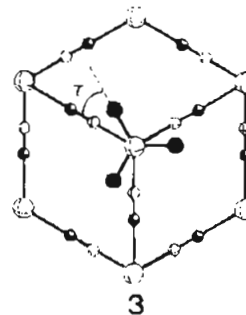


Figure 2. Structure of the $\text{Cd}(\text{CN})_2 \cdot \text{CCl}_4$ clathrate, with full occupation of the adamantanoid units by CCl_4 molecules. Large white spheres represent Cd atoms, small white spheres C atoms, black spheres N atoms, and the gray ones Cl atoms. The short guest \cdots guest distances correspond to $\text{C1} \cdots \text{C2} = \text{C1} \cdots \text{C3} = 5.506 \text{ \AA}$ and $\text{C2} \cdots \text{C2}' = 8.997 \text{ \AA}$.

other cavities resulting from $\text{CdA}_{4-n}\text{B}_n$ tetrahedra, not represented in our model structure, should show intermediate behavior between the C- and N-cavities present in the model structure. In the neopentane clathrate, the guest molecules sit at the centers of the two types of cavities, as shown in Figure 2 for the case of CCl_4 . The C–C bonds are aligned with the local C_3 axes of the adamantanoid units (**2**). The CCl_4 molecules, on the other



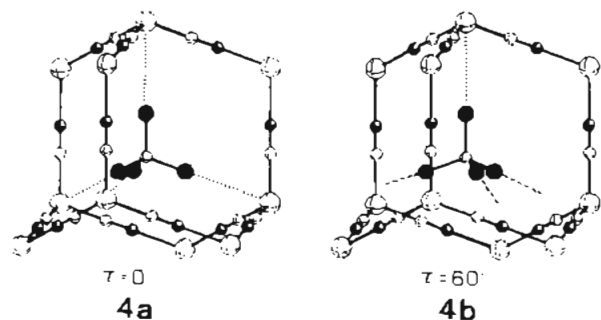
hand, are also sitting at the center of the cavities, but the Cl atoms are disordered around the 3-fold axes. The different behavior of the two guests can be defined by the rotation angle τ , shown in **3** in a projection along z and in a perspective view



for the two extreme orientations: $\tau = 0^\circ$ (**4a**) and $\tau = 60^\circ$ (**4b**).

(18) Nishikiori, S.; Ratcliffe, C. I.; Ripmeester, J. A. *J. Phys. Chem.* **1990**, *94*, 8908.

(19) Hoskins, B. F.; Robson, F. *J. Am. Chem. Soc.* **1990**, *112*, 1546.



For neopentane, a single orientation is found ($\tau = 0^\circ$), whereas several orientations around each trigonal axis are possible for CCl_4 .

Electronic Structure of the $\text{Cd}(\text{CN})_2$ Host Lattice

The electronic structure of the host lattice, as represented by its density of states (DOS), is relatively simple (Figure 3). The occupied levels are associated with the σ and π bonds of the cyanides and with their lone pairs. The lowest unoccupied band (LUB) is built up from the π^*_{CN} orbitals, and the empty levels at ~ 0 eV are centered at the Cd atoms and have $\sigma^*(\text{Cd}-\text{N})$ character. The $\sigma^*(\text{Cd}-\text{C})$ levels fall outside the energy window shown in Figure 3 (between +17 and +30 eV). According to the different atomic contributions to the DOS, the Cd-C and Cd-N bonds are fairly ionic, but the Cd-C bond is less so. This result allows us to distinctly assign the different energy bands to Cd^{2+} or CN^- ions and is important for the modeling of the clathrate needed later for the ab initio calculations.

Interaction between the $\text{Cd}(\text{CN})_2$ Lattice and a CCl_4 Guest

In this section we first discuss the geometrical results of our theoretical study, such as site preference and orientation of the guest. Later we will go into more detail and try to find the orbital basis for the host • • guest interaction. First, we have calculated the energies for the hypothetical clathrate $\text{Cd}_8(\text{CN})_{16} \cdot \text{CCl}_4$, in which only one-eighth of the cavities are occupied by a guest molecule. In that way, N- or C- cavities are selectively occupied and no significant interaction between neighboring guest molecules is present, allowing the interpretation of the results in terms of only host • • guest interactions. Calculations were also carried out for full occupation of the cavities (one guest molecule per Cd atom).

