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Inorganic−Organic Hybrid Molecular Architectures of Cyanometalate Host and Organic Guest Systems: Specific Behavior of the Guests

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ABSTRACT
Molecular architectures built of inorganic cyanometalate building blocks provide variegated host structures with several organic guest molecules. The strategies to derive novel structures are presented briefly. The formation of a charge-transfer (CT) complex as the guest inside the cavity and the photochemistry of the CT complexes are discussed. The chemical pressure that the guest experiences inside the cavity is also discussed based on the vibrational spectroscopic results.

Introduction

The term “molecular architecture” seems to be ambiguous. In terms of methodology, one interpretation is to build up a complicated molecular structure like the complex structures of the building architect Antoni Gaudi I Cornet; another is to use ordinary molecules as building blocks to create something new made of the molecules. The product of the first is a discrete “Avogadro” molecule, such as DNA or something else, and the product of the second has an infinite polymeric structure like silicate minerals in nature. An Avogadro molecule is a discrete chemical species, regardless of electric charge, comprised of definite numbers of atoms belonging to certain elements. The nature of the work presented in this Account belongs to the second category; the main building blocks are linear dicyanoargentate(I), tetrahedral tetracyanocadmate(II), square-planar tetracyanonickelate(II), etc. Most of the products exhibit clathrate structures: the multidimensional cyanometal complex hosts generate cavities of molecular scale in which organic guest molecules are included.

The prototype of our cyanometalate structures is Hofmann’s benzene compound, $Ni(CN)_2{\cdot}NH_3{\cdot}C_6H_6$, discovered by chance in 1897,[1−3] the clathrate structure of which was determined half a century after the discovery.[4,5] The host has a layered structure made up of two-dimensional networks, which consist of an array of alternating square-planar $[Ni(CN)_4]^{2-}$ and octahedral Ni^{2+} centers. The flat and square-meshed networks, from which two NH_3 ligands protrude at every octahedral Ni^{2+}, are stacked on top of one another to generate the interlayer cavities for the guest benzene molecules. The formula $[Ni(NH_3)_2Ni(CN)_4]{\cdot}2C_6H_6$ denotes the presence of the two kinds of Ni atoms, which differ in their coordination mode. Our work on the molecular architectures involving cyanide ligands started from the development of the series of Hofmann-type clathrates, $[M(NH_3)_2M'(CN)_4]{\cdot}2G$ ($M = Mn$, Fe, Co, Ni, Cu, Zn, or Cd; $M' = Ni$, Pd, or Pt; $G = PhNH_2$, PhOH, C_6H_6, C_4H_4S, or C_4H_5N).[6,7] That work, however, involved only the replacement of the two metals to produce the isostructural series. As is illustrated in Figure 1, the first step in crystal engineering to develop novel architectures was materialized for the Hofmann-en-type, $[Cd(en)M'(CN)_4]{\cdot}2C_6H_6$, clathrate; a three-dimensional host was derived from the Hofmann-type by replacing the pair of ammine ligands facing each other in the interlayer space of the two-dimensional networks by a bridging ethylenediamine.[8] Since then, various novel architectures have been developed. The building blocks from which the Hofmann-type architecture is constructed are divided into three moieties: (a) the square-planar $[M'(CN)_4]^{2-}$, that is, a moiety comprised of the primary coordination center M′ and the primary ligand CN; (b) the octahedral M as the second coordination center; (c) the NH_3 as the complementary ligand coordinated to M.

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Hirofumi Yoshikawa, born in 1975, received his B.Sc. and Ph.D. degrees in chemistry from the University of Tokyo in 1998 and 2003, respectively. His Ph.D. thesis involved synthetic, structural, spectroscopic, and theoretical studies of polycyano-polycadmate host clathrates including a methyl viologen as a cationic guest. He is currently a postdoctoral fellow supported by the 21st century COE program in Prof. K. Awaga’s research group at Nagoya University. His current research interests are magnetic properties of metal complexes and nano materials.

Yuriko Sano earned her M.S. degree in chemistry from the University of Tokyo in 2004, on studies of PCPC clathrates including diquat. She is now working for Japan Institute of Invention and Innovation.

Toschitake Iwamoto, born on 29th June 1935 in Tokyo, received his B.Sc. in 1958 and D.Sc. (Ph.D.) in 1963 from the University of Tokyo. From 1963 to 1996, he had stayed in the University of Tokyo as Research Associate and Lecturer at Department of Chemistry in Hongo Campus and Associate and Full Professor in Komaba Campus, before he moved to the present position. He received the award for younger chemist of the Chemical Society of Japan in 1969 for the study on the clathrate compounds formed between metal complex hosts and organic guest molecules, having pioneered inorganic supramolecular chemistry, in particular, the crystal engineering technique to develop novel host structures. Since 1980, he has been on the board of the International Advisory Committee of the International Symposia on Supramolecular Chemistry and was appointed as a lifetime member in 2000. He had worked as the editor of *J. Coord. Chem., Sect. B* from the middle of the 1980s to the 1990s and has currently been named as an emeritus editor.

