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Polycyano–polycadmate host clathrates including a methylviologen dication. Syntheses, crystal structures and photo-induced reduction of methylviologen dication †

Hirofumi Yoshikawa,[a] Shin-ichi Nishikiori,*[a] Tokuko Watanabe,[b] Toshimasa Ishida,[c] Go Watanabe,[c] Makoto Murakami,[c] Kinga Suwinska,[d] Roman Luboradzki[d] and Janusz Lipkowski[d]

[a] *Department of Basic Science, Graduate School of Arts and Sciences, The University of Tokyo, 3-8-1, Komaba, Meguro, Tokyo 153-8902, Japan. E-mail: cnskor@mail.ecc.u-tokyo.ac.jp*
[b] *Tokyo University of Fisheries, 4-5-7, Konan, Minato-ku, Tokyo 108-8477, Japan*
[c] *Applied Science, Faculty of Engineering, Shizuoka University, Hamamatsu 432-8561, Japan*
[d] *Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01224 Warsaw, Poland*

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A series of polycyano–polycadmate host clathrates including a methylviologen dication (MV^{2+}), which is a strong electron acceptor, and an organic molecule, such as alcohols, haloalkanes, ethers and small aromatics, and two complexes built of a polycyano–polycadmate and MV^{2+} have been synthesized. Single crystal X-ray diffraction experiments on ten clathrates and the two complexes revealed their 3-D network polycyano–polycadmate structures constructed with Cd^{2+} ions and CN^- bridges. The network structures are classified into five structure types. Type I, II and III were found in the clathrates, and Type IV and V were found in the two complexes. Type I and II have cage-like cavities and each of the cavities includes one guest, MV^{2+} or an organic molecule. Type III has a channel-like cavity where MV^{2+} ions and organic molecules are included. Type IV and V have 3-D cavities, the shape of which is neither cage-like nor channel-like, for embracing MV^{2+}. Although all compounds were colorless and the formation of a charge transfer complex between MV^{2+} and a neutral guest in the clathrates was not confirmed from the crystal structure data and diffuse reflectance spectra, some of them showed a color change from colorless to blue on UV irradiation, which arose from the reduction of MV^{2+} to a methylviologen radical cation $MV^{+\bullet}$.

Introduction

The polycyano–polycadmate host clathrate consists of a polycyano–polycadmate host, a cationic guest and a neutral guest.[1] The polycyano–polycadmate host is built of Cd^{2+} ions and cyano ligands that link two Cd^{2+} ions as ambidentate ligands. In many cases the Cd^{2+} ions adopt tetra- or a hexa-coordination. As a result, the polycyano–polycadmate host has a 3-D network structure. The length of the Cd–CN–Cd bridge is *ca.* 5.5 Å, so that the 3-D network has void space in its inside, and which is large enough to accommodate a guest molecule. The general formula of the polycyano–polycadmate host is represented by $[Cd_x(CN)_y]^{2x-y}$.[1–7] The electric charge of the host depends on the numbers of Cd^{2+} and CN^-, or the coordination form of Cd^{2+}. In many cases, the electric charge has a minus value, so that counter cations are necessary and they are included in the 3-D network. Such counter cations are denoted cationic guests and monopositive cations such as $N(CH_3)_4^+$, $S(CH_3)_3^+$, $NH_2(CH_2)_3NH(CH_3)_2^+$, *etc.*, are usually used. Besides a cationic guest, the host can include small organic molecules with no electric charge. These organic molecules are denoted neutral guests. As a neutral guest, many small organic compounds can be used, such as aromatics, haloalkanes, ethers and alcohols.

Researches concerning polycyano–polycadmate host clathrates have concentrated on their structural interest and no reports about their applications can be found. We believe that developing functionalized materials with chemical and physical properties using polycyano–polycadmate hosts is of worth. For this purpose, to introduce a chemically active guest molecule into the host is necessary, because it is not expected to observe chemically interesting properties from the polycyano–polycadmate host itself. However, attempts to synthesize clathrates including such neutral guest molecules have given no useful results so far. There seem to be limitations upon the size of the neutral guest for a polycyano–polycadmate host. Another possible way is to use a chemically active cationic guest. According to this line, we chose a methylviologen dication MV^{2+} (1,1′-dimethyl-4,4′-bipyridinium dication, Fig. 1) as a cationic guest. MV^{2+} is known as a strong electron acceptor and is easily reduced to a monopositive cation radical $MV^{+\bullet}$ by chemical and photo-chemical treatment. For this reason, MV^{2+} has been widely used in photochemistry, electrochemistry, solar energy conversion and in related fields.[8,9] Using MV^{2+} as a cationic guest, we have synthesized a series of polycyano–polycadmate host clathrates including MV^{2+} and a neutral guest. In these clathrates both colorless [10] and colored species were observed.[11] In our recent paper, charge-transfer (CT) interactions between MV^{2+} and a neutral guest has been revealed in the colored clathrates,[11] and details will be reported elsewhere. In this paper we concentrate upon the colorless

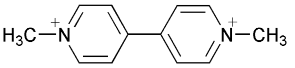

Fig. 1 Methylviologen dication (MV^{2+}).