Several conclusions can be drawn from the results of our calculations (Table 1). The enclathration of CCl_4 is more favorable in the N- than in the C- cavities by 0.7 eV (~ 16 kcal/mol). This may be why CCl_4 occupies approximately half of the N- cavities in $[\text{NMe}_4^+ \cdot \text{CCl}_4][\text{CuCd}(\text{CN})_4]$, in spite of the clear preference of the cationic guest NMe_4^+ for the N- cavities in $[\text{NMe}_4][\text{CuCd}(\text{CN})_4]$, in which the C-ones remain empty. If no guest • • guest interactions are considered, the most stable conformations are different at the two types of cavities, with a tiny barrier for rotation in the N-cavity. However, for full occupation of the cavities and considering the simultaneous rotation of all guest molecules, the preferred conformation is the eclipsed one ($\tau = 0^\circ$, 4a) and the barrier for rotation is large. We can therefore conclude that the orientation of the guest molecules is mostly determined by guest • • guest interactions. Nevertheless, partial rotation of the guest molecules ($\tau = 30^\circ$) requires very little energy: if only one type of guest molecules are rotated, a much smaller barrier is calculated (~ 4 kcal/mol for the C-guests, ~ 15 kcal/mol for the N-guests). All these results are consistent with the rotational disorder of

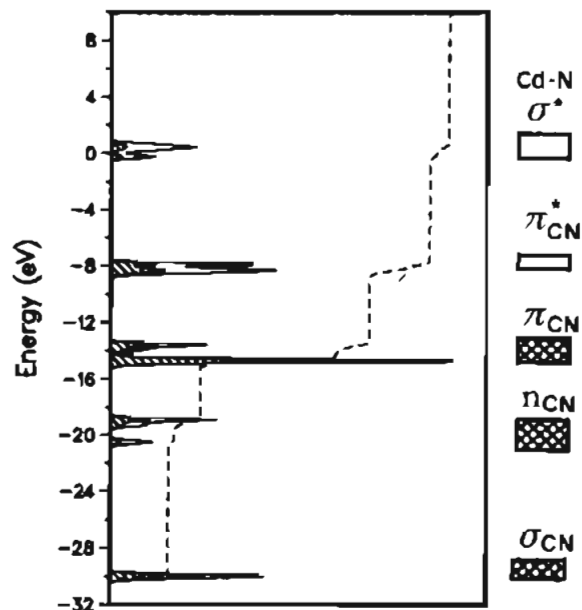


Figure 3. Density of states (DOS) for the $\text{Cd}(\text{CN})_2$ host lattice. The shaded areas indicate the contribution of the C atoms. Shown at right is a block scheme of the bands labeled according to their major contributions. All bands below -12 eV are occupied.

Table 1. Calculated Variations of the One-Electron Energies (EHTB) in the $\text{Cd}(\text{CN})_2 \cdot \text{CCl}_4$ Clathrate upon Rotation of the CCl_4 Molecules (All Energies in kcal/mol of CCl_4)^a

τ (deg)	rotation of CCl_4 molecules				
	one cavity occupied		all cavities occupied		
	N-cavity	C-cavity	N-cavity	C-cavity	all cavities
0	0.0	16.1	0.0	0.0	0.0
30	1.2	11.1			4.2
60	3.2	7.6	1.8	0.5	14.3

^a The values with only one type of cavity occupied (first two columns) were calculated with a Cd: CCl_4 ratio of 8. Those with both types of cavities occupied (last three columns; energies relative to $\tau = 0^\circ$) include guest • • guest repulsions and correspond to one CCl_4 molecule per Cd atom.

the CCl_4 molecules found in the experimental structure. Even if the extended Hückel results should not be trusted in their quantitative aspects, the orbital analysis of the interactions presented below provides a sound basis for some of these qualitative conclusions, showing that they stem from fundamental properties of the system studied and are not mere artifacts of the computational approach used.

The calculated DOS for the $\text{Cd}(\text{CN})_2 \cdot \text{CCl}_4$ clathrate is presented in Figure 4, where the contributions from the guest CCl_4 molecules (shaded areas) appear at the same energies as the molecular orbitals of an isolated CCl_4 molecule. The white areas correspond to the contributions of the $\text{Cd}(\text{CN})_2$ lattice and appear at the same energies as those of the isolated lattice (Figure 3). Apparently, thus, the DOS of the clathrate is just the superposition of the DOS of the two sublattices. But this is just a consequence of the weak nature of the host • • guest interactions that appear hidden among the large number of noninteracting orbitals of the clathrate, and an adequate tool to analyze such interactions is provided by the *crystal orbital displacement* (COD) diagrams¹² (see Appendix for a brief description of the COD functions).