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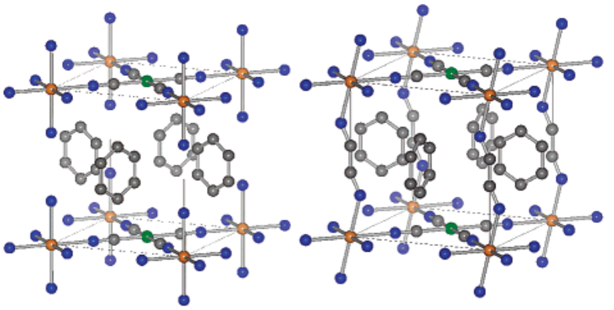


FIGURE 1. From Hofmann-type $[Cd(NH_3)_2Ni(CN)_4]\cdot 2C_6H_6$ to Hofmann-en-type $[Cd(NH_2CH_2CH_2NH_2)Ni(CN)_4]\cdot 2C_6H_6$.

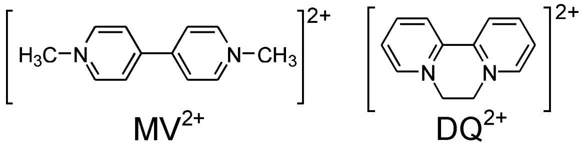
The strategies that we have applied to obtain new clathrate structures are summarized as follows: (1) to replace the NH_3 by other unidentate ligands, H_2O, alkylamine, etc., to regulate the lipo- or hydrophilic characters of the interlayer cavities; (2) to replace two NH_3 ligands facing each other in the interlayer space by a bridging ligand, such as α,ω-diaminoalkanes ($NH_2(CH_2)_nNH_2$), to increase the lipophilic character of the cavities and to regulate the interlayer distance in the three-dimensional host; (3) to replace the square-planar $[M'(CN)_4]^{2-}$ by a tetrahedral tetracyanometalate, such as $[Cd(CN)_4]^{2-}$ or $[Hg(CN)_4]^{2-}$, to build up three-dimensional hosts with CN bridges only; (4) to replace the octahedral *trans*-$[M(NH_3)_2]^{2+}$ entity by two phenylalkylammonium cations, $Ph(CH_2)_nNH_3^+$, in order to increase the lipophilic character of the interlayer space; (5) to replace the −CN− span with a −NC−Ag−CN− span, that is, to replace the $[Ni(CN)_4]^{2-}$ by $\{[Ag(CN)_2]^-\}_2$ in the formula to elongate the span distance. In cases 4 and 5, the derived structures are too complicated to explain briefly, but these are exemplified by $[\{Ph(CH_2)_2NH_3\}_2Ni(CN)_4]\cdot PhNMe_2$ [9] and *trans*-$[Cd(dppn)_2\{Ag(CN)_2\}_2]_n$ [dppn = 1,3-di(4-pyridyl)propane].[10] The results have been reviewed successively, including those of cyanide-linked multidimensional nonclathrate structures.[11−16]

The main component CN group is approximated to an ellipsoid of 4 Å length and 3.2 Å thickness. These dimensions lead to a span length between two coordination centers of ca. 5.2−5.5 Å. In the case of linear $[Ag(CN)_2]^-$, the effective span length becomes ca. 10.5 Å. The polyhedra edged by these M′−CN−M spans may generate a void of considerable volume inside, which is occupied by a guest species, a complementary ligand voluminous enough to stabilize the whole crystal structure, or both. Various combinations of the coordination mode of cyanometalate, complementary ligand, and guest species have been materialized to give a number of variegated CN-linked structures. As for the secondary coordination center, that is, that bridged at the N atom of CN, Cd^{2+} is extremely versatile for all the compounds obtained so far, except for the Hofmann-type clathrates.

Mineralomimetic Structures

Varieties of the multidimensional structures consisting of both octahedral Cd^{2+} as the secondary coordination center and tetrahedral $Cd(CN)_4$ moieties have been obtained with the apparent compositional formulas of polycyano-polycadmates (PCPC), $[Cd_x(CN)_z]^{2x-z}$ or more exactly $[Cd^{(o)}{}_{x-y}\{Cd^{(t)}{}_y(CN)_z\}]^{2x-z}$ where $Cd^{(o)}$ and $Cd^{(t)}$ denote octahedral and tetrahedral Cd atoms, respectively. Similarities have been observed between such pairs as $Cd^{(t)}(CN)_4$ and SiO_4, $Cd^{(t)}{}_y(CN)_z$ and Si_yO_z, and $Cd(CN)_2$ and SiO_2, in molecular structure, in condensation behavior, and in crystal structure. A potassium salt of a discrete (isolated) silicate-like $[Cd(CN)_4]^{2-}$ unit was described as a "cyanospinel" $K_2Cd(CN)_4$, owing to the compositional (Al_2MgO_4) and the structural ($Fd\bar{3}m$) similarity to the spinel.[17] In our series of PCPC structures, dimeric pyrosilicate-like $Cd_2(CN)_7$ both in staggered and in eclipsed forms, polymeric chains of linear inosilicate-like $[Cd(CN)_3]_n$, oligomeric rings of ring-silicate-like $[Cd(CN)_3]_4$ and $[Cd(CN)_3]_6$, pentameric clusters of $Si(OSiO_3)_4$-like $[Cd\{(CN)Cd(CN)_3\}_4]$, etc. have been observed together with those frameworks similar to rutile (TiO_2), pyrite (FeS_2), cooperlite (PtS), etc. From observations on these variegated structures, the concept of mineralomimetic chemistry has been derived to denote a field of chemistry where mineralomimetic structures are developed by using materials that never give stable minerals in nature. This contrasts with biomimetic chemistry, which aims at developing biofunctional systems using nonbiotic materials.[18] Mineralomimetic chemistry is not only limited to the field of supramolecular chemistry but also extends to a new field of coordination chemistry, that is, the field of coordination polyhedra.