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† Electronic supplementary information (ESI) available: the results of elementary analysis, a table of selected inter-atomic distances, figures of crystal structures, a picture of dichroism and EPR spectrum. See http://www.rsc.org/suppdata/dt/b1/b111059d/

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clathrates. In these some showed a color change from colorless to blue on UV irradiation. However, the degree of the color change was different for each clathrate. This finding indicates that the properties of MV^{2+} as an electron acceptor are retained in polycyano–polycadmate hosts but are affected by the clathrate structure.

In this work, two Cd cyano complexes, which have a 3-D network of a polycyano–polycadmate surrounding MV^{2+} but contain no neutral guest, have been also prepared. Crystal structures of ten colorless clathrates and the two Cd complexes are presented below. All network structures revealed here show zeolite-like structures.[4] They are also new structures and are classified into five structure types (Types I–V). After the description of the crystal structures, their response to light will be demonstrated. The reduction from MV^{2+} to $MV^{+\bullet}$ on UV irradiation and the stability of $MV^{+\bullet}$ generated in the clathrates will be discussed based on results of UV–VIS, EPR and IR spectroscopy.

Experimental

Syntheses and characterization

Type I, II, III clathrates and the Cd complex $[MV^{2+}][Cd_3(CN)_7Cl]$ (IV-1). $K_2Cd(CN)_4$ (5 mmol, 1.47 g), $CdCl_2\cdot 2.5H_2O$ (5 mmol, 1.14 g) and $MVCl_2$ (methylviologen dichloride, 2 mmol, 0.50 g) were dissolved in water (50 ml). After the solution was filtered, a neutral guest compound: ethers, alcohols, haloalkanes, benzene, toluene, *etc.*, was poured onto the filtrate, and then the mixture was left at room temperature. After several days colorless clathrates were obtained in a crystalline or powdered state. Crystals of **IV-1** were obtained from the host solution with no neutral guest at 277 K after several days. When benzene was used as a neutral guest, two types of benzene clathrates were obtained. One was a new benzene clathrate denoted **III-1** while the other was $[MV^{2+}][Cd_{3.5}(CN)_9(H_2O)]\cdot C_6H_6$ that had been already described in our previous report.[10] The above procedure always gave $[MV^{2+}][Cd_{3.5}(CN)_9(H_2O)]\cdot C_6H_6$. However when the pH of the host solution was adjusted to 8.1–8.3 by addition of citric acid, $[MV^{2+}][Cd_{3.5}(CN)_9(H_2O)]\cdot C_6H_6$ was obtained in most cases, but occasionally **III-1** appeared. The reproducibility of the production of **III-1** was poor and definitive preparative conditions for **III-1** were unclear.

Cd complex $[MV^{2+}][Cd_2(CN)_6]$ (V-1). An $AgNO_3$ aqueous solution ($AgNO_3$, 0.55 g, 3.24 mmol and water 5 ml) was added to an aqueous solution of $MVCl_2$ ($MVCl_2$ 0.34 g, 1.08 mmol and water 5 ml). After the white precipitate of AgCl was filtered off, $K_2Cd(CN)_4$ (2.06 g, 6.99 mmol) was added to the filtrate. The solution was left for one day at 277 K and colorless column crystals of **V-1** were obtained.

All clathrates and Cd cyano complexes prepared in this study are listed in Table 1. All compounds were colorless before UV irradiation. The presence of cyano groups and neutral guests was confirmed by IR spectroscopy.

Single crystal X-ray diffraction and structure determination

In the compounds listed in Table 1, the crystal structures of ten clathrates, **Ia-1** (1-butanol clathrate), **Ia-2** (nitromethane clathrate), **Ib-1** (1,2-dichloroethane clathrate), **IIa-1** (chloroform clathrate), **IIa-2** (acetonitrile clathrate), **IIa-3** (2-propanol clathrate), **IIb-1** (diethyl ether clathrate), **IIb-2** (ethanol clathrate), **III-1** (benzene clathrate), **III-2** (toluene clathrate), and two Cd complexes, **IV-1** and **V-1**, were determined by single crystal X-ray diffraction and their crystallographic and experimental data are summarized in Table 2. Each crystal was coated with epoxy resin in order to prevent spontaneous liberation of the neutral guest. For the collection of the diffraction data, a Rigaku AFC-5S four-circular diffractometer, a Rigaku R-AXIS RAPID imaging plate diffractometer and an Enraf-Nonius CCD diffractometer were used. All measurements were carried out at room temperature. The positions of Cd^{2+} ions were determined by the direct method using the SHELXS-86 program.[12] The crystal structures were refined by successive difference Fourier syntheses and full-matrix least-squares procedure using the SHELXL-97 program.[12] All atoms of the host were refined anisotropically. Hydrogen atoms were generated geometrically.