In order to decide which orbitals should be analyzed via their COD diagrams, we look at the integrated values (ICOD) at the Fermi level, $\Omega_i(\mathcal{E}_F)$. These numbers tell us by how much a particular occupied orbital of, e.g., the guest molecules, mixes

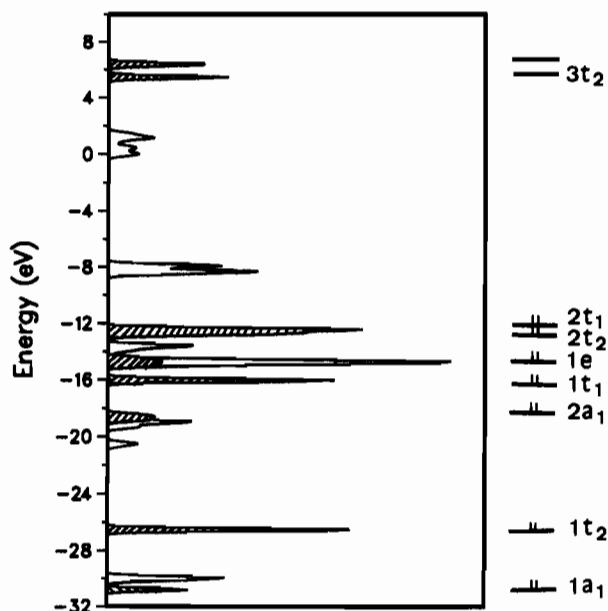


Figure 4. Total density of states (DOS) and CCl_4 contributions (shaded areas) for the $\text{Cd}(\text{CN})_2 \cdot \text{CCl}_4$ clathrate. Shown at right are the MO levels of the isolated CCl_4 molecule.

Table 2. Most Significant Values of the Integrals of the COD Functions Up to the Fermi Level, $\Omega_i(\mathcal{E}_F)$, for the Molecular Orbitals of CCl_4 in the $\text{Cd}(\text{CN})_2 \cdot \text{CCl}_4$ Clathrate^a

mol orbital	N-guest		C-guest	
	$\tau = 0^\circ$	$\tau = 60^\circ$	$\tau = 0^\circ$	$\tau = 60^\circ$
1a ₁	-8	-3	-7	-2
1t ₂	-84	-24	-63	-18
2a ₁	-133	-38	-83	-28
1t ₁	-240	-68	-150	-50
1e	-2	-22	-12	-16
2t ₂	-345	-130	-279	-105
2t ₁	-15	-15	-66	-34
3t ₂	+1	+1	+3	+2
3a ₁	+1	+1	+1	+1
total	-825	-298	-656	-250

^a Notice that CCl_4 molecules in N- or C-cavities present different values. Results are given for the two extreme rotamers of the guest molecules.

with all the empty orbitals of the host sublattice. The most significant values are presented in Table 2. The first important point to note is that the integral over all the orbitals of CCl_4 is negative, indicating that there is mostly mixing of its occupied orbitals with empty levels of the host sublattice. The positive values for the high-energy orbitals of CCl_4 are all negligible. Only three sets of molecular orbitals, 2a₁, 1t₁, and 2t₂ (symmetry-adapted combinations of the lone-pair orbitals of the Cl atoms), are responsible for most of the host••guest interaction (between 73 and 87%) regardless of the type of cavity and the rotation angle. Only these lone-pair orbitals point outward, toward the Cd atoms of the host sublattice, whereas the remaining lone-pair orbitals, 1e and 2t₁, do not have the appropriate topology and do not significantly interact with the host. The host••guest interaction is stronger for the eclipsed conformation ($\tau = 0^\circ$) in the two different cavities, confirming that the choice of orientation of the guest molecule found above does not depend only on the host••guest interactions.

Having identified the CCl_4 orbitals involved in the host••guest interaction, we now attempt to determine with which host orbitals they interact. To that purpose we plot the COD diagrams for the 2a₁ orbital and for one orbital of each degenerate set, 1t₁ and 2t₂, of the CCl_4 molecule in the N-

(Figure 5) and C-cavities (Figure 6). In the N-cavity only one intense peak appears at ~ 0 eV, in the region of the $\sigma^*(\text{Cd}-\text{N})$ band of the host (see Figure 3), indicating that the host••guest interaction can be described as occurring between lone-pair orbitals of CCl_4 (2a₁, 1t₁, and 2t₂) and the empty orbitals of the Cd^{2+} ions with $\sigma^*(\text{Cd}-\text{N})$ character.²⁰ The COD diagrams for the same orbitals of the guest molecules in C-cavities (Figure 6) show peaks at four different energies: one of them (at -9 eV) corresponds to interaction with the π^*_{CN} orbitals of the host; the three remaining peaks (between +20 and +30 eV) result from interaction with different $\sigma^*(\text{Cd}-\text{C})$ orbitals of the host.

