Host···Guest Interactions in the Pyrrole and Aniline Hofmann Clathrates. A Theoretical Study

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Extended Hückel tight binding (EHTB) band calculations are reported for the Hofmann clathrates $Ni(NH_3)_2Ni$-$(CN)_4·2G$ (G = pyrrole or aniline) and $Ni(en)Ni(CN)_4·2C_6H_6$ (en = ethylenediamine). The *crystal orbital displacement* (COD) and *integrated crystal orbital displacement* (ICOD) functions were used to detect the nature of the interacting orbitals and to study the role of the different building blocks of the host lattice in the host···guest interaction. The main orbital interactions identified correspond to electron density donation from the π system of the guest molecules to empty orbitals of the host lattice, mostly $\sigma^*(N-H)$, and from the $\pi(C-N)$ orbitals of the host to the $\sigma^*(C-H)$ orbitals of the guest, with no significant participation of the transition metal atoms. Changes in bond distances of the host and guest sublattices and variations of vibrational frequencies, such as CN and N−H stretches of the host lattice produced by enclathration are correlated with variations in the calculated overlap populations, accounting for the axial elongation of the pyrrole guest molecule, in contrast to the compression predicted for benzene.

The Hofmann clathrates, first prepared in 1897 by Hofmann and Küspert,[1−4] have the general formula[5,6] $M(NH_3)_2M'$-$(CN)_4·2G$, with M = Mn, Fe, Co, Ni, Cu, Zn, or Cd; M′ = Ni, Pd, or Pt; and G = benzene, pyrrole, thiophene, dioxane, aniline, or biphenyl.[7] These compounds have been the subject of a large number of experimental studies because of the selectivity shown toward different potential guests, as well as for the stereochemical preferences of the enclathrated molecules. In recent papers,[8,9] we presented theoretical studies on the orbital nature and the energetics of the host···guest interactions in the archetype of the Hofmann clathrates, $Ni(NH_3)_2Ni(CN)_4·2C_6H_6$. These studies showed that a good qualitative description of the host···guest interactions can be obtained through band calculations within the extended Hückel tight binding (EHTB) formalism, which accounts for structural and spectroscopic changes associated with enclathration and for substituent effects. In this paper we extend our previous studies to different guest molecules (pyrrole and aniline), and to a modified host lattice in which two NH_3 groups are substituted by an ethylenediamine molecule.

Crystal Structure of the Hofmann Clathrates. The Hofmann clathrates consist of a host lattice of amminated nickel cyanide formed by $Ni(CN)_2(NH_3)$ layers (**1**) and guest molecules occupying the approximately cubic cavities formed by the host lattice. A three dimensional perspective of the structure showing the layers and enclathrated benzene molecules is shown in Figure 1. In the host lattice there are two nonequivalent sets of Ni atoms. One of them, Ni_C, is tetragonally coordinated by the carbon ends of the cyano ligands. The nitrogen ends of the

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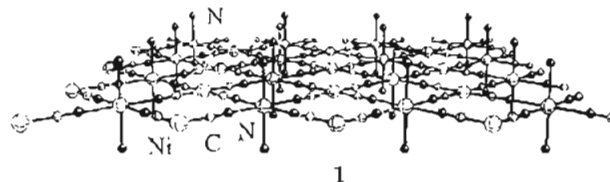
cyano groups are bound to another set of Ni atoms (Ni_N), which complete a pseudooctahedral coordination sphere by linking two NH_3 ligands at the axial positions. The separation between layers clearly depends on the size of the guest molecule,[6] but not every aromatic molecule is enclathrated: toluene and xylene are examples of simple benzene derivatives which do not form Hofmann clathrates with the nickel−ammonia host lattice. The reason for this is probably not merely steric, since larger molecules such as biphenyl have been enclathrated.[7,10] The interlayer separation *c*, on the other hand, is not significantly altered when Ni_C or Ni_N atoms are substituted by metal atoms of different sizes.[11]

As far as the guest molecule is concerned, it is practically always found in the middle of the interlayer cavities. Its orientation relative to the host sublattice is in most cases found to deviate from the most symmetrical orientations ($\varphi = 0°$ or $\varphi = 90°$, Figure 1) and correspond to angles $\varphi \approx 60°$ (Table 1). In such an orientation, the plane of the guest molecule is pointing approximately toward the carbon atoms of the cyano groups. Iwamoto and co-workers[12] have increased the number of families of inclusion compounds related to the Hofmann clathrates by substituting other amines for the ammonia groups. Typically, bidentate amines $NH_2-(CH_2)n-NH_2$ (e.g., ethylenediamine, *en*, or hexanediamine) or hydroxylamines, such as monoethanolamine (*mea*)[13−17] have been employed as ligands,

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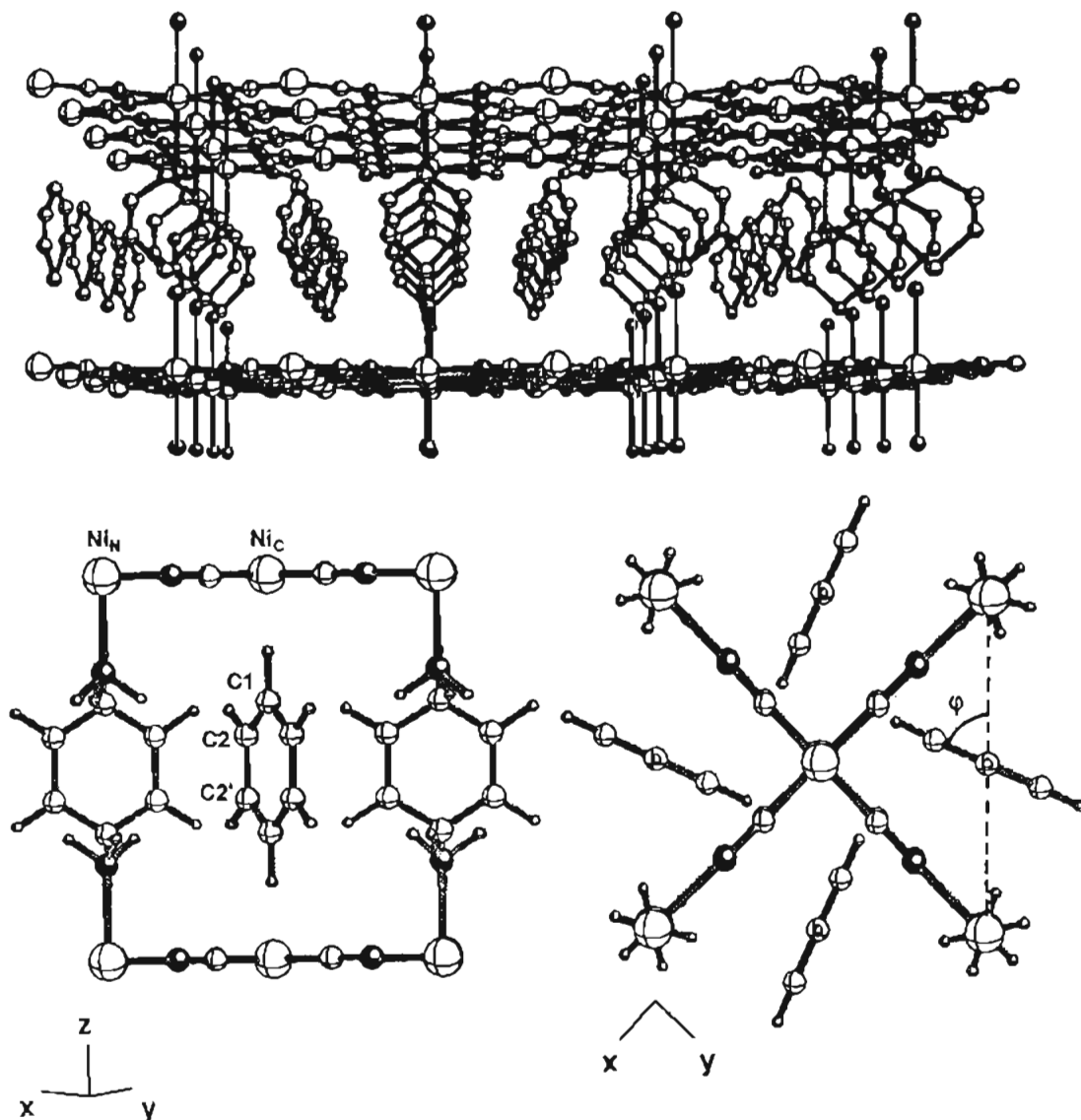(15) Nishikiori, S.; Iwamoto, T. *Chem. Lett.* **1983**, 1129.