Structural distortion of a neutral guest molecule was observed in certain cases. Such distortion has often been seen in previous studies of polycyano–polycadmate host clathrates, where some of non-H guest atoms could not be positioned and in the worst case no guest atoms could be refined. The distortion arises from orientational disorder of the guest molecule. The main reason for the disorder is the non-coincidence of the molecular symmetry with the site symmetry of the crystal[4] and/or motional behavior of the guest molecule.[13]

Another problem in the structure determination of polycyano–polycadmate compounds is the difficulty in identifying C and N atom in a CN^- bridge linking two Cd^{2+} ions.[7,14] We here applied a reasonable criterion that the N atom of a cyano ligand was attached to an octahedral Cd^{2+} and the Cd–N distance is longer than the Cd–C distance.[4] In another case where a symmetrical feature, such as an inversion center or a mirror plane at the center of a CN^- bridge, exists, we adopted a hybrid atom (50% carbon and 50% nitrogen) for both atoms of the CN^- bridge.[4]

CCDC reference numbers 175538–175549.

See http://www.rsc.org/suppdata/dt/b1/b111059d/ for crystallographic data in CIF or other electronic format.

UV irradiation, physical measurements and theoretical calculations

The crystals of all samples were washed with ethanol and acetone, dried, powdered then irradiated for 90 min in the air with a Toshiba SHL100UV 100 W low-pressure mercury lamp (λ/nm = 365) and their color was checked visually with results listed in Table 1. UV–VIS diffuse reflectance spectra were measured on a JASCO V-570 UV–VIS spectrometer equipped with an ISN-470 integrating sphere accessory. The samples were washed with ethanol and acetone, powdered and packed into a flat cylindrical cell JASCO PSH-001 with a quartz window. Absorption spectra of a blue crystal of **IIb-1**, which is a 0.8 × 0.3 × 0.1 mm size single crystal irradiated by UV light for 90 min, were recorded on an Olympus BX60 polarizing microscope attached with a JASCO CT-25C spectrophotometer and a Hamamatsu photoelectron multiplier R316 detector. The orientation of the single crystal was confirmed by an X-ray diffraction method. EPR spectra were recorded on a JEOL JES-TE300 EPR spectrometer with a 100 kHz magnetic field modulation of 1 G and a microwave power of 1 mW at room temperature. The production yield of $MV^{+\bullet}$ was determined using a TEMPOL (4-hydroxy-2,2,6,6-tetramethyl piperidine-1-oxyl) radical benzene solution as a reference.[15] Microscopic IR spectra of a 0.4 × 0.3 × 0.1 mm size single crystal of **IIb-1** were recorded on a JASCO FT/IR-350 IR spectrometer equipped with a JASCO MICRO-20 microscopic measurement accessory. The energies of MV^{2+} and $MV^{+\bullet}$ were calculated at HF/6–31G** level, varying their dihedral angles of the two pyridinium rings in the range of 0 to 90° every 15°. The calculations were performed using a Gaussian98 program.[16]

Results and discussion

Crystal structures

General. In previous studies, it is demonstrated that the structure of the polycyano–polycadmate host can be of two types: "zeolite-like structure" and "clay-like structure". The

Table 1 Ionization energies of neutral guests, photo-responses and structural data for the prepared MV^{2+}–neutral guest clathrates

Neutral guest	[a]	I[b]/eV	[c]	ω[d]/°	Neutral guest	[a]	I[b]/eV	[c]	ω[d]/°
No guest	**IV-1**	—	B	59.9(4)	Ethyl acetate		10.01	D	
No guest	**V-1**	—	B	52.3(2)	1-Butanol	**Ia-1**	10.06	C	76.5(4)
Benzyl alcohol		8.5	A		2-Propanol	**IIa-3**	10.12	B	0
Toluene	**III-2**	8.82	B	0	2-Methyl-1-propanol		10.12	D	
Chlorobenzene		9.06	B		1-Propanol		10.22	B	
p-Difluorobenzene		9.16	B		Ethanol	**IIb-2**	10.47	C	0
Fluorobenzene		9.20	B		Methanol		10.85	C	
Diisopropyl ether		9.20	B		1,2-Dichloropropane		10.87	B	
Benzene	**III-1**	9.25	B	0	Nitromethane	**Ia-2**	11.02	D	71.9(2)
Diethyl ether	**IIb-1**	9.51	A	0	1,2-Dichloroethane	**Ib-1**	11.04	D	73.8(5)
Benzonitrile		9.62	B		Dichloromethane		11.32	D	
Acetone		9.71	B		Chloroform	**IIa-1**	11.37	C	0
2-Methyl-2-butanol		9.80	B		Carbon tetrachloride		11.47	D	
2-Butanol		9.88	B		Acetonitrile	**IIa-2**	12.13	D	0
2-Methyl-2-propanol		9.97	D						

[a] Compound number. [b] Ionization energy of the neutral guest. [c] Color after UV irradiation; A: deep blue, B: blue, C: slightly blue, D: no change. [d] Dihedral angle of MV^{2+} determined by the X-ray diffraction method.