The different interactions of the guest molecules in the two types of cavities can be easily understood. The fact that interaction with π^*_{CN} is important at the C-cavity but irrelevant at the N-cavity stems from the larger contribution of the carbon atom to this molecular orbital. Since there are two perpendicular π^*_{CN} orbitals at every cyanide, these can follow the rotation of the CCl_4 molecule without a dramatic loss of interaction. This might explain why the interaction is much more affected by rotation of CCl_4 in the N- than in the C-cavity (Table 2). The other empty orbitals of the host lattice available for interaction with CCl_4 are the atomic orbitals of the Cd^{2+} ions, bearing Cd-N or Cd-C σ^* character. Of these, only $\sigma^*(\text{Cd}-\text{N})$ levels are available in the N-cavity, but only $\sigma^*(\text{Cd}-\text{C})$ orbitals in the C-cavity. Given the much lower energy of the former, its energy match with the chlorine lone pairs is much better. Consequently, the host••guest interaction associated with the σ^* orbitals is more favorable at the N-cavity, as seen in Table 2. Now it becomes obvious that the orientation in which the C-Cl bonds are aligned with the Cd atoms ($\tau = 0^\circ$, 4a) is the most favorable one for host••guest interaction.

Given such simple orbital description of the host••guest interaction, one should expect that enclathration would affect in predictable ways the strengths of the different bonds of the two sublattices. Partial occupation of σ^* orbitals should result in a weakening of the Cd-N (or Cd-C) bonds in the N-cavity (C-cavity) upon enclathration. Likewise, electron density donation to the π^*_{CN} orbital should result in a slight weakening of the CN bond. Finally, the 2a₁, 1t₁, and 2t₂ orbitals of CCl_4 incorporate some C-Cl bonding character and such bonds should appear somewhat weaker after electron donation to the host lattice. All these qualitative expectations are reflected in the calculated overlap populations for the different bonds (Table 3). The changes to be expected in bond strengths are indeed small and might be detectable in the vibrational spectra,¹² but these have not been reported. Due to the disorder found in the structural determination for the clathrate, it is not possible to identify individual bond lengths, but the Cd-CN-Cd distance is well-known for both the isolated $\text{Cd}(\text{CN})_2$ and the clathrate. The different bonds of the host lattice are expected to be elongated to varying degrees upon enclathration (Table 3), and the Cd-CN-Cd distance is expected to be longer in the clathrate than in $\text{Cd}(\text{CN})_2$. The experimental values of 5.505(1) and 5.460(1) Å for the clathrate and the host, respectively, are thus consistent with our calculations. Of course, the slight expansion of the host lattice upon enclathration can be attributed to a steric origin. We think that the steric effects are implicit

(20) The small peak at ~ 4 eV is not indicative of a host••guest interaction, but is an artifact of the model used. Since the guest molecules have less symmetry in the clathrate than free carbon tetrachloride, other orbitals mix with 1t₁ and 2t₂ on lowering the symmetry, thus giving a small peak in the COD curves. Before making an assignment of a COD peak to the interaction between a host orbital and a guest orbital, one must check that a peak also appears in the COD diagram of the host orbitals at the energy corresponding to the guest orbital.

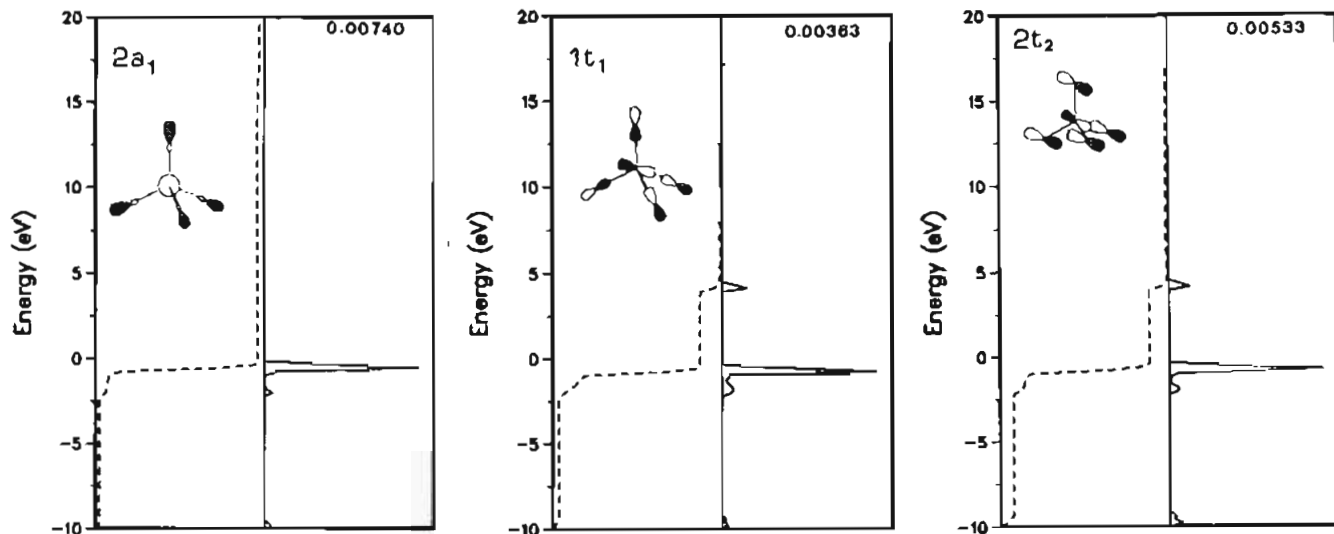


Figure 5. Crystal orbital displacement (COD, solid line) and integrated COD (dashed line) curves for the $2a_1$ and one of the $1t_1$ and $2t_2$ orbitals of the CCl_4 molecules upon intercalation at the N-cavities in $\text{Cd}(\text{CN})_2 \cdot \text{CCl}_4$ with an orientation of $\tau = 0^\circ$. The scale for the COD curves is indicated in the upper right corner of each diagram.