Figure 1. Perspective view and two projections of the structure of the Hofmann clathrates of the type $M(NH_3)_2M'(CN)_4 \cdot 2C_6H_6$. Black balls represent nitrogen atoms, large white balls nickel atoms, and small white balls carbon atoms.

Table 1. Experimental Orientation of the Guest Molecules in Hofmann Clathrates of the Type $M(B)_2Ni(CN)_4 \cdot 2G$, Where the Orientation Angle φ is defined in Figure 1

M	B	G	φ (deg)	refs
Ni	NH_3	C_6H_6	65.9	14, 16
Cd	NH_3	C_6H_6	58.5	14
Cd	NH_3	C_6H_6	67.7	19
Mn	NH_3	C_6H_6	66.5	14
Cu	NH_3	C_6H_6	64.3	18
Cd	en	C_6H_6	90	21
Cd	en	C_4H_5N	90	22
Cd	NH_3	dioxane	46.3	23
Cd	mea	C_6H_6	90	24

thus allowing one to fine-tune the interlayer distance and to modify the size of the cavities.[18,19] It is in these cases that clearly different values of φ have been found (~90°, Table 1), due probably to steric interactions.

In the following sections we will examine the interactions of the host lattice $Ni(NH_3)_2Ni(CN)_4$ with two different guest

molecules—pyrrole and aniline—and compare the results with those previously reported for the benzene guest.[8] Then, we will analyze the interaction between an ethylenediamine-containing host lattice and the benzene guest in the $Ni(en)Ni(CN)_4 \cdot 2C_6H_6$ clathrate. The interaction of the tetrahedral host lattice Cd-$(CN)_2$ with nonaromatic molecules will be discussed elsewhere.[20] For our theoretical study we use extended Hückel tight-binding (EHTB) calculations and the derived *crystal orbital displacement* (COD) curves. The computational details and a brief introduction to the COD curves are presented in the Appendix.

Electronic Structure of the Host Lattice, $Ni(NH_3)_2Ni(CN)_4$. Let us briefly summarize the main aspects of the electronic structure of the host sublattice[8] $Ni(NH_3)_2Ni(CN)_4$. Its total density of states (DOS) is presented in Figure 2, together with block band diagrams for the contributions of the different building blocks: the cyanide ions, the ammonia ligands, the tetragonally coordinated Ni atom (Ni_C) and the octahedrally

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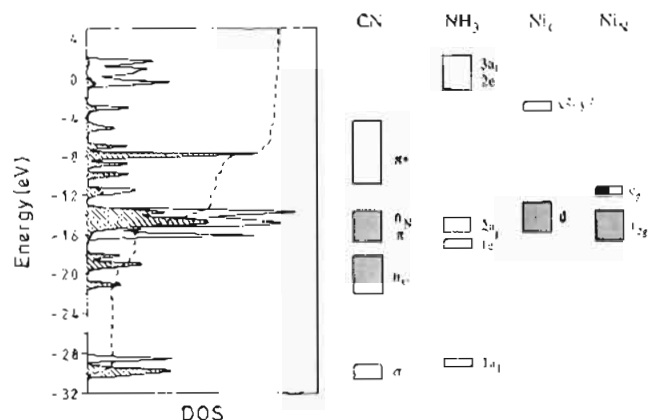
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Figure 2. Left: Total density of states of the host lattice $Ni(NH_3)_2$-$Ni(CN)_4$, with the contributions of the cyanide groups represented by the shaded areas. Right: Block representation of the band levels associated with each fragment—cyano (CN) and ammonia ligands (NH_3), carbon-bound nickel atom (Ni_C), and nitrogen-bound nickel atom (Ni_N). The highest occupied band, at *ca.* −12 eV, is half occupied.

coordinated Ni atom (Ni_N). The shaded blocks represent occupied bands. The e_g-like band of Ni_N is half-occupied, according to the magnetic behavior of such systems.[25]

How does the electronic structure of the host sublattice change upon enclathration of benzene and formation of $Ni(NH_3)_2Ni$-$(CN)_4 \cdot 2C_6H_6$? The analysis of the COD (*crystal orbital displacement*) diagrams showed[8] that the most important orbital interactions are those between the occupied π orbitals of benzene, $1a_{2u}$ and $1e_{1g}$, and empty orbitals of the host lattice, notably the $\sigma^*(N-H)$ orbitals of the NH_3 groups. Relevant interactions occur also between the occupied π-orbitals of the cyano groups and the empty $\sigma^*(C-H)$ orbitals of benzene. These results have been confirmed through ab initio MP2 calculations on bimolecular complexes,[9] and are consistent with the existence of numerous reports of C···HN, CH···N, and CH···O hydrogen bonds.[26-28] The changes produced by enclathration in the bond lengths and vibrational spectra of both the host and the guest sublattices are consistent with the calculated variations in overlap populations and fragment orbital occupations.

The Clathrate of Pyrrole, $Ni(NH_3)_2Ni(CN)_4 \cdot 2C_4H_5N$

In this section we report on our theoretical study of the effect of substituting a pyrrole guest for benzene. Although the structure of the pyrrole clathrate $Ni(NH_3)_2Ni(CN)_4 \cdot 2C_4H_5N$ has not been solved, the unit cell parameters have been determined.[25] Hence, we will keep the host lattice the same as in the benzene clathrate, adjusting the interlayer distance to the c parameter of the pyrrole clathrate, obtained from X-ray powder diffraction data. For the pyrrole molecule, we use its geometry in the Cd-(en)$Ni(CN)_4 \cdot 2C_4H_5N$ clathrate,[29] since the structures of the guest molecules are not substantially modified when ethylenediamine is substituted for NH_3, as observed for the case of benzene.[22,30]