Table 2 Crystallographic and selected experimental data

Compound	**Ia-1**	**Ia-2**	**Ib-1**	**IIa-1**	**IIa-2**	**IIa-3**
Neutral guest	1-Butanol	Nitromethane	1,2-Dichloroethane	Chloroform	Acetonitrile	2-Propanol
Formula	$C_{28}H_{24}N_{14}OCd_5$	$C_{26}H_{22}N_{16}O_5Cd_5$	$C_{27}H_{20}N_{14}Cl_3Cd_5$	$C_{28}H_{16}N_{16}Cl_6Cd_6$	$C_{30}H_{20}N_{18}Cd_6$	$C_{32}H_{36}N_{16}O_5Cd_6$
Formula weight	1134.65	1200.62	1208.96	1463.73	1307.08	1399.21
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*Cccm* (no. 66)	*Cccm* (no. 66)	*Pncm* (no. 53)[b]	*Pbca* (no. 61)	*Pbca* (no. 61)	*Pbca* (no. 61)
a/Å	10.970(6)	11.0655(2)	10.946(3)	13.6454(2)	13.794(8)	13.724(4)
b/Å	23.744(8)	23.9517(7)	23.705(3)	27.2037(4)	26.990(6)	27.269(6)
c/Å	15.906(5)	15.7838(3)	15.847(4)	13.5497(2)	13.665(5)	13.569(5)
U/Å^3	4143(3)	4183.3(2)	4112(1)	5029.7(1)	5088(3)	5078(2)
Z	4	4	4	4	4	4
μ(Mo-Kα)/mm^{-1}	2.545	2.536	2.756	2.825	2.482	2.500
Unique reflections,	3138	2480	4900	5660	7429	7409
Used reflections	1897 ($F_o > 3\sigma(F_o)$)	2480 (all reflections)	1885 ($F_o > 3\sigma(F_o)$)	5660 (all reflections)	2658 ($F_o > 3\sigma(F_o)$)	3516 ($F_o > 3\sigma(F_o)$)
$R(F)$, $wR(F^2)$	0.0586, 0.1466	0.0346,[a] 0.0995	0.0716, 0.1356	0.0379,[a] 0.1121	0.0776, 0.1807	0.0745, 0.1956

Compound	**IIb-1**	**IIb-2**	**III-1**	**III-2**	**IV-1**	**V-1**
Neutral guest	Diethyl ether	Ethanol	Benzene	Toluene	—	—
Formula	$C_{34}H_{38}N_{16}O_4Cd_6$	$C_{30}H_{36}N_{16}O_7Cd_6$	$C_{30}H_{20}N_{14}Cd_5$	$C_{31}H_{22}N_{14}Cd_5$	$C_{19}H_{18}N_9O_2ClCd_3$	$C_{18}H_{14}N_8Cd_2$
Formula weight	1409.25	1407.19	1138.64	1152.67	777.10	567.19
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Triclinic	Monoclinic
Space group	*Pbca* (no. 61)	*Pbca* (no. 61)	*Icmm* (no. 74)[b]	*Icmm* (no. 74)[b]	$P\bar{1}$ (no. 2)	*C*2/*c* (no. 15)
a/Å	13.718(7)	13.740(6)	11.1290(5)	11.4002(4)	8.668(2)	10.015(4)
b/Å	27.232(5)	27.03(1)	23.697(1)	23.404(1)	24.15(1)	14.675(3)
c/Å	13.639(5)	13.647(6)	15.7539(6)	15.6457(4)	8.438(2)	15.034(1)
α/°	—	—	—	—	96.96(4)	—
β/°	—	—	—	—	116.23(2)	93.17(2)
γ/°	—	—	—	—	115.54(3)	—
U/Å^3	5095(3)	5068(3)	4154.7(3)	4174.4(3)	1319(1)	2206.1(9)
Z	4	4	4	4	2	4
μ(Mo-Kα)/mm^{-1}	2.491	2.508	2.537	2.526	2.513	1.935
Unique reflections	7422	7380	2484	3229	7697	3233
Used reflections	3443 ($F_o > 3\sigma(F_o)$)	4117 ($F_o > 3\sigma(F_o)$)	2484 (all reflections)	3229 (all reflections)	4691 ($F_o > 3\sigma(F_o)$)	2265 ($F_o > 3\sigma(F_o)$)
$R(F)$, $wR(F^2)$	0.0702, 0.1770	0.0623, 0.1706	0.0605,[a] 0.1741	0.0276,[a] 0.0741	0.0553, 0.1358	0.0388, 0.0871

[a] Calculated using reflections with $F_o^2 > 2\sigma(F_o^2)$. [b] A non-standard setting was used for easy comparison of the crystal structures.