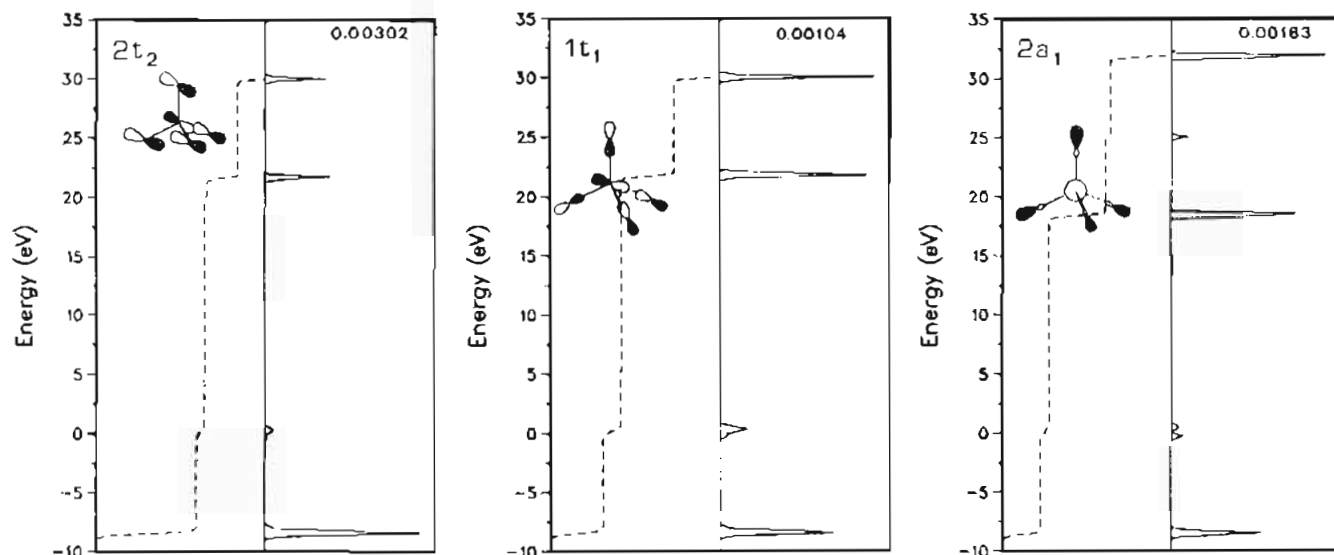


Figure 6. Crystal orbital displacement (COD, solid line) and integrated COD (dashed line) curves for the $2a_1$ and one of the $1t_1$ and $2t_2$ orbitals of the CCl_4 molecules upon intercalation at the C-cavities in $\text{Cd}(\text{CN})_2 \cdot \text{CCl}_4$ with an orientation of $\tau = 0^\circ$. The scale for the COD curves is indicated in the upper right corner of each diagram.

Table 3. Calculated Variations of the Overlap Populations for the Bonded Atoms Produced upon Formation of the Clathrate $\text{Cd}(\text{CN})_2 \cdot \text{CCl}_4$

bond	N-cavity		C-cavity	
	$\tau = 0^\circ$	$\tau = 60^\circ$	$\tau = 0^\circ$	$\tau = 60^\circ$
Cd–C	0	–0.0004	–0.0048	–0.0004
Cd–N	–0.0055	–0.0018	+0.0002	–0.0002
C–N	–0.0001	–0.0001	–0.0008	–0.0003
C–Cl	–0.0038	–0.0010	–0.0025	–0.0010

in our calculations, since the size of the CCl_4 molecule is given by the spread of its outermost electrons, which are essentially the Cl lone pairs. Likewise, the size of the cavity is given by the valence electron cloud of the host lattice. Changes in the size of the cavity are performed related to changes in the electron density of the host, and changes in internuclear distances are intimately tied to changes in electron density distribution.