Scheme 1. MV^{2+} and DQ^{2+}



$[Cd(CN)_2]\cdot G$ clathrates are the simplest in composition among all known inclusion compounds. However, the $Cd(CN)_2$ host framework shows polymorphism just like silica, SiO_2, depending upon the shape and size of the guest G; host lattice structures similar to high-cristobalite (the high-temperature phase of cristobalite), low-cristobalite, high-tridymite, etc. have been obtained.[19−23]

Charge-Transfer Complex Formation in Clathrate Cavities

A cavity formed in a PCPC (polycyano-polycadmate) host structure may provide a field of interaction with a donor and acceptor pair to give a charge-transfer (CT) complex, if the environmental conditions are appropriate inside the molecular architecture. The PCPC host species, $[Cd_x(CN)_z]^{2x-z}$, tends to be anionic ($z > 2x$) so that a cationic guest is often incorporated in the clathrate structure to neutralize the negative charge of the host. Methyl viologen dication, MV^{2+} (1,1′-dimethyl-4,4′-bipyridinium dication), and diquat dication, DQ^{2+} (6,7-dihydrodipyrido[1,2-*a*:2′,1′-*c*]pyrazinium dication), were chosen as cationic guests (Scheme 1). They are well-known as strong electron acceptors that are often used in the fields of electrochem-

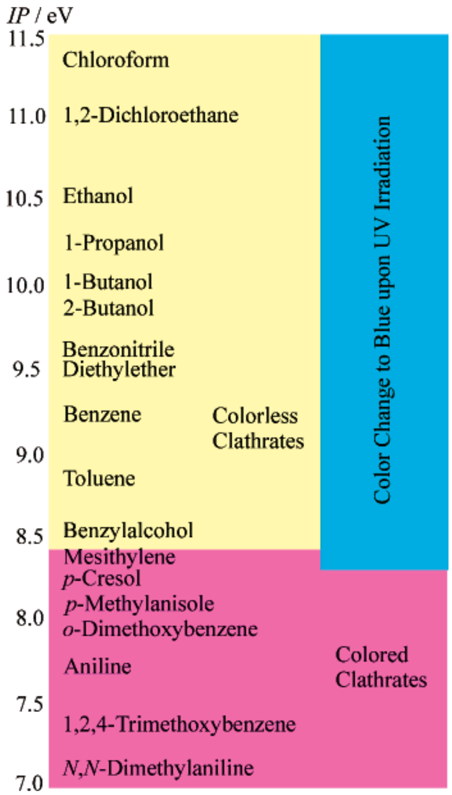


FIGURE 2. Some examples of MV^{2+}−G PCPC clathrates. The neutral guest (G), its ionization potential (IP), and the classification are indicated.

istry and photochemistry (MV^{2+}, $E° = -0.45$ V vs SCE; DQ^{2+}, $E° = -0.39$ V vs SCE). The donor−acceptor interaction is tuned by changing the donor, which is the neutral guest (G), such as aromatics, halocarbons, and alcohols.

MV^{2+}−G Clathrates.[24−28] Several clathrates synthesized using MV^{2+} and various kinds of neutral organic compounds are shown in Figure 2. These clathrates were classified into two groups, colorless and colored, each of which also has distinct structural features. Typical examples for both groups are illustrated in Figure 3. In the colored clathrates, MV^{2+} and G are included together in one cavity and are so close to each other as to form a CT complex. On the other hand, in the colorless clathrates MV^{2+} and G are included separately in their own cavities. The color classification thus also reflects whether the inclusion mode has coupled or separated MV^{2+} and G guests.

In Figure 4, the energies at the absorption maxima of the colored clathrates are plotted against the ionization potentials (*IP*) of their neutral guests. The plots satisfy the Mulliken linear relationship, $h\nu_{CT} = IP - EA + \text{const}$, *EA* being the electron affinity of MV^{2+}. This finding suggests that the origin of the color is a CT complex formed between MV^{2+} and G in the cavity. X-ray structural analysis carried out for several colored clathrates revealed the formation of such CT complexes as illustrated in Figure 5. Their basic structure is a $\pi-\pi$ stacking, which is an ordinary structure formed with a π donor and a π acceptor. One feature found here was a remarkable red shift of their CT transition energies. Compared with the