Even if no structural data is available for comparison, it might be worth commenting on the orientation and internal rotation of the pyrrole molecule, since previous EHTB calculations[8] have
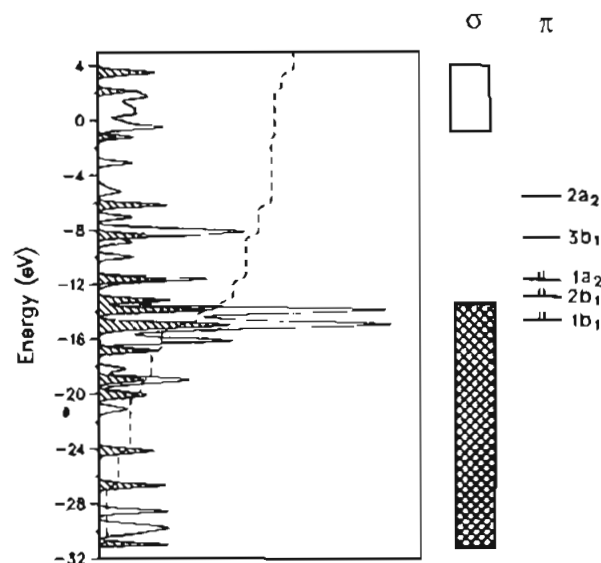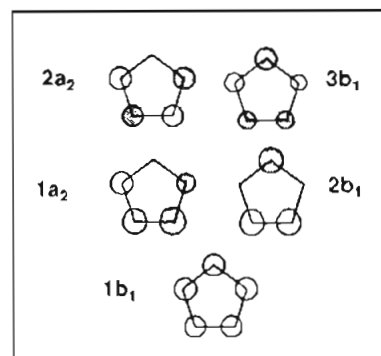
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Figure 3. Molecular orbitals of pyrrole (right) and their contributions to the DOS of the Hofmann clathrate $Ni(NH_3)_2Ni(CN)_4 \cdot 2C_4H_5N$ (left, shaded curve). All the bands above −11 eV are empty.

proved to reproduce very well the orientation of the benzene molecule in the corresponding Hofmann clathrate. The optimum rotation angle is calculated to be $\varphi = 72°$, a bit larger than for benzene, probably indicating weaker guest···guest interaction, due to the smaller size of the pyrrole ring. However, the calculated barrier for rotation around the c-axis is quite small (2 kJ/mol) in this case, compared to that of benzene (16 kJ/mol). Difficulties in solving the structure of this clathrate might therefore be associated with orientational disorder, including the possibility of aligning the pyrrole molecule with the nitrogen atom in one of two alternative directions, i.e., with the nitrogen atom of the pyrrole pointing upward or downward.

Interaction between Pyrrole and the Host Lattice. In Figure 3 we show the DOS of the pyrrole clathrate, as well as the molecular orbitals of the isolated pyrrole molecule. The $1a_2$ band of pyrrole (corresponding to an occupied MO of the free molecule) is superimposed on the partially occupied e_g bands of the octahedral metal atom (at −11.5 eV). The pyrrole clathrates show anomalous values of their magnetic moments, as in the Cu compound, for which $\mu_{eff} = 2.5\ \mu_B$,[25] in contrast with an expected value for a d^9 ion of 1.7 μ_B. Maybe these anomalies are related to the superposition of these bands, but we cannot rule out that this result is an artifact of the EH parametrization. To avoid the artificial emptying of the pyrrole $1a_2$ band, we have used a rigid band model, keeping the atomic parameters of Ni, but filling its d orbitals to give the d^{10} configuration appropriate for the Cd compound. Let us recall that both experimental data and our previous calculations show that the structural parameters are insensitive to the electron configuration of the octahedral metal atom.

Table 2. Values of the ICOD Functions of Molecular Orbitals of Pyrrole at the Fermi Level, $\Omega_i(\mathscr{E}_F)$ ($\times 10^4$) in the Clathrate Ni(NH)$_3$Ni(CN)$_4$·2C$_4$H$_5$N, in Increasing Order of Energy[a]

| pyrrole occupied orbitals		pyrrole empty orbitals	
lowest σ orbitals [7]	−9	3b$_1$ (π)	4
1b$_1$ (π)	−13	2a$_2$ (π)	4
5b$_2$	0	10a$_1$	8
6b$_2$	−6	remaining σ^* orbitals [9]	26
9a$_1$	−4		
2b$_1$(π)	−12		
1a$_2$ (π)	−22		

[a] Number of orbitals given in brackets.

In order to analyze the host· ·guest interactions we have calculated ICOD functions for a model clathrate with only one pyrrole molecule per unit cell; their values at the Fermi level are shown in Table 2. As in the case of benzene, the most important individual interactions involve the π system of the aromatic molecule, mainly through the occupied π orbitals 1b$_1$, 2b$_1$ and 1a$_2$. On the other hand, the largest amount of charge transfer from the hsot to the empty orbitals of the guest corresponds to the combined interaction with several pyrrole σ^* orbitals. Of these, the most relevant one is the 10a$_1$ orbital, centered at the pyrrole N atom and of N−H antibonding character.

Once we have identified some orbitals relevant for the host· ·guest interaction, let us look in more detail at the orbital interactions. For that purpose, we represent in Figure 4 the COD curves for the three occupied π orbitals of pyrrole (1b$_1$, 2b$_1$ and 1a$_2$). These are similar to the COD curves of benzene,[8] the most intense peak in the region between −1 and 3 eV being that of the 2e$^+$ orbitals of NH$_3$ (**2b**). In summary, all this reveals

a
b
c

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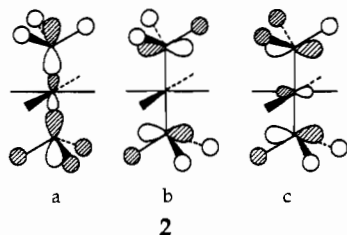
a weak donor−acceptor interaction from the occupied π orbitals of pyrrole (1b$_1$, 2b$_1$, and 1a$_2$) to the σ^*(N−H) orbitals of NH$_3$ in the host lattice (mainly 2e$^+$). As for the σ system of pyrrole, the analysis of the corresponding COD curves (not shown here) indicate that the most relevant interactions in this system occur between occupied orbitals of the host lattice and σ^* empty orbitals of the pyrrole (see Table 2). These interactions are stronger than in the case of benzene because the 10a$_1$ orbital of pyrrole, N−H antibonding, is at lower energy than the σ^*(C−H) ones. Conversely, the interaction of the occupied σ orbitals of pyrrole with the host lattice is weaker than in benzene, although the same host orbitals are involved: π^* (C−N), 3a$_1$ of NH$_3$ (**2a**) and 2e of NH$_3$ (**2b,c**). All the interactions between pyrrole and host lattice are schematically summarized in **3**.

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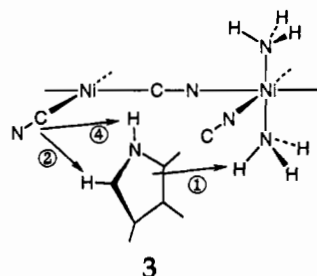
From the analysis of the changes in atomic charges upon enclathration, it is concluded that the host· ·guest interactions are in essence analogous to those found in the benzene clathrate. There is charge transfer from the pyrrole π system to the NH$_3$ groups in the host lattice (sketched as ① in **3**), as in benzene, the shortest H· ·pyrrole distances being approximately 3.0 Å. Such interaction may also be described as a C· ·H−N hydrogen bond. In the opposite direction, one finds charge transfer from the cyano groups (π bonding orbitals) of the host lattice to the N−H antibonding orbital 10a$_1$ (interaction ④ in **3**), as well as to C−H antibonding orbitals (interactions of type ② in **3**).