term " zeolite-like structure" indicates structural similarities to zeolites, although hexa- and penta-coordinated centers exist in the polycyano–polycadmate network besides tetrahedral connecting centers.[1,4] On the other hand, "clay-like structure" means a layered structure host like clay minerals.[1,5] All structures of the twelve polycyano–polycadmate networks here belong to zeolite-like structure in which Cd^{2+} ions and CN^- bridges make an infinite 3-D network. Moreover, they are classified into five structure types based on similarity of their actual crystal structures: Type I (**Ia-1**, **Ia-2**, **Ib-1**); Type II (**IIa-1**, **IIa-2**, **IIa-3**, **IIb-1**, **IIb-2**); Type III (**III-1**, **III-2**); Type IV (**IV-1**) and Type V (**V-1**). Besides this classification, it is also helpful for understanding the 3-D network structure to classify the zeolite-like structure into three categories from the viewpoint of the dimension and structure of the cavity. The first category is a 3-D network with cage-like cavities, whose structural dimension is zero. The second is a 3-D network with a channel-like cavity whose shape is a tube running one dimensionally. The third is a 3-D network with a 3-D structure cavity. The cavity structure of the third category is neither cage-like nor channel-like, and their boundaries cannot be determined clearly. These three categories have been found in the twelve compounds. Type I and II

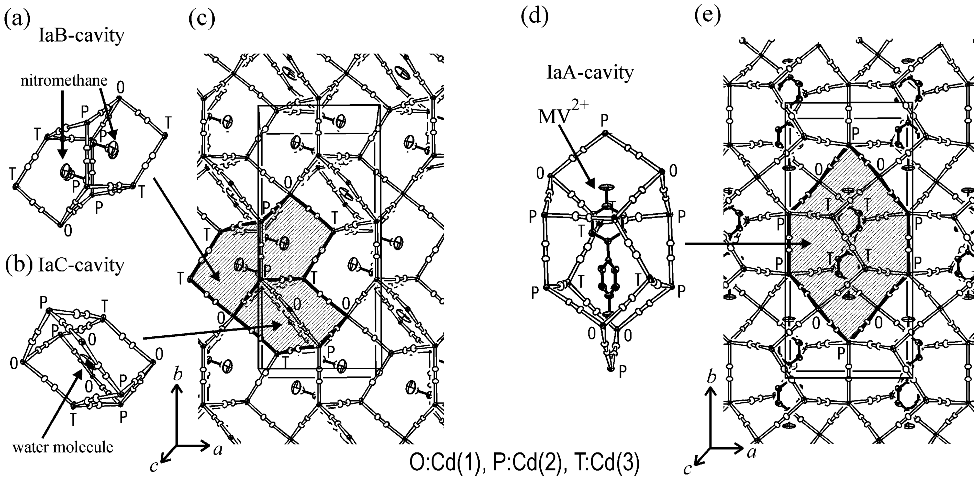

Fig. 2 Crystal structure of the nitromethane clathrate **Ia-2**. (a) IaB cage-like cavity and two guest nitromethane molecules. (b) IaC cage-like cavity and a guest water molecule. (c) Crystal structure in the range $c = -0.25$ to $+0.25$ viewed along the *c* axis. The arrangement of IaB and IaC cavities is shown. (d) IaA cage-like cavity and MV^{2+}. (e) Crystal structure in the range $c = 0$ to $+0.5$ viewed along the *c* axis. The arrangement of IaA cavities is shown.

have cage-like cavities of the first category, and in Type III there is a channel-like cavity of the second category. Type IV and V belong to the third category.

In polycyano–polycadmate 3-D network structures a number of structural variations exist. A method for describing the structures of the 3-D networks and the cavities is necessary. In this paper we apply a method similar to that used for the discussion of the structures of zeolites[17] and $[Cd_3(CN)_7]^-$ type host clathrates in previous work.[4] In our method, a polycyano–polycadmate 3-D network is considered to be assembly of polygons that are defined by vertices of Cd^{2+} ions and edges of Cd–CN–Cd linkages. It should be noted that the polygon defined in the above way is not always planar. The cavity formed in the 3-D network is considered to be a polyhedron made of the polygons. The polygons must act as a cavity wall that divides space into the inside and outside of the cavity. However, the span between two Cd^{2+} ions in a Cd–CN–Cd edge is *ca.* 5.5 Å, so that a window is generated at the center of the polygon. If the window is large the polygon cannot act as a partition. We considered that a quadrangle and a pentagon could be a cavity wall based on our investigation of the twelve crystal structures; for a hexagon, however, it depends on each situation. Each actual case will be treated in the following sections. For the first and second category, this method works well and is useful to understand cavity structures. However, for the third category it does not work well; indeed where this method does not work well can be defined as the third category.