An analysis of the COD diagrams for the neopentane clathrate indicates that the main interactions in this case appear between the occupied π_{CN} orbitals of the host and the $\sigma^*(\text{C}-\text{H})$ orbitals

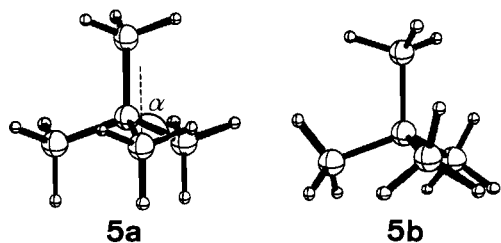
of the guest, analogous to one of the interactions present in the Hofmann clathrates.¹² This interaction may be described as a weak hydrogen bond. It is noteworthy that the host lattice acts as an acceptor toward CCl_4 but as a donor toward CMe_4 . Such ambivalent behavior of the $\text{Cd}(\text{CN})_2$ sublattice could probably explain the existence of two such interpenetrated networks in the cuprite structure of $\text{Cd}(\text{CN})_2$.

Ab Initio MP2 Study of Bimolecular Models

The size of the unit cell of the clathrates excludes presently the possibility of carrying out a periodic calculation at the Hartree–Fock level or beyond. Therefore we have chosen to study discrete bimolecular models of the clathrates, in an attempt to verify the qualitative conclusions based on the EHTB calculations and to obtain semiquantitative estimates of some relevant contributions to (a) the interaction energies and (b) the relative stabilities of the different orientations of the guest molecules. These calculations have been carried out by performing ab initio calculations with a second-order Møller–Plesset treatment of the electron correlation (see Appendix for computational details).

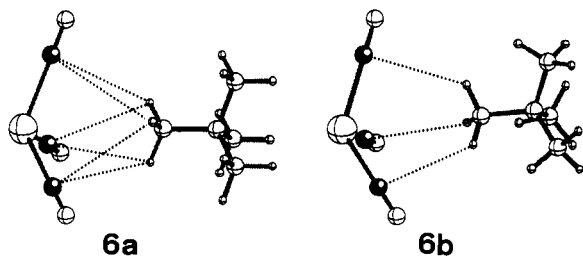
Host · · Guest Models. According to the above results, the smallest systems needed to model the host · · guest interactions occurring in the extended structure must include one CX_4 molecule and a $[Cd(CN)_3]^-$ fragment (**6**). Omitting the Cd atom from the model results in unreasonably high values of the host · · guest interaction energies (in excess of 34 kcal/mol per CX_4 molecule, compared to less than 8 kcal/mol when Cd is considered). On the other hand, considering a full $[Cd(CN)_4]^{2-}$ unit would represent better the host part of the electronic structure. Check calculations using this larger model show that the effect of the fourth cyanide ion might be important at the quantitative level (Table 4), but can be left out of the calculations without affecting the qualitative and semiquantitative conclusions, making the calculations affordable. Therefore, we chose the bimolecular systems $X_3CX \cdot \cdot [Cd(NC)_3]^-$ ($X = Cl, Me$) as models for the host · · guest interactions in the N-cavities, and $X_3CX \cdot \cdot [Cd(NC)_3]^-$ for the C-cavities, with the geometries fixed at the experimental structure of the clathrates. Note that such models mimic the interactions at $\tau = 0^\circ$.

In the structure of the $Cd(CN)_2 \cdot CMe_4$ clathrate, determined from its X-ray diffraction data, the CCl_4 skeleton of the guest molecule has been found to present an eclipsed conformation ($\tau = 0^\circ$) but the hydrogen atoms have not been located. However, the neopentane molecule has been found experimentally^{21,22} to present the staggered structure (**5a**), and a theoretical



study²³ found it to be more stable than the eclipsed one (**5b**). Our calculations also predict the staggered structure to be more stable than the eclipsed one by 25.4 and 27.9 kcal/mol at the EHTB and MP2 (using a 6-31+G* basis set) levels, respectively. We have therefore adopted the staggered conformation **5a** for the enclathrated molecule in the sequel.

For the case of neopentane, we have used two different models, considering two different conformations of the methyl group facing the $[Cd(CN)_3]^-$ unit: in one (staggered model **6a**),



the C–H bonds are staggered with respect to the Cd–C bonds and the neopentane molecule is also staggered (as in **5a**); in the other model (eclipsed model **6b**), the C–H bonds are eclipsed to the Cd–C bonds and the four methyl groups are also in the eclipsed conformation (as in **5b**). This latter model has been chosen to simulate the relative orientation of the methyl groups and the cyanides in the case $\tau = 60^\circ$ (**4b**). One must

Table 4. Total (E_{tot}) and Interaction Energies (E_{int} , Corrected for the BSSE) for the Bimolecular Models of the Host · · Guest and Guest · · Guest Contacts, Calculated at the Hartree–Fock (HF) and Second-Order Moeller–Plesset (MP2) Levels^a