Structural Changes Produced by Enclathration. We analyze here the structural changes observed in the molecule of pyrrole[31] in the Cd(en)Ni(CN)$_4$·2C$_4$H$_5$N clathrate.[32] Remember that the most important charge transfer contribution comes from the 1a$_2$ orbital of pyrrole (Figure 3), C2−C3 bonding and C3−C3′ antibonding. Partial depopulation of this orbital is therefore predicted to slightly weaken the C2−C3 bonds but to strengthen the C3−C3′ one (calculated changes in the corresponding overlap populations are -8×10^{-4} and $+7 \times 10^{-4}$, respectively, calculated with a double-ζ basis set for all but the hydrogen atoms, see Appendix). Note that the effect of enclathration on the pyrrole molecule is an elongation along the crystallographic c axis, whereas in the case of benzene the result is a compression along the same direction. The structural data (experimental bond distances change from 1.382(5) to 1.49-(11) Å and from 1.417(5) to 1.27(11) Å, respectively) seem to be consistent with our prediction, although the large standard deviations in the case of the clathrate make the structural comparison inconclusive.

The Nickel−Aniline Clathrate, Ni(NH$_3$)$_2$Ni(CN)$_4$·2C$_6$H$_5$-NH$_2$

Orientation of the Guest Molecule. The behavior of the aniline guest molecule with regard to rotation around the c-axis is similar to that of benzene. The minimum in energy is calculated at $\varphi = 60°$ and the barrier for rotation is calculated to be 18.4 kJ/mol, only slightly larger than that for the benzene clathrate (15.3 kJ/mol). Rotation of the NH$_2$ group with the aromatic ring fixed also shows a preference for the conformation in which the lone pair is pointing toward the ammonia molecule, with a rotational barrier of ~27 kJ/mol, clearly suggesting the existence of a N(aniline)· ·H(NH$_3$) hydrogen bond.

Interaction of Aniline with the Host Lattice. The contribution of aniline to the DOS of the clathrate Ni(NH$_3$)$_2$Ni(CN)$_4$·2-(aniline) is shown in Figure 5. Similarly to what was found above for pyrrole, the π (9a″) band of aniline (at *ca.* −12 eV) is interspersed with the e$_g$ band of the octahedral nickel atom. Consequently, that orbital, occupied in aniline, may become empty in the calculations. Although this peculiar situation might be associated with the anomalous magnetic behavior[25] of the aniline clathrate, there is a possibility that this situation is an artifact of our calculations. Therefore, we choose to carry out all calculations on a model clathrate with two extra electrons, leading to the d^{10} configuration for the octahedral metal atom, appropriate for Cd(NH$_3$)$_2$Ni(CN)$_4$·2(aniline), so that full occupation of both bands is unambiguous.

We have analyzed the host· ·guest interactions by means of the ICOD functions, and their values at the Fermi level, $\Omega_i(\mathscr{E}_F)$. The most relevant difference from the cases of benzene and

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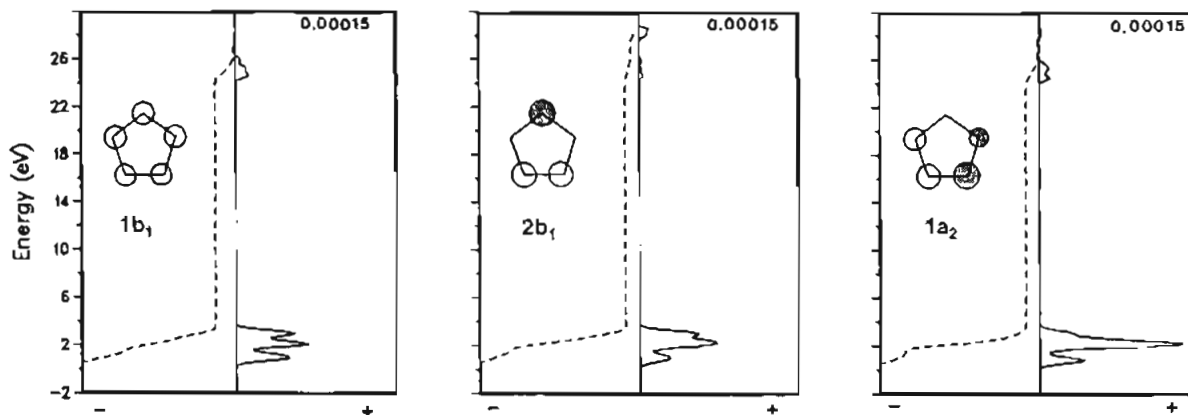
Figure 4. COD curves for the occupied $1b_1$, $2b_1$, and $1a_2$ orbitals of pyrrole in the energy range of the empty orbitals of the host lattice in the $Ni(NH_3)_2Ni(CN)_4\cdot2C_6H_6$ clathrate. The full scale for the COD curve corresponds to the number indicated in the upper right corner in units of number of displaced levels per unit cell.
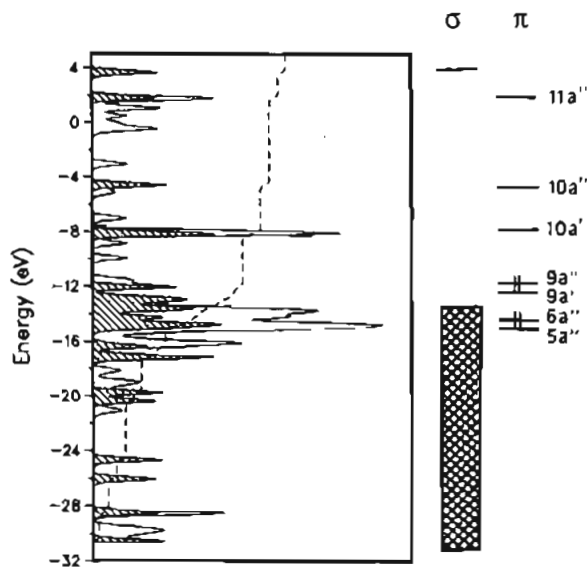

Figure 5. Contribution of the molecular orbitals of aniline (shaded areas) to the DOS of the Hofmann clathrate $Ni(NH_3)_2Ni(CN)_4\cdot2C_6H_5$-$NH_2$. The energies of the molecular orbitals in the isolated aniline molecule are shown at the right-hand side, together with their symmetry labels in the C_s point group. All the bands above -11 eV are empty.

pyrrole resides in the larger amount of charge transfer from (i) the σ-type orbitals of aniline toward the host lattice (0.0120, 0.0046, and 0.0038 electrons for aniline, benzene, and pyrrole, respectively), and (ii) from the host lattice toward the σ^* orbitals of aniline (0.0104, 0.0044, and 0.0068 electrons for aniline, benzene and pyrrole, respectively). This enhanced charge transfer may be responsible for the higher enclathration energy of aniline (50—60 kJ/mol)[33] compared to benzene and pyrrole (36 and 46 kJ/mol, respectively).