In following sections, the following notations will be used: O for a hexa-coordinated (octahedral) Cd^{2+}, P for a penta-coordinated Cd^{2+}, T for a tetra-coordinated (tetrahedral) Cd^{2+}; (–O–T– ··· –) for a polygon, for example, (–T–O–T–O–) for a quadrangle whose periphery is made of a cyclic chain of –NC–Cd(T)–CN–Cd(O)–NC–Cd(T)–CN–Cd(O)– linkage; $[4^a\ 5^b\ 6^c]$ for an *n*-hedron ($n = a + b + c$), for example, $[4^3\ 6^3]$ for a hexahedron with three quadrangular faces and three hexagonal faces.[17]

Type Ia: $[MV^{2+}][Cd_5(CN)_{12}]\cdot CH_3(CH_2)_3OH$ (Ia-1) and $[MV^{2+}][Cd_5(CN)_{12}]\cdot 2CH_3NO_2\cdot H_2O$ (Ia-2). Type I structures have a common formula $[MV^{2+}][Cd_5(CN)_{12}]\cdot n\text{G}\cdot m\text{H}_2\text{O}$, but are divided into two sub-groups, Type Ia and Type Ib, based on the difference of their space groups. A Type Ia host consists of three independent Cd^{2+} ions, hexa-coordinated Cd(1)(O), penta-coordinated Cd(2)(P), and tetra-coordinated Cd(3)(T) in a ratio of 1 : 2 : 2. Their site symmetries are 2/*m* for Cd(1)(O), 2 for Cd(2)(P) and *m* for Cd(3)(T), respectively. All cyano groups act as CN^- bridges between the Cd^{2+} ions to build a 3-D network, in which three types of cage-like cavities, IaA, IaB, IaC, are formed. The IaA cavity has an octahedral shape with four (–O–P–P–T–T–) and four (–O–P–O–T–P–) pentagonal faces, so that IaA cavity is denoted as $[5^8]$. The IaB cavity is a hexahedron $[4^2 5^4]$ with two (–O–P–T–P–) quadrangles and four (–O–P–P–T–T–) pentagonal faces. The IaC cavity is a hexahedron $[4^2 5^4]$ with two (–O–P–T–P–) quadrangles and four (–O–P–T–O–P–) pentagons, and its shape is similar to that of a IaB cavity. The IaA and IaB cavities include MV^{2+} and a neutral guest, respectively. In **Ia-1**, the IaC cavity is empty, but in **Ia-2** the IaC cavity includes one water molecule. Fig. 2(a), (b) and (d) illustrate the structures of the three cavities of **Ia-2**. Fig. 2(c) and (e) are the projective views of the crystal of **Ia-2** along the *c* axis. They illustrate the crystal structure in the range $c = -0.25$ to $+0.25$ and that in the range $c = 0$ to $+0.5$, respectively. Fig. 2(c) shows the arrangement of the IaB and IaC cavities. The IaB and IaC cavities share a (–O–P–T–P–) quadrangular face. In Fig. 2(e) the arrangement of IaA cavities is shown. Four IaB and four IaC cavities are in contact with one IaA cavity from the front and the rear sides of the Ia-A cavity.

The site symmetry at the center of MV^{2+} trapped in IaA cavity is 222, and the long molecular axis of MV^{2+}, which is the axis runs from one methyl group to the other one, is on a two-fold axis parallel to the *b* axis. Therefore, MV^{2+} has a non-planar geometry. The dihedral angles of the two pyridinium rings of MV^{2+} are 76.5(4) and 71.9(2)° in **Ia-1** and **Ia-2**, respectively. The nearest distance between MV^{2+} and the polycyano–polycadmate host is 2.79(1) Å for **Ia-1** and 2.858(7) Å for **Ia-2**.

In **Ia-1** the electron density for the neutral guest 1-butanol was found on the mirror plane of IaB cavity, whose symmetry is 2/*m*. However, the molecular shape of 1-butanol was unclear because of the reasons mentioned in the Experimental section. In the IaB cavity of **Ia-2**, two nitromethane molecules, which are related to each other by the inversion center of the cavity, were found. Their N–C bonds lie on the mirror plane and this plane bisects their O–N–O angles. The nitromethane molecules have no structural disorder as shown in Fig. 2(a). The guest water molecule of **Ia-2** lies at the center of a IaC cavity, whose site symmetry is 2/*m*.

Type Ib: $[MV^{2+}][Cd_5(CN)_{12}]\cdot 1.5\ ClCH_2CH_2Cl$ (Ib-1). Although the crystal symmetry of **Ib-1**, space group *Pncm*, is lower than that of Type Ia, space group *Cccm*, the host of **Ib-1** has the same topology of Type Ia. The effect of the low symmetry appears in the number of independent Cd^{2+} ions. There are five Cd^{2+} ions, Cd(1)(O1), Cd(2)(O2), Cd(3)(P), Cd(4)(T1) and Cd(5)(T2). The octahedral Cd^{2+} ions lie at independent sites with 2/*m* symmetry and the tetrahedral ones lie at