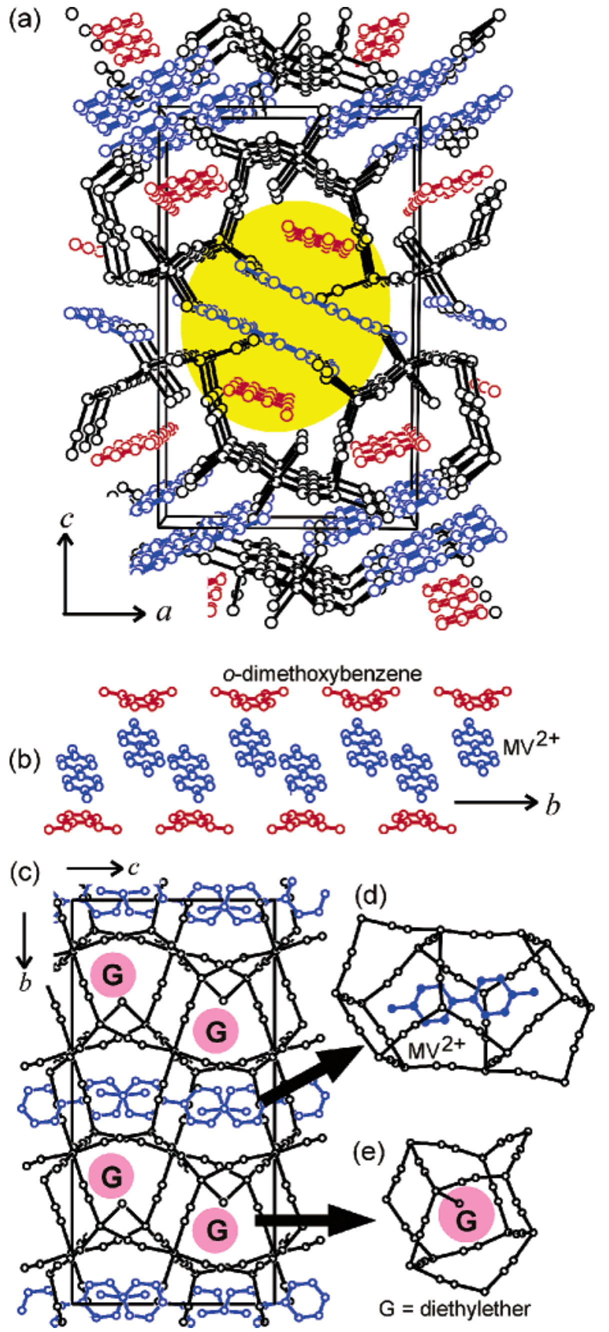


FIGURE 3. Crystal structures of a MV^{2+}−*o*-dimethoxybenzene clathrate,[27] $[Cd_3(CN)_{6.553}Cl_{1.447}(H_2O)]\cdot[MV^{2+}\cdot C_6H_4(OCH_3)_2]$, and a MV^{2+}−diethyl ether clathrate,[25] $[Cd_6(CN)_{14}(H_2O)_2]\cdot[MV^{2+}\cdot 2CH_3CH_2OCH_2CH_3]$, as typical examples of colored and colorless clathrates, respectively. Host complex is depicted in black, MV^{2+} in blue, and G in red. Panel a shows a perspective view along the *b* axis of the MV^{2+}−*o*-dimethoxybenzene clathrate. The host is a layered structure of largely waved 2D networks of cadmium cyanide complex. Between the networks, a 1D channel structure running along the *b* axis is formed. The yellow area is the section of the 1D channel. Panel b shows the array of CT complexes of MV^{2+} and *o*-dimethoxybenzene in the 1D channel cavity. In this arrangement, MV^{2+} ions are in contact with each other. Panel c shows a perspective view along the *a* axis of the MV^{2+}−diethyl ether clathrate. MV^{2+} and diethyl ether are included separately, each in its own cage-like cavity. Panel d shows the cage-like cavity for MV^{2+}; panel e shows the cage-like cavity for diethyl ether. The shape of the diethyl ether is unclear because of isotropic reorientational motion.

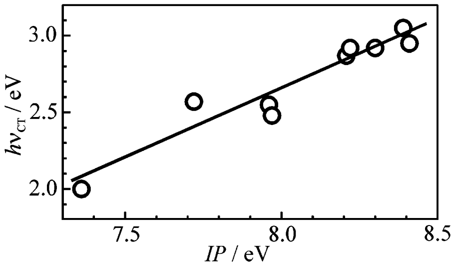


FIGURE 4. Plot of the energy at the absorption maximum of the MV^{2+} colored clathrate against the ionization potential (IP) of its neutral guest. The plots show the Mulliken linear relationship. The neutral guest and chemical formula of its clathrate are as follows (IP given in eV in parentheses): 1,2,4-trimethoxybenzene, $[Cd_5(CN)_{11.28}Cl_{1.72}]\cdot[^3/_2MV^{2+}\cdot C_6H_3(OCH_3)_3]$ (7.36); aniline, $[Cd_6(CN)_{14}(C_6H_5NH_2)]\cdot[MV^{2+}\cdot 2C_6H_5NH_2]$ (7.72); *o*-dimethoxybenzene, $[Cd_3(CN)_{6.553}Cl_{1.447}(H_2O)]\cdot[MV^{2+}\cdot C_6H_4(OCH_3)_2]$ (7.96); 1-methylnaphthalene, $[Cd_3(CN)_{6.384}Cl_{1.616}]\cdot[MV^{2+}\cdot C_{10}H_7CH_3]$ (7.97); pyrrole, $[Cd_{7/2}(CN)_9(H_2O)]\cdot[MV^{2+}\cdot C_4H_4NH]$ (8.21); *p*-cresol, $[Cd_3(CN)_7Cl]\cdot[MV^{2+}\cdot 2CH_3C_6H_4OH]$ (8.22); *o*-cresol, $[Cd_3(CN)_8(H_2O)_2]\cdot[MV^{2+}\cdot 2CH_3C_6H_4OH]$ (8.30); *m*-cresol, $[Cd_3(CN)_8]\cdot[MV^{2+}\cdot ^3/_2CH_3C_6H_4OH\cdot 2H_2O]$ (8.39); mesitylene, $[Cd_3(CN)_6Cl_2]\cdot[MV^{2+}\cdot C_6H_3(CH_3)_3]$ (8.41).