The COD curves for two of the occupied π orbitals of aniline ($9a'$ and $9a''$) are shown in Figure 6. As in the previously discussed clathrates, the interaction between these orbitals and the σ^* orbitals of NH_3 ($3a_1$ and $2e$) shows up in the peaks between -1 and $+3$ eV. A weaker interaction gives place to a smaller peak at $24-28$ eV, in the region of the $4a_1$ orbital of ammonia. In the COD curves for the $9a''$ and $6a''$ orbitals (not shown), small peaks between -9 and -6 eV indicate some charge transfer to the π^* of the cyano groups. It is not easy to ascribe the interactions of the aniline lone pair to a single molecular orbital, since the σ and π orbitals of this molecule are allowed to mix by symmetry. We therefore computed the

ICOD function of the lone pair orbital of the NH_2 fragment at the Fermi level, which turns out to be negative ($\Omega_n(\mathscr{E}_F) = -0.0037$), indicative of a charge transfer from this orbital to the lattice.

The COD curve for all empty σ^* orbitals of aniline is shown in Figure 7 (left). A charge transfer can be deduced from the occupied π orbitals of the cyano groups (between -15 and -12 eV) to the σ^* orbitals of aniline. This interaction is stronger than the analogous one in the benzene clathrate, a fact which can be attributed to the presence of some hydrogen bonding between the amino group of aniline and the host lattice, resulting in a tiny decrease of the C—N overlap population by 0.0004. The experimental evidence is in good agreement with this result, the shift of the $\nu(CN)$ frequency to lower frequency upon enclathration being somewhat more pronounced for aniline than for benzene.[34] Some interaction is also seen between the σ^* orbitals of benzene and the lone pairs of the cyanides, centered at their carbon atoms and mixing in some nickel d-character. The COD curve for the occupied σ orbitals of aniline (Figure 7, right) is quite similar to those of the clathrates studied above, as detected from the corresponding values of $\Omega_i(\mathscr{E}_F)$: the donation goes mainly to the $\pi^*(CN)$ system (between -9 and -5 eV) and to the $\sigma^*(NH_3)$ orbitals $3a_1$ and $2e$ (between -1 and 3 eV).

The analysis of the changes in electron densities upon enclathration shows a behavior analogous to that of the pyrrole clathrate, and is in agreement with the existence of hydrogen bonds between the hydrogen atoms of the NH_2 group of the aniline guest and the host lattice (mainly the cyanides), and between the hydrogen atoms of the NH_3 ligands in the host and the nitrogen of the amino group of the guest, as seen, e.g., in the decreased overlap population of the N—H bonds of ammonia (calculated shift associated with enclathration is -0.0014). The stretching and bending vibrations of ammonia are consistently shifted to smaller frequencies ($\nu_a = 3385$ cm^{-1}, $\nu_s = 3309$ cm^{-1}, $\delta_s = 1230$ cm^{-1} in the host lattice; $\nu_a = 3379$ cm^{-1}, $\nu_s = 3283$ cm^{-1}, and $\delta_s = 1191$ cm^{-1} in the clathrate). The stronger binding of the amino group of aniline to the host lattice is consistent with the finding that the aniline molecules do not rotate freely in the clathrates,[35] in contrast with the low activation barrier found for benzene.

In summary, besides the charge transfer components previously identified for the benzene and pyrrole clathrates (①

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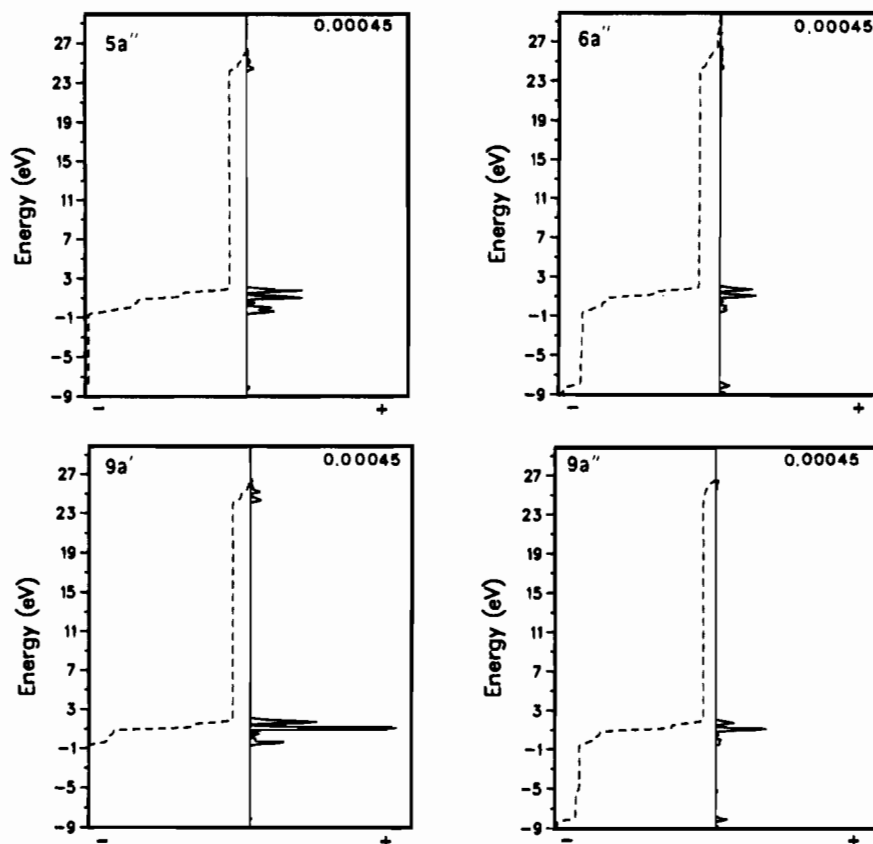
Figure 6. COD (solid line) and ICOD (dashed line) curves for the occupied π orbitals of aniline in the $Ni(NH_3)_2Ni(CN)_4 \cdot 2C_6H_5NH_2$ clathrate. The full scale for the COD curve corresponds to the number indicated in the upper right corner in units of number of displaced levels per unit cell.
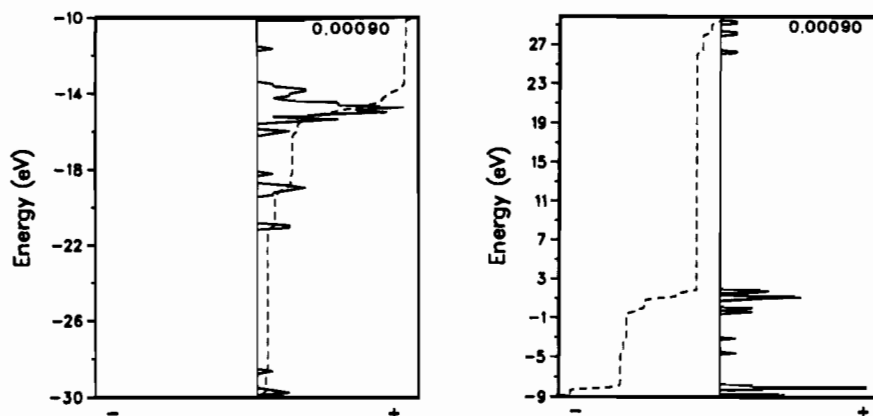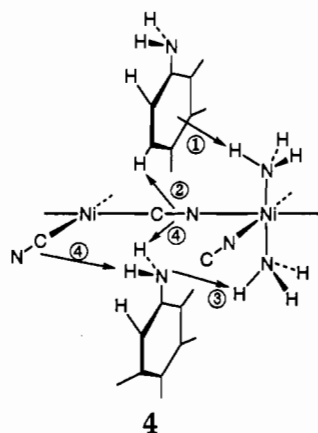