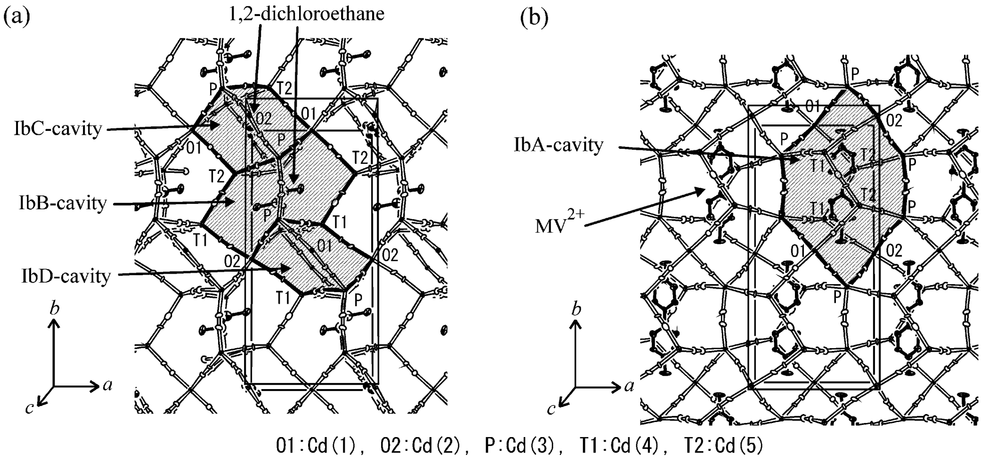

Fig. 3 Crystal structure of the 1,2-dichloroethane clathrate **Ib-1**. (a) Crystal structure in the range $c = -0.3$ to $+0.3$ viewed along the c axis. The arrangement of IbB, IbC and IbD cavities is shown. Each of the IbB and IbC cavities includes a guest 1,2-dichloroethane molecule. (b) Crystal structure in the range $c = 0$ to $+0.5$. The arrangement of the IaA cavities, which include MV^{2+}, is shown.

independent sites with m symmetry while Cd(3)(P) lies at a general position. The low crystal symmetry reflects on its cavity structure. In **Ib-1**, there are four types of cage-like cavities, IbA, IbB, IbC and IbD. The IaA and IaB cavities of Type Ia correspond to IbA and IbB cavities of **Ib-1**, respectively; their respective guests are MV^{2+} and a 1,2-dichloroethane molecule. On the other hand, IaC cavities of Type Ia are divided into two types of cavities, IbC and IbD, in **Ib-1**. The structures of both cavities are similar to each other, but they are not equivalent. The IbC cavity includes another different 1,2-dichloroethane molecule but the IbD cavity is empty. As a result, **Ib-1** has a formula of $[MV^{2+}][Cd_5(CN)_{12}]\cdot 1.5ClCH_2CH_2Cl$. Fig. 3(a) and (b) illustrate the arrangement of the IbB, IbC and IbD cavities, and that of IbA cavities, respectively, in a way similar to Fig. 2. The center of MV^{2+}, which is also the center of IbA cavity, is on a two-fold axis parallel to the a axis. The dihedral angle of the two pyridinium rings is 73.8(5)°. The nearest distance between MV^{2+} and the polycyano–polycadmate host is 2.79(3) Å.

The IbB cavity has a mirror symmetry, and the 1,2-dichloroethane molecule in the IbB cavity has a *trans* conformation and lies on the mirror plane. The IbC cavity, which traps another 1,2-dichloroethane molecule, has $2/m$ symmetry. Although the 1,2-dichloroethane molecule has a *trans* form, its molecular plane is perpendicular to the mirror plane of IbC cavity so that the structure of the guest is considerably disordered.

Type II: $[MV^{2+}][Cd_6(CN)_{14}]\cdot 2CHCl_3$ (IIa-1), $[MV^{2+}][Cd_6(CN)_{14}]\cdot 2CH_3CN$ (IIa-2), $[MV^{2+}][Cd_6(CN)_{14}]\cdot 2(CH_3)_2CHOH\cdot 3H_2O$ (IIa-3), $[MV^{2+}][Cd_6(CN)_{14}(H_2O)_2]\cdot 2CH_3CH_2OCH_2CH_3$ (IIb-1) and $[MV^{2+}][Cd_6(CN)_{14}(H_2O)_2]\cdot 2CH_3CH_2OH\cdot 3H_2O$ (IIb-2). Type II has a common space group *Pbca*, but is divided into two sub-groups, Type IIa and Type IIb, arising from the difference of the host component: $[Cd_6(CN)_{14}]^{2-}$ for Type IIa (**IIa-1**, **IIa-2**, **IIa-3**) and $[Cd_6(CN)_{14}(H_2O)_2]^{2-}$ for Type IIb (**IIb-1**, **IIb-2**). The host of Type IIa has three types of Cd^{2+} ions, hexa-coordinated Cd(1)(O), tetra-coordinated Cd(2)(T1) and Cd(3)(T2) in a 1 : 1 : 1 ratio. All Cd^{2+} ions are at general positions. In the host of Type IIb there are three types of Cd^{2+} ions, hexa-coordinated Cd(1)(O), penta-coordinated Cd(2)(P′) and tetra-coordinated Cd(3)(T) in a ratio of 1 : 1 : 1. However, Cd(2)(P′) is coordinated by four CN^- bridges and one unidentate aqua ligand, so that Cd(2)(P′) acts as a tetrahedral 4-connecting center. Therefore, the 3-D networks of Type IIa and Type IIb have the same topology. The following description is for the Type IIa host structure, but the same description is applicable to Type IIb hosts except the aqua ligand. The host of Type IIa has two types of cage-like cavities, IIA and IIB in a ratio of 1 : 2. The IIA cavity is a decahedron $[4^25^8]$ with two (O–T2–O–T2) quadrangles, six (O–T1–T2–O–T2) pentagons and two (O–T1–T2–O–T1) pentagons, and includes MV^{2+}. The IIB cavity is a hexahedron $[5^6]$ with five (O–T1–T2–O–T1) and one (O–T1–T2–O–T2) pentagonal faces, and includes a neutral guest. The structures of the IIA and IIB cavities is shown in Fig. 4, which is a projective view along the a axis of **IIa-1**. One IIA cavity is surrounded by six other IIA cavities from the directions of the a and the c axis, and the IIA cavity shares two (O–T2–O–T2) and four (O–T1–T2–O–T2) faces with the adjacent six IIA cavities. As a result, IIA cavities are arranged two-dimensionally to make a monolayer perpendicular to the b axis. IIB cavities are also arranged two-dimensionally to make a monolayer in a manner similar to the case of the IIA cavity. The crystal structure of Type IIa is a layered structure of the two mono-layers stacked alternately along the b axis. IIA cavities are arranged around the ac plane and its equivalent positions, and IIB cavities are sandwiched between the layers of IIA cavities.