	E_{tot} (hartrees)		E_{int} (kcal/mol)	
	HF	MP2	HF	MP2
Host · · Guest				
$Cl_3CCl \cdot \cdot [Cd(NC)_4]^{2-}$	-2291.6257	-2293.5095	+0.01	-2.07
$Cl_3CCl \cdot \cdot [Cd(CN)_4]^{2-}$	-2291.5792	-2293.5229	-0.79	-4.03
$Cl_3CCl \cdot \cdot [Cd(NC)_3]^-$	-2199.3046	-2200.8971	+1.89	-0.12
$Cl_3CCl \cdot \cdot [Cd(CN)_3]^-$	-2199.3062	-2200.9474	+1.80	-0.82
$Me_3CMe \cdot \cdot [Cd(NC)_3]^-$ (staggered, 6a)	-519.8867	-521.4751	+0.18	-1.51
$Me_3CMe \cdot \cdot [Cd(NC)_3]^-$ (eclipsed, 6b)	-519.8417	-521.4315	-0.12	-1.99
$Me_3CMe \cdot \cdot [Cd(CN)_3]^-$ (staggered, 6a)	-519.8880	-521.5246	+0.36	-1.56
$Me_3CMe \cdot \cdot [Cd(CN)_3]^-$ (eclipsed, 6b)	-519.8431	-521.4809	+0.04	-2.00
Guest · · Guest				
$CCl_4 \cdot \cdot CCl_4$ (staggered)	-3751.4943	-3752.8410	+0.24	-0.73
$CCl_4 \cdot \cdot CCl_4$ (eclipsed)	-3751.4940	-3752.8413	+0.46	-0.58
$CMe_4 \cdot \cdot CMe_4$ (staggered)	-392.6525	-392.9936	+0.72	-0.70
$CMe_4 \cdot \cdot CMe_4$ (eclipsed)	-392.6517	-393.9934	+1.28	-0.32

^a The notation “eclipsed” and “staggered” corresponds to the relative orientation of the methyl C–H bonds and the Cd–X ($X = C, N$) bonds in the host · · guest calculations and to the relative orientation of two neighboring tetrahedra (**6**) in the guest · · guest calculations.

keep in mind that these models are rather crude, since the cyanides which are bridging in the host structure are considered here as terminal, and only the interaction of one X group of the CX_4 molecules with its environment is taken into account.

The results of our calculations on the models for the host · · guest interactions in the CX_4 clathrates ($X = Cl, Me$) are presented in Table 4. The first thing to note is that all interactions are attractive when electron correlation is taken into account (MP2 results). Considering that every guest molecule interacts with four neighboring $Cd(CN)_3$ units, the interaction energies given in Table 4 must be multiplied by 4 to obtain a rough estimate of the interaction energy per formula unit. The preference for the N-cavity found with the EHTB calculations is now reversed, and the C-cavity is predicted to be more stable for CCl_4 . The MP2 level of computation used for the model chosen is far more rigorous than the EH band calculations, but the model extracted from the extended structure is probably oversimplified. In a previous work,¹⁴ it was found that the interaction of the C-end of the cyano group with a benzene molecule is 3–5 kcal/mol more stabilizing than that of the HCN molecule with benzene in the same relative orientation. This is probably due to the fact that the cyanide orbitals centered at the carbon atom are readily available for intermolecular interactions in the case of CN^- , but not so in HCN or in bridging cyanides. Since there is a clear orbital reason for the N-cavity preference predicted by the EHTB calculations, supported by experimental evidence discussed above, it might well be that in this case the MP2 calculations are not giving the right result because of the poor quality of the molecular model used to simulate a solid. The present results are therefore not conclusive as to the preference of the guest for the N- or C- cavities.

For the neopentane case, the present model MP2 calculations for either a staggered or an eclipsed arrangement (**6a** or **6b**)

(21) Bartel, L. S.; Bradford, W. F. *J. Mol. Struct.* **1977**, *37*, 113.

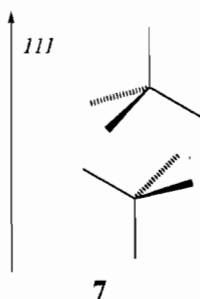
(22) Beagley, B.; Brown, D. P.; Monhagen, J. J. *J. Mol. Struct.* **1969**, *4*, 233.

(23) Guth, J. R.; Hess, A. C. *Chem. Phys.* **1988**, *124*, 29.

predict stronger host • • guest interactions than for CCl_4 at both cavities. The interaction is stronger for eclipsed $\text{Cd}-\text{X}$ ($\text{X} = \text{C}, \text{N}$) and $\text{C}-\text{H}$ bonds of the proximal methyl group, thus confirming the importance of hydrogen bonding for the host • • guest interaction in this case. Even if the interaction energy is somewhat larger for the eclipsed model (**6b**), this is not sufficient to overcome the preference of neopentane for the staggered conformation, which remains the most stable after interaction with the $\text{Cd}(\text{CN})_3^-$ fragment (Table 4). However, these results must be taken cautiously, given the limitations of the bimolecular model used.