Figure 7. COD curve for the empty σ^* (left) and occupied σ (right) orbitals of aniline in the $Ni(NH_3)_2Ni(CN)_4 \cdot 2C_6H_5NH_2$ clathrate. The full scale for the COD curve corresponds to the number indicated in the upper right corner in units of number of displaced levels per unit cell.

and ② in **4**), two new interactions appear for aniline: (a) a

4

donation of the aniline lone pair toward the ammonia molecule (labelled ③ in **4**) and (b) hydrogen bonding between the amino group and the cyanides of the host lattice (labelled ④ in **4**). As a result, the calculated N–H overlap population of the amino group decreases by 0.0010 upon enclathration. The experimental evidence also supports this interpretation, since the stretching frequencies of the amino group, ν_a (and ν_s) are shifted from 3500 (and 3418) cm^{-1} in the vapor phase to 3460 (and 3370) cm^{-1} in the clathrate.[34] A similar shift appearing in liquid aniline has also been attributed to the formation of intermolecular hydrogen bonds.[36]

Overall, the carbon atoms of the phenyl ring of aniline behave as donors toward the host lattice, as in the clathrates studied above, whereas the ortho hydrogen atoms are sterically protected by the amino group and show weaker interactions. As a

(36) Evans, J. C. *Spectrochim. Acta* **1960**, *16*, 428.

consequence, the net loss of electron density for the aniline molecule is -0.006, sensibly smaller than that calculated for benzene (-0.017). A connected experimental observation has to do with the out of plane vibrations of the aromatic ring, which are shifted to lower frequency by *ca.* 30 cm^{-1} in the benzene clathrate, but only half of that in the aniline clathrate.[34] In summary, the unsubstituted part of the ring interacts with the host lattice in the same way as the benzene guest, while the amino group makes two types of hydrogen bonds: N—H(aniline)···CN(host) and N—H(NH$_3$, host)···N(aniline).

Electronic Structure of the Benzene Clathrate with Ethylenediamine, Ni(en)Ni(CN)$_4$·2C$_6$H$_6$

Orientation of the Guest Molecule. In this case, the only parent compound known, Cd(en)Ni(CN)$_4$, presents a peculiar structure, in which ethylenediamine (*en*) acts as a chelate ligand to the hexacoordinate metal atom. The host lattice obtained through enclathration of a guest molecule differs from that of the parent compound in that the ethylenediamine ligands are coordinated in a monodentate mode to two metal atoms, bridging two successive layers of metal cyanide.[37] The *en* ligands are in a transoid conformation (**5**) and the NH$_2$ groups are disor-
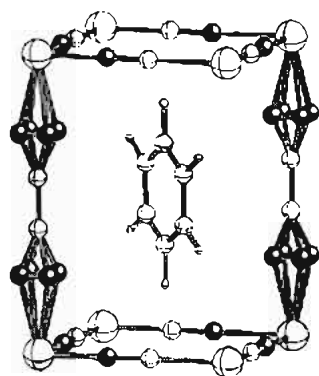
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dered.[21,38] The presence of the *en* ligand induces a different orientation of the guest molecules: $\varphi = 90°$ in the benzene and pyrrole clathrates with the ethylenediamine host[30,39] as compared to $\varphi = 58-66°$ (Table 1) and 72° (calculated) in the benzene and pyrrole clathrates with ammonia, respectively. This is probably a result of the steric bulk introduced in the axial positions of the octahedral metal atom by the bridging ligand.

The geometry adopted for the calculations on the ethylenediamine clathrate is shown in **6**, with two nonequivalent benzene molecules (labeled 1 and 2). With the idealized rotation angle, $\varphi = 90°$, benzene-1 is nearly parallel to the plane of the neighboring *en* molecule (the NCCN plane in the transoid conformation), whereas benzene-2 is roughly perpendicular to the same *en*. Since the amino groups appear disordered in the X-ray structure, the experimental data for the benzene guest corresponds to an average of the two nonequivalent benzene molecules of the model clathrate used in the present calculations.

The calculated energy of Cd(en)Ni(CN)$_4$·2(benzene) as a function of the rotation angle of either of the benzene molecules (Figure 8) has a minimum at $\varphi = 90°$, in excellent agreement with the experimental data. This rotation angle, much larger than the one found for the benzene and pyrrole clathrates of
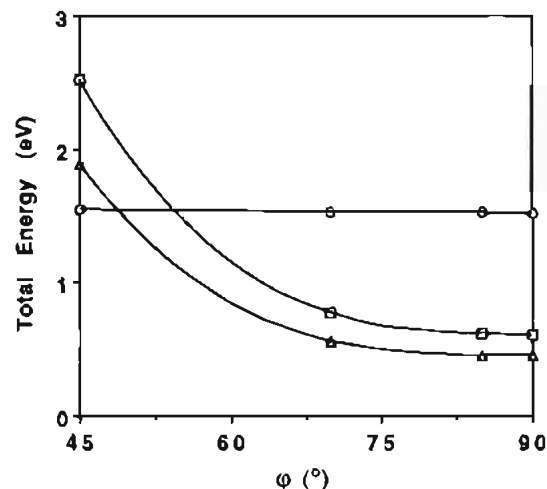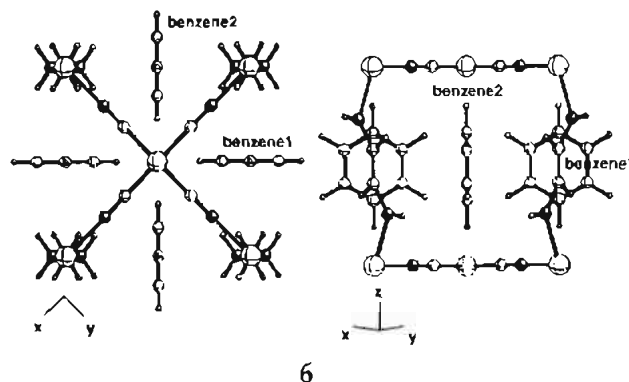

Figure 8. Total one-electron energy of the clathrate Cd(en)$_2$Ni-(CN)$_4$·C$_6$H$_6$ (within a rigid band approximation, see Appendix) as a function of the orientation angle φ (see Figure 1) of the benzene-1 (triangles) and benzene-2 (squares) molecules. The energy calculated in the absence of ethylenediamine ligands is also shown (circles).

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the ammoniated cyanide, is imposed by the greater bulk of the *en* ligand in the neighborhood of the octahedral M atom. This can be verified by looking at the energy curve obtained in the absence of ethylenediamine, which is practically invariant with φ (Figure 8). Ab initio calculations on bimolecular complexes of ethylenediamine and benzene[9] confirm that the conformation adopted by the guest molecule corresponds either to the maximum attraction between benzene-1 and ethylenediamine or to the minimum repulsion between benzene-2 and ethylenediamine. Therefore, the orientation of the benzene guest in the ethylenediamine host is predicted to correspond to $\varphi = 90°$ regardless of the position occupied by the disordered ethylenediamine molecules.