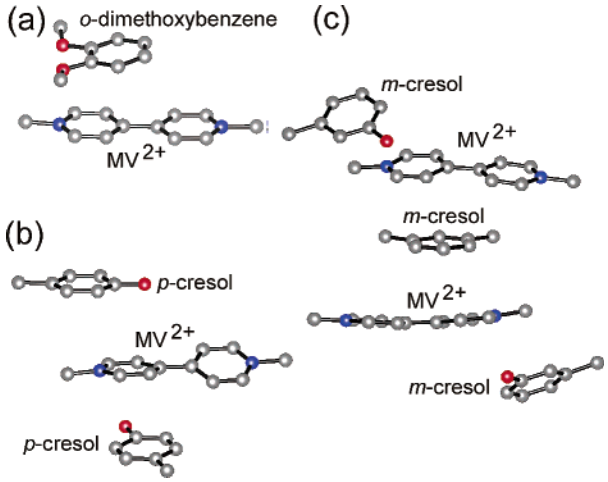


FIGURE 5. Examples of CT complexes found in the MV^{2+}–G clathrates: (a) $MV^{2+}/G = 1:1$ complex; the donor is *o*-dimethoxybenzene; (b) $MV^{2+}/G = 1:2$ complex; the donor is *p*-cresol; (c) $MV^{2+}/G = 2:3$ complex; the donor is *m*-cresol.

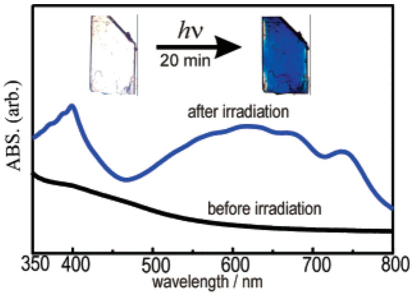


FIGURE 6. The change of diffuse reflectance spectra of the MV^{2+}–diethyl ether clathrate before and after UV irradiation.

CT transitions observed in acetonitrile solutions, those in the colored clathrates were ca. 0.6 eV lower on average. It is well-known that the excitation energy of a CT complex is lowered when the distance between donor and acceptor is decreased, and this is true in cases of ordinary neutral CT complexes. In a clathrate, a decrease in the donor–acceptor distance might occur due to encapsulation of the CT complex. However, in our clathrates, this effect cannot be the reason for the red shift. In the excited state, where MV^{2+} and G become $MV^{+\bullet}$ and G^+, respectively, due to one electron transfer from G to MV^{2+}, the electrostatic repulsion between $MV^{+\bullet}$ and G^+ will cause an increase in the energy of the excited state as the donor–acceptor distance is decreased. This effect introduces a blue-shift rather than a red shift.[27,28] Our ab initio calculations on the MV^{2+}–*o*-dimethoxybenzene CT complex, surrounded by the host framework and other CT complex guests, revealed that the array structure of the CT complex guests plays an important role in the red shift. The arrangement of MV^{2+} ions in this clathrate is very characteristic; the MV^{2+} ions line up and the adjacent MV^{2+} ions are in contact with each other (Figure 3b). This situation increases the energy of the ground state of the CT complex. On the other hand, this electrostatic repulsion is relaxed in the excited state because MV^{2+} receives one electron from *o*-dimethoxybenzene to become a mono-positive cation, $MV^{+\bullet}$. This scheme reduces the energy gap between the ground and the excited state, giving rise to the large red shift in the excitation energy of the CT complex. The arrangement of MV^{2+} ions found here is peculiar to the PCPC host clathrate. A column structure with MV^{2+} and a donor stacked alternately is usual for such a CT complex formed with a planar donor and acceptor. Probably, the energy of the repulsion between MV^{2+} ions is absorbed in the lattice energy of the negatively charged PCPC host.

The colorless clathrates become blue upon irradiation with UV or sunlight in air.[24,25] The spectral change in this photoinduced color change is shown in Figure 6. The spectrum after the color change indicated the presence of $MV^{+\bullet}$, which is the product of the one electron reduction of MV^{2+}. Electron spin resonance (ESR) spectra supported the generation of the mono-positive radical. The yield of the radical was estimated to be 2–3%. The degree of this color change depends on the ionization potential of the neutral guest. The generation of $MV^{+\bullet}$ indicates that an electron is withdrawn from somewhere. Presumably, the host complex is involved in this electron transfer because after the color change a new weak signal appeared in the IR spectrum at 30 cm^{-1} higher than the original stretching mode of the cyanide ligand. There has been no clear evidence indicating that the electron source is the neutral guest. After the blue clathrate was left in the air for 5 days, the color was bleached. This bleaching was not observed under a N_2 atmosphere. Thus it appears that the bleaching is caused by O_2 in the air oxidizing $MV^{+\bullet}$ to MV^{2+}. The coloration and bleaching can be repeated but is limited to several cycles (Figure 7). In this cyclic process, other complicated radical species, which have not been assigned, were generated.