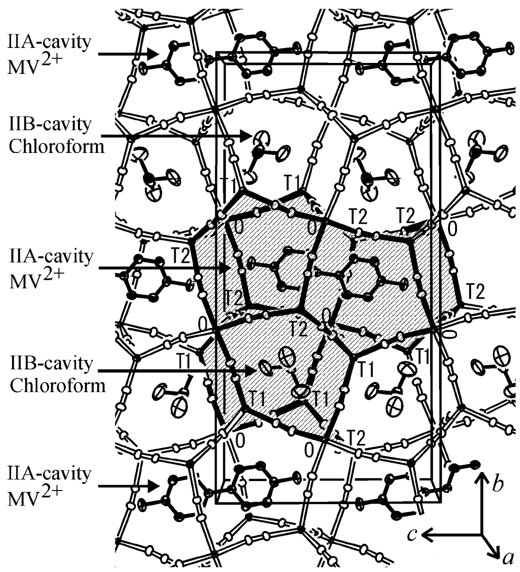

Fig. 4 Crystal structure of the chloroform clathrate **IIa-1**. A projective view along the a axis shows a layered structure, where mono-layers of IIA cage-like cavities and those of IIB cage-like cavities are stacked alternately along the b axis. IIA and IIB cage-like cavities include MV^{2+} and a chloroform molecule, respectively.

The center of IIA cavity lies on an inversion center of the crystal, so that MV^{2+} has an inversion center at the center C–C bond and has a planar structure. The shortest distance between MV^{2+} and the polycyano–polycadmate host is 2.698(9) Å for

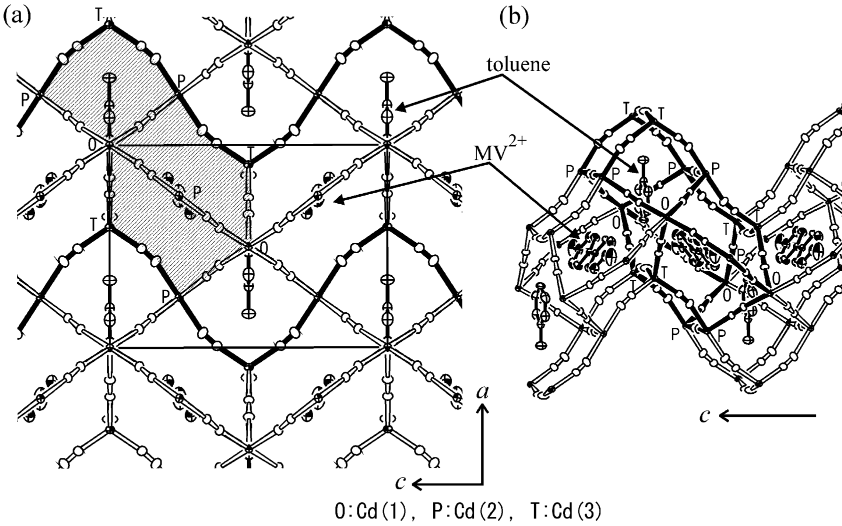

Fig. 5 Crystal structure of the toluene clathrate **III-2**. (a) Crystal structure in the range $b = -0.17$ to $+0.67$ viewed along the *b* axis. The thick bonds indicate a zigzag shaped channel-like cavity. (b) A perspective view of the channel-like cavity including MV^{2+} ions and toluene molecules.