Interaction of Benzene with the Ethylenediamine Host. The electronic structure of the host lattice changes in a predictable way when substituting ethylenediamine for ammonia, as seen in the contributions of the corresponding NH$_2$ and CH$_2$ fragments to the DOS (Figure 9). The contributions relevant for the subsequent discussion are (a) the bands appearing between -18 and -10 eV, associated with the N—H and C—H bonds of *en*; (b) the first two unoccupied bands of ethylenediamine (between -2 eV and $+2$ eV), corresponding to C—H antibonding orbitals with a contribution of the NH$_2$ lone pair in the lowest one, reminiscent of the $3a_1$ orbital of ammonia; (c) the two superimposed bands at 3.5 eV, mostly localized at the amino group, N—H antibonding and similar to the 2e bands of ammonia; and, finally, (d) a band at $\sim$4.7 eV, delocalized through the NH$_2$ and CH$_2$ groups, essentially N—H and C—H antibonding.

(37) Kitazawa, T.; Mizushima, Y.; Shiraha, J.; Ryoko, T.; Katoh, A.; Hasegawa, T.; Nishikiori, S.-I.; Iwamoto, T. *J. Incl. Phenom.* **1991**, *11*, 29.
(38) Nishikiori, S.; Ratcliffe, C. I.; Ripmeester, J. A. *J. Phys. Chem.* **1991**, *95*, 1589.
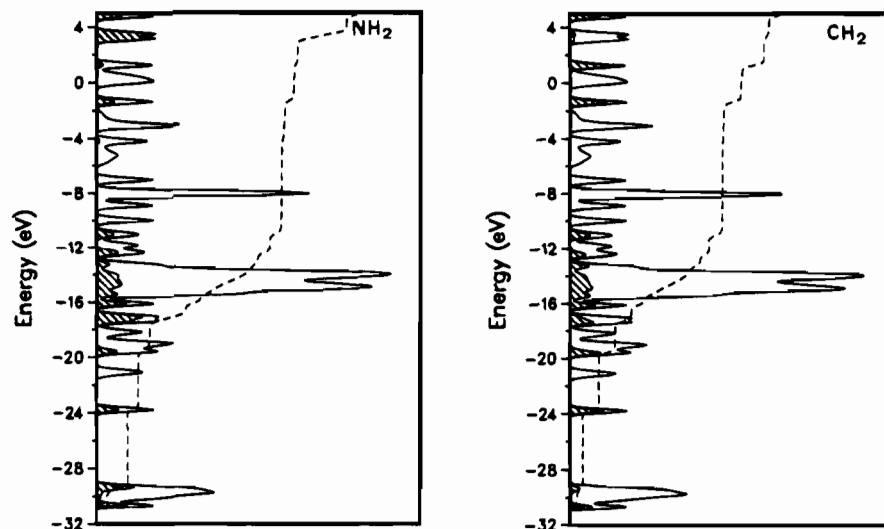(39) Miyoshi, T.; Iwamoto, T.; Sasaki, Y. *Inorg. Chim. Acta* **1972**, *6*, 59.

Figure 9. Contributions of the NH₂ and CH₂ groups of ethylenediamine to the DOS of Cd(en)Ni(CN)₄.
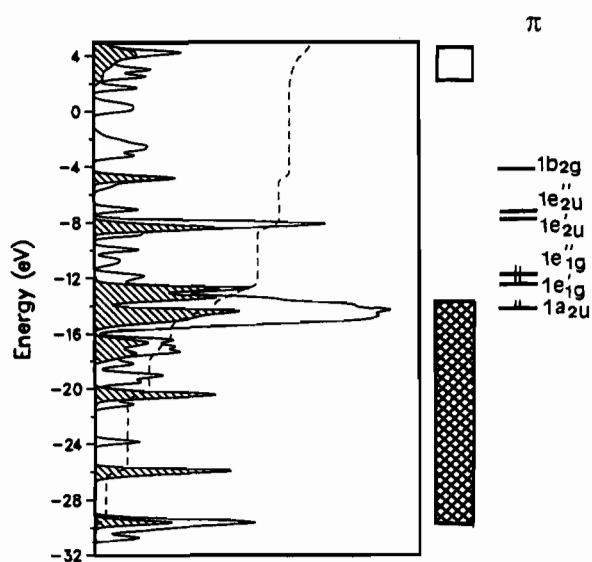

Figure 10. Contribution of the benzene molecules to the DOS of the ethylenediamine clathrate, Cd(en)Ni(CN)₄·2C₆H₆.

The contribution of the benzene molecules to the total DOS of the ethylenediamine clathrate is shown in Figure 10, together with the energy levels of the molecular orbitals calculated for the isolated benzene molecule. There is a clear correspondence between the MO energies of the molecule and their contributions to the bands of the clathrate, indicating that only weak interactions may exist between benzene and the host lattice, which cannot be easily identified in a DOS diagram. We therefore turn to COD and ICOD diagrams in order to analyze the host···guest interactions.

The values of $\Omega_i(\mathcal{E}_F)$ of the two types of benzene molecules are shown in Table 3, where also the corresponding values for the ammonia host are given for comparison. It is clear that benzene-2, oriented perpendicular to the ethylenediamine molecules (**6**), undergoes stronger charge transfer interactions with the host lattice than benzene-1. The COD curves for those orbitals in benzene-1 with the largest $\Omega_i(\mathcal{E}_F)$ values (1a₂ᵤ and 1eg″) are shown in Figure 11. These, together with the knowledge of the composition of the bands at 1, 3, and 5 eV (see above) yield a simple orbital description of the host···guest interactions: The occupied π orbitals of benzene-1 interact with C−H and N−H antibonding bands of *en*, (equivalent to forming hydrogen bonds between the π system of benzene and the methylene and amino groups of the *en* ligand, ① in **7**). The

Table 3. Calculated Values for the ICOD Functions of Molecular Orbitals of Benzene at the Fermi Level, $\Omega_i(\mathcal{E}_F)$ ($\times 10^4$), in the Ammonia and Ethylenediamine Clathrates of Benzene, in Increasing Order of Energy[a]

		L = ethylenediamine	
	L = NH₃	benzene-1	benzene-2
Benzene Occupied Orbitals			
other σ orbitals [9]	−17	−20	−30
1a₂ᵤ (π)	−19	−17	−38
1b₂ᵤ	−1	−2	−7
3e₂g′	−2	−6	−5
3e₂g″	−3	−10	−9
1e₁g′ (π)	−17	−7	−28
1e₁g″ (π)	−19	−26	−56
Benzene Empty Orbitals			
1e₂ᵤ′ (π*)	6	4	25
1e₂ᵤ″ (π*)	2	7	19
1b₂g (π*)	1	0	3
other σ* orbitals [12]	22	23	32

[a] Number of orbitals given in brackets.

σ* system of benzene (COD curves not shown), on the other hand, interacts predominantly with the π orbitals of the cyano groups of the host lattice (interaction ② in **7**). In addition, the σ system of benzene interacts mostly with the empty π* orbitals of the cyano groups (interaction ⑥ in **7**).