DQ^{2+}–G Clathrates.[29] In the case of DQ^{2+}, more than 40 new clathrates were obtained (Figure 8). Among them, nine crystal structures have been solved. Interestingly, the structures solved were all isostructural independent of the neutral guest species. The cavity has a 1D channel

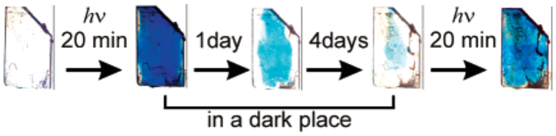


FIGURE 7. The UV irradiation and bleaching cycle of the MV^{2+}–diethyl ether clathrate. The cycle was performed in air.

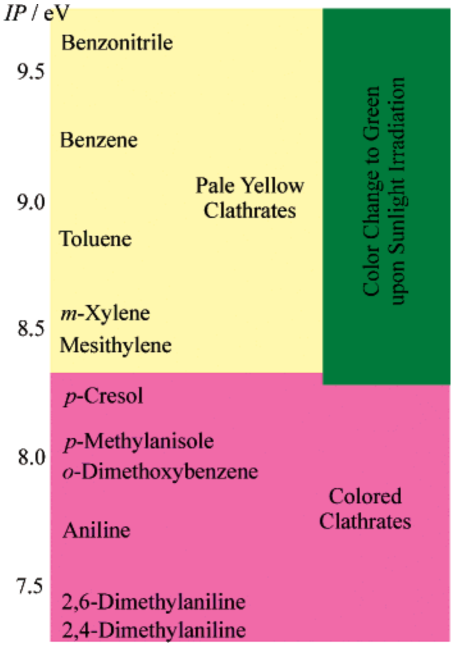


FIGURE 8. Some examples of DQ^{2+}–G PCPC clathrates. The neutral guest (G), its ionization potential (IP), and the classification are indicated.

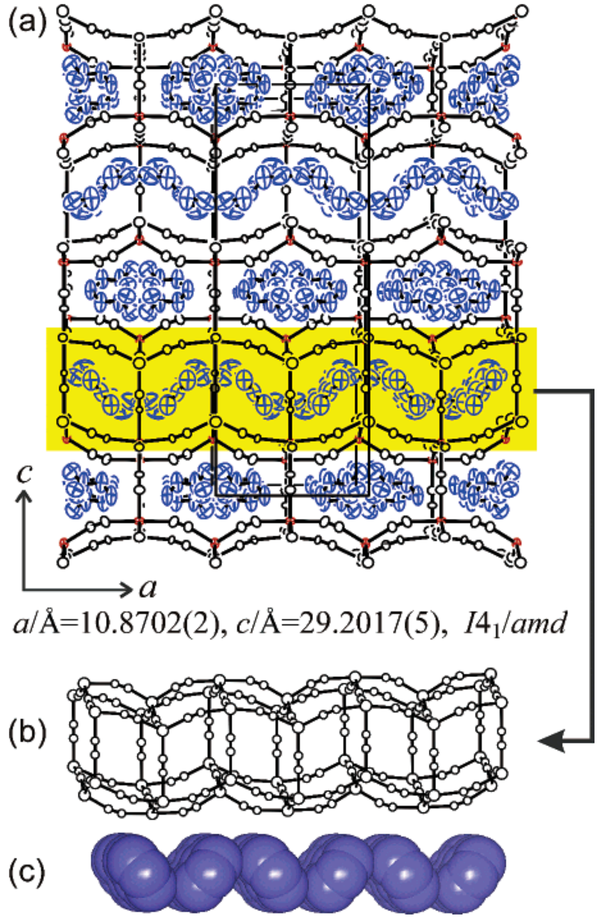


FIGURE 9. Crystal structure of a DQ^{2+}–*m*-xylene clathrate, $[Cd_4(CN)_{10}]\cdot[DQ^{2+}\cdot C_6H_4(CH_3)_2]$: (a) a perspective view along the *b* axis showing that 1D channel cavities stack along a 4_1 screw axis parallel to the *c* axis; (b) the structure of the 1D channel cavity; (c) the array of the guests DQ^{2+} and *m*-xylene found in the 1D channel cavity. A precise view of the guests is unclear because of a structural disorder coming from the crystal symmetry.

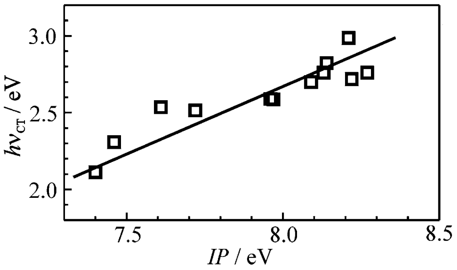


FIGURE 10. Plot of the energy at the absorption maximum of the DQ^{2+} colored clathrate $[Cd_4(CN)_{10}]\cdot[DQ^{2+}\cdot G]$ against the ionization potential (IP) of its neutral guest (G). The plots show the Mulliken linear relation. Guests are as follows (IP in eV given in parentheses): 2,4-dimethylaniline (7.40); 2,6-dimethylaniline (7.46); 3,5-dimethylaniline (7.61); aniline (7.72); *o*-dimethoxybenzene (7.96); 1-methylnaphthalene (7.97); *p*-methylanisole (8.09); 1-chloronaphthalene (8.13); *m*-methylanisole (8.14); anisole (8.21); *p*-cresol (8.22); 1,2,4-trimethylbenzene (8.27).