Guest • • Guest Models. The guest • • guest interactions are more difficult to model, since different pieces of the host lattice intrude between neighboring guest molecules, depending on the crystallographic direction and the rotation angle τ . We have chosen to study the interaction between two neighboring CX_4 molecules along the crystallographic (111) direction in which no intervening host atoms exist and present the shortest guest • • guest distance (see Figure 2).

If all the guest molecules have the same orientation, as defined by the angle τ , the neighbors along the (111) direction are oriented face to face, with a rotated conformation (**7**). The



eclipsed guest • • guest conformation is only found if the guests in one type of cavities are rotated with respect to the surrounding adamantanoid skeleton ($\tau = 60^\circ$), while those in the other type of cavities are eclipsed ($\tau = 0^\circ$).

The results of our calculations for $(\text{CCl}_4)_2$ and $(\text{neopentane})_2$ (Table 4), indicate that such interactions are weakly attractive and favor a structure in which the guest molecules are staggered along the c direction; i.e., they must have all the same rotation angle τ , in agreement with the experimental structures. The different behavior of CCl_4 should then be attributed to the different rotation angles preferred by the molecules in the C- and N-cavities as imposed by the host • • guest interaction.

Appendix: Computational Aspects

Extended Hückel tight-binding band calculations^{24,25} were carried out using the modified Wolfsberg–Helmholz formula²⁶ on the host, guest, and clathrate lattices under discussion, including up to 176 atoms

and 418 valence atomic orbitals per unit cell. Standard atomic parameters were used for C, H, and O.¹⁶ For Cd, the atomic parameters were taken from previous work, with no 4d orbitals included in the basis set.²⁷ COD and ICOD functions were calculated from DOS obtained by averaging throughout the irreducible edge of the Brillouin zone, using meshes of 120K points. For the MP2 calculations we used a 6-31+G* basis set for C, N, Cl, and H. Hay and Wadt's "large-core" pseudopotentials²⁸ and the Dunning–Huzinaga D95V double- ζ basis set for the valence orbitals²⁹ were used for Cd. The interaction energies were calculated by using the counterpoise method³⁰ to correct for the basis set superposition error.

The experimental structure of the host lattice in $\text{Cd}(\text{CN})_2 \cdot \text{CCl}_4$ was used throughout,⁴ and the experimental data for $\text{Cd}(\text{CN})_2 \cdot \text{CCl}_4$ and $\text{Cd}(\text{CN})_2 \cdot \text{CMe}_4$ were used for the structure of the guest molecules.

COD Functions. The crystal orbital displacement function¹² for a given molecular orbital of the guest molecule at a given energy $\Delta_i(\mathcal{E})$ corresponds to the number of levels shifted in the clathrate relative to the free molecule and is defined as

$$\Delta_i(\mathcal{E}) = n_i^C(\mathcal{E}) - n_i^G(\mathcal{E})$$

where n_i^C is the contribution of the i th molecular orbital to the density of states of the clathrate and n_i^G its contribution to the DOS of the isolated guest molecules. Hence, positive values of $\Delta_i(\mathcal{E})$ indicate the existence of levels at the particular energy \mathcal{E} in the clathrate that appear at different energy values in the free molecule. Inversely, negative values indicate that some molecular levels have been wiped out by interaction with the host lattice.

The integral of the COD function $\Omega_i(\mathcal{E})$ also provides relevant information. In particular, its value at the Fermi level, $\Omega_i(\mathcal{E}_F)$, gives a numerical indication of the direction and the degree of charge transfer between host and guest. Mixing of an occupied MO of the guest molecule with empty levels of the host (guest to host charge transfer) results in a negative value of $\Omega_i(\mathcal{E}_F)$, whereas the mixing of an empty MO of the guest with occupied levels of the host (host to guest charge transfer) gives a positive value.

Acknowledgment. Financial support to this work was provided by the DGICYT through Grant PB92-0655. Computer resources in the Centre de Supercomputació de Catalunya (CESCA) were made available to the authors through a grant from Fundació Catalana per a la Recerca. The authors are grateful to P. Alemany for suggestions and enlightening discussions and to F. Vilardell for expert help with the drawings.

IC950523L

- (24) Whangbo, M.-H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 6093.
- (25) Whangbo, M.-H.; Hoffmann, R.; Woodward, R. B. *Proc. R. Soc. London, Ser. A.* **1979**, *366*, 23.
- (26) Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686.
- (27) Alemany, P.; Alvarez, S. *Solid State Commun.* **1992**, *83*, 447–450.
- (28) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270.
- (29) Dunning, T. H.; Hay, P. J. *Modern Theoretical Chemistry*; Plenum: New York, 1976; pp 1–28.
- (30) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 270.