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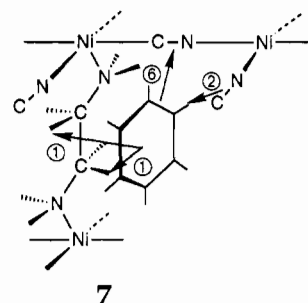
The interactions of benzene-2 with the perpendicular molecules of ethylenediamine are somewhat different, as can be deduced from the COD curves (not shown). The occupied π orbitals of benzene interact with the bands of ethylenediamine centered on the NH₂ groups (interaction ① in **8**). It is to be noted, however, that the e₁g′ and e₁g″ orbitals (degenerate in free benzene) interact with different bands of ethylenediamine. In this case the empty π* orbitals of benzene show important interactions with several bands of the host lattice, in contrast to
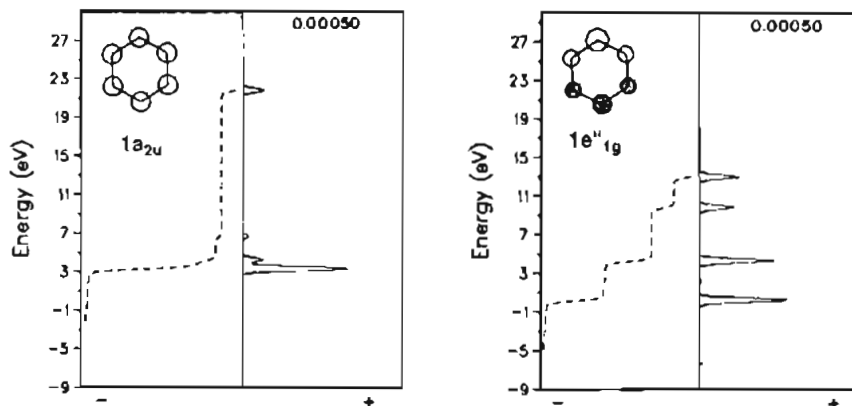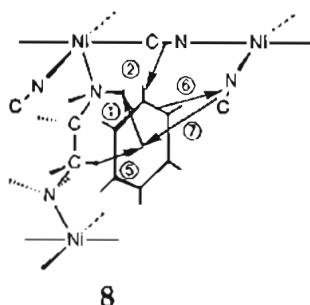
Figure 11. COD (solid line) and ICOD (dashed line) curves for two occupied π orbitals of benzene in the Ni(en)$_2$Ni(CN)$_4$·2C$_6$H$_6$ clathrate. The full scale for the COD curves corresponds to 0.0005 displaced levels per unit cell.

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what has been found for other clathrates (see above): the occupied orbitals of the cyanides, both π and carbon-centered lone pair (interaction ⑦ in **8**), and the N−H and C−H bonding orbitals of ethylenediamine (⑤ in **7**). The σ orbitals of benzene-2 interact with the host lattice in much the same way as those of benzene-1 (⑥ in **7** and **8**), though more intensely.

Conclusions

Band calculations have been carried out on Hofmann clathrates Ni(NH$_3$)$_2$Ni(CN)$_4$·2G with two different guest molecules (G = pyrrole, aniline), and on the related ethylenediamine clathrate, Ni(en)Ni(CN)$_4$·2C$_6$H$_6$, by using the extended Hückel tight-binding approximation. The crystal orbital displacement (COD) and integrated crystal orbital displacement (ICOD) functions appear to be very useful for abstracting the relevant levels from a large set of noninteracting wave functions, therefore facilitating the detection of weak interactions between two sublattices in complex systems such as the Hofmann clathrates.

The orientation of the guest molecule is predicted to correspond to a rotation angle $\varphi = 72°$ (pyrrole), 60° (aniline), and 90° (benzene, with ethylenediamine in the host). The last value is in excellent agreement with the experimental angle found by X-ray diffraction (90°). The orientation angle is seen to result from the interplay between the guest··guest and guest··axial ligand interactions. The calculated barriers for rotation of the guest molecule around the crystallographic c axis are 2.0, and 18.4 kJ/mol for G = pyrrole and aniline, respectively.

The changes produced in the M−C and C−N bond distances of the host lattice, and in the C−C distances of the guest pyrrole molecule upon enclathration are nicely paralleled by the calculated changes in the corresponding overlap populations in EHTB calculations. An orbital explanation can be found for the fact that the benzene molecule is compressed along the c axis and stretched in the perpendicular direction, whereas the pyrrole guest molecule is elongated along the c axis.

A resulting simplified description of the host··guest interactions would be that of hydrogen bonds between the guest and ammonia, and between cyanide and benzene. In contrast, the metal atom does not participate significantly in the host··guest interaction. For the aniline clathrate, the unsubstituted part of the ring interacts with the host lattice in the same way as the benzene or pyrrole guests, while the amino group participates in two types of hydrogen bonds: N−H(aniline)··CN(host) and N−H(NH$_3$, host)··N(aniline). The resulting enhanced charge transfer may be responsible for the higher enclathration energy of aniline compared to those of benzene and pyrrole, and for its nondynamical behavior.

Appendix

Computational Details. Extended Hückel calculations of molecular orbitals[40] and tight-binding bands[41,42] were carried out using the modified Wolfsberg−Helmholz formula[43] and standard atomic parameters.[40,44] including single-ζ basis sets for all atoms except for the transition metals, for which a double-ζ basis was used. Check calculations were carried out using double-ζ basis set for all except hydrogen atoms. DOS and COD diagrams were calculated by averaging throughout the Brillouin zone using a mesh of 120 k-points.

The experimental structure of the Ni(NH$_3$)$_2$Ni(CN)$_4$·2C$_6$H$_6$ clathrate[45] was used in general for the host lattice. The complete unit cell of the Ni(NH$_3$)$_2$Ni(CN)$_4$·2G clathrates (G = pyrrole, aniline) was used for calculating properties. For the calculation of COD functions, we used the simpler model Ni(NH$_3$)$_2$Ni-(CN)$_4$·G, in which only half of the cavities are occupied by guest molecules, to analyze the host··guest, but not the guest··guest interactions. The interlayer distance in the clathrates was adjusted according to the unit cell parameter c obtained from powder diffraction patterns.[25] The structural parameters used for pyrrole correspond to the structure[29] of Cd(NH$_3$)Ni-

(40) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.
(41) Whangbo, M.-H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 6093.
(42) Whangbo, M.-H.; Hoffmann, R.; Woodward, R. B. *Proc. R. Soc. London, A.* **1979**, *366*, 23.
(43) Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686.
(44) Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 7240.
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$(CN)_4·2C_4H_5N$, and for the aniline guest, the structure of pure aniline was employed.[46,47] Finally, for the ethylenediamine clathrate, the experimental structure[21] was used. The method employed for calculating properties for the $t_{2g}^6 e_g^n$ electron configurations has been reported previously.[8]

COD Functions. The crystal orbital displacement function[8] for a given molecular orbital of the guest molecule at a given energy, $\Delta_i(\epsilon)$ corresponds to the number of levels shifted in the clathrate relative to the free molecule, and is defined as

$$\Delta_i(\epsilon) = n_i^C(\epsilon) - n_i^G(\epsilon)$$

where n_i^C is the contribution of the ith molecular orbital to the

density of states of the clathrate and n_i^G its contribution to the DOS of te isolated guest molecules. Hence, positive values of $\Delta_i(\epsilon)$ indicate the existence of levels at the particular energy ϵ 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 $\Omega_i(\epsilon)$ also provides relevant information. In particular, its value at the Fermi level, $\Omega_i(\mathscr{E}_F)$, 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 $\Omega_i(\mathscr{E}_F)$, 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 of $\Omega_i(\mathscr{E}_F)$.

(46) Fukuyo, M.; Hirotsu, K.; Higuchi, T. *Acta Crystallogr., B* **1982**, *38*, 640.
(47) Lister, D. G.; Tyler, J. K. *Chem. Commun.* **1966**, 152.