structure, and the stacking of these 1D channel cavities is guided by a 4_1 screw axis. The host structure of a clathrate of DQ^{2+} and *m*-xylene is shown in Figure 9. The precise shape and position of the DQ^{2+} and the *m*-xylene guest could not be determined because of a structural disorder. Probably, DQ^{2+} and the neutral guest are arrayed alternately in the 1D channel. The contact between the adjacent guests in the 1D channel occurs at peripheral parts of the guests because the 1D channel runs not straight but zigzag. The DQ^{2+} clathrates also were classified into two groups based on color, colored or pale yellow. (The original color of DQ^{2+} is pale yellow rather than colorless.) The plot of excitation energy vs *IP* of G for the colored clathrates showed the Mulliken linear relationship (Figure 10), which indicates the existence of CT interaction between DQ^{2+} and G. The CT transition observed here showed a red shift similar to that observed in the MV^{2+} clathrates. The pale yellow clathrates changed to light green upon sunlight irradiation under a N_2 atmosphere (Figure 11). In the air, no color change occurred. However, the light green color was not bleached for several months in the air. The host works well as a shield from air oxidation. The origin of the light green color is $DQ^{+\bullet}$ that was generated from the one electron reduction of DQ^{2+}. The electron source of this electron transfer has not been determined. X-ray analysis of the light green clathrate, however, showed a slight distortion over the whole host framework with a lowering of the crystal symmetry. Undoubtedly, the host received structural damage in the photoinduced color change. This might suggest that the host is involved in the electron transfer.

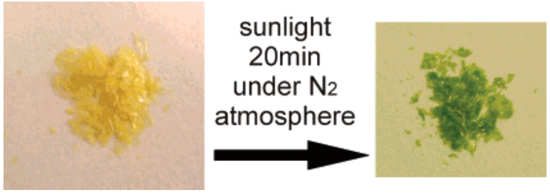


FIGURE 11. Color change of the DQ^{2+}–*m*-xylene clathrate upon sunlight irradiation.

Table 1. Spectral and Structural Data for the CCl_4-Guest Clathrates

	spectral data, ν/cm^{-1}			
compound^b	A_1	E	F_2 ^{a}	F_2
neat	459	218	785, 761; *773*	314
I	460 (+1)	218 (0)	789, 766; *778* (+5)	316 (+2)
II	460 (+1)	223 (+5)	790, 766; *778* (+5)	315 (+1)
III	459 (0)	222 (+4)	793, 765; *779* (+6)	319 (+5)
IV	460 (+1)	225 (+7)	796, 773; *785* (+12)	321 (+7)

	structural data				
compound^b	a, Å	V_{cell}, Å^3	V_{cav}, Å^3	V_{molec}, Å^3	P_c
neat				160.7	1
I	12.714(1)	2055.2(5)	131.9	160.7	1.22
II	12.243(1)	1835.1(5)	114.7	160.7	1.41
III	12.189(2)	1810.9(9)	113.2	160.7	1.43
IV	11.771(2)	1631(1)	101.9	160.7	1.59

^{a} The band is observed as a doublet due to Fermi resonance; the average value has been listed in italics. The band shift from that observed for the neat CCl_4 is shown in parentheses. ^{b} **I** = $[Cd(CN)_2]\cdot CCl_4$; **II** = $[CdZn(CN)_4]\cdot 2CCl_4$; **III** = $[CdCu(CN)_4]\cdot[NMe_4\cdot CCl_4]$; **IV** = $[ZnCu(CN)_4]\cdot[NMe_4\cdot CCl_4]$.

Chemical Pressure against Guest Molecule

It is not unusual in clathrate structures that a guest molecule is imprisoned in a cavity the effective volume, V_{cav}, of which is considerably smaller than the volume of the molecule, V_{molec}, in the condensed phase under ambient conditions. For example, the cubic high-cristobalite-like host of $[Cd(CN)_2]\cdot CCl_4$ provides V_{cav} of 131.9 Å^3 with the guest CCl_4 molecule, which occupies 160.7 Å^3 as the mean V_{molec} (V_{molec} = [molar volume]/[Avogadro constant]) in its neat liquid state at 25 °C (see Table 1). Thus, the guest CCl_4 molecule is imprisoned in the cavity with a volume 18% smaller than that in the neat liquid state. To the zeroth-order approximation, we may define the chemical pressure, P_c, in the clathrate cavity as follows: first, assume PV = constant under ambient conditions; second, the external pressure P being at 1 atm, $P_c/\text{atm} = (V_{mol}/V_{cav})/(P/\text{atm}) = |V_{mol}/V_{cav}|$; the CCl_4 guest in the $[Cd(CN)_2]$ host is seen to be under the chemical pressure of 1.22 (= 160.7/131.9) atm. Certainly, this isotropic definition of P_c is too rough for the guest enclathrated in an essentially anisotropic crystal structure. The real "chemical pressure" should be anisotropic in the crystal phase. In other words, the host–guest and guest–guest interactions are well interpreted in terms of the chemical pressure in the anisotropic crystal structure.

Effects of chemical pressure may be observed in the vibrational spectroscopic behavior of guest molecules, including the anisotropic character of the cavity. IR spectroscopy is a convenient tool to ascertain the enclathration of a guest in a newly prepared clathrate based on the appearance of IR bands characteristic of the guest molecule. For example, in Hofmann-type benzene clathrates, the A_{2u} out-of-plane CH bending mode has been observed shifted to higher frequency by ca. 20–40 cm^{-1} than the band at 675 (673) cm^{-1} observed for the solid (liquid) C_6H_6. We may ascribe a high-frequency shift (high shift) to higher chemical pressure and a low-frequency shift (low shift) to lower chemical pressure with respect to the relevant vibrational modes of the guest molecule.

The FT-Raman and FT-IR (ν_3 only) bands observed for CCl_4 in the high-cristobalite-like host clathrates $[Cd(CN)_2]\cdot CCl_4$ (**I**), $[CdZn(CN)_4]\cdot 2CCl_4$ (**II**), $[CdCu(CN)_4]\cdot[N(CH_3)_4\cdot CCl_4]$ (**III**), and $[ZnCu(CN)_4]\cdot[N(CH_3)_4\cdot CCl_4]$ (**IV**) are compared with those for the neat CCl_4 in Table 1. The $Fd\bar{3}m$ unit cell lattice constant, a, decreases from 12.714 Å for **I** to 11.771 Å for **IV**; the resulting decrease of the cavity volume implies an increase of chemical pressure in the cavity. Although the totally symmetric A_1 mode appears not to be affected by the chemical pressure, the other three modes do show a high shift with the smaller V_{cav}, that is, under the higher chemical pressure.

The anisotropic character of chemical pressure has been exemplified distinctly for another series of isostructural host clathrates, $[Cd\{HN(CH_2CH_2)_2NH\}Ni(CN)_4]\cdot CH_2X_2$ (X = Cl, Br, or I). The guest CH_2X_2 molecules are arrayed linearly with respect to the X–C–X in the zigzag channel cavities, as is shown in Figure 12.[30] Although the unit cell dimensions increase successively from Cl to I, the intermolecular distance between adjacent X atoms, $r_{X\cdots X}$, decreases in comparison to the van der Waals contact, $2r_{vdW}$, as listed in Table 2. For CH_2Cl_2, the $r_{X\cdots X}$ distance is longer than the van der Waals contact, $2r_{vdW}$, for CH_2Br_2, both are nearly equal to each other, and for CH_2I_2, the distance is shorter than the contact distance. These geometries lead to a lower chemical pressure for CH_2Cl_2, almost the same for CH_2Br_2, and a higher one for

Table 2. Spectral and Structural Data for $[Cd\{HN(CH_2CH_2)_2NH\}Ni(CN)_4]\cdot CH_2X_2$ (X = Cl, Br, or I)

	CH_2Cl_2			CH_2Br_2			CH_2I_2		
vibrational mode	ν (cm^{-1}) neat	ν (cm^{-1}) guest	$\Delta\nu$ (cm^{-1})	ν (cm^{-1}) neat	ν (cm^{-1}) guest	$\Delta\nu$ (cm^{-1})	ν (cm^{-1}) neat	ν (cm^{-1}) guest	$\Delta\nu$ (cm^{-1})
CX str. A_1	705	695	−10	577	576	−1	486	487	+1
CX str. B_2	740	728	−12	640	636	−4	572	579	+7
CX_2 bend A_1	286	289	+3	173	177	+4	120	129	+9

	CH_2Cl_2	CH_2Br_2	CH_2I_2
$r_{X\cdots X}$ (Å)	3.755(8)	3.699(3)	3.670(2)
$2r_{vdW}$ (Å)	3.50	3.70	3.96

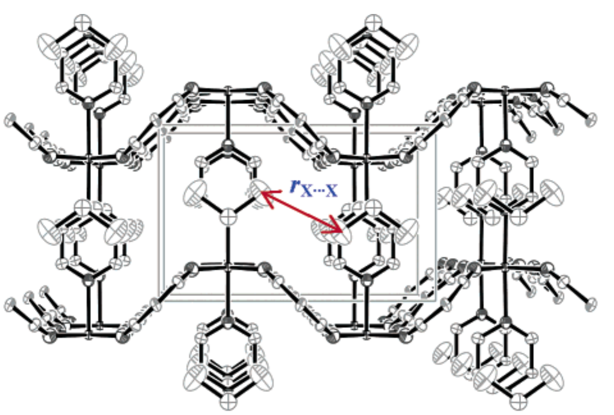


FIGURE 12. Structure of $[Cd\{HN(CH_2CH_2)_2NH\}Ni(CN)_4]\cdot CH_2Cl_2$; projection along the *c* axis.

CH_2I_2, with respect to the molecular contact along the cavity channel. Both symmetric and antisymmetric C−X stretching modes shift to lower frequency for X = Cl, to lower frequency but to a lesser extent for Br, and to higher frequency for I. The X−C−X bending modes are, however, observed with high shifts for all three. The *c* dimension of the unit cell is ca. 7.5 Å for all three clathrates,[30] and the three guest molecules are sandwiched in a similar manner by the piperazine ligands in the channel cavity. Hence the steric hindrance from the cavity wall to the X−C−X bending mode causes the high shift, the higher for the greater X. Thus, the spectral behavior reflects the anisotropic character of the channel cavity, that is, the anisotropy of the chemical pressure.

Since both guest dihalogenomethane and host piperazine ligand contain CH_2 groups, it is difficult to evaluate in detail the chemical pressure effect on the spectral shifts in the CH_2 stretching, bending, twisting, wagging, and rocking modes; observations for the deuterated CD_2X_2 guests are in progress.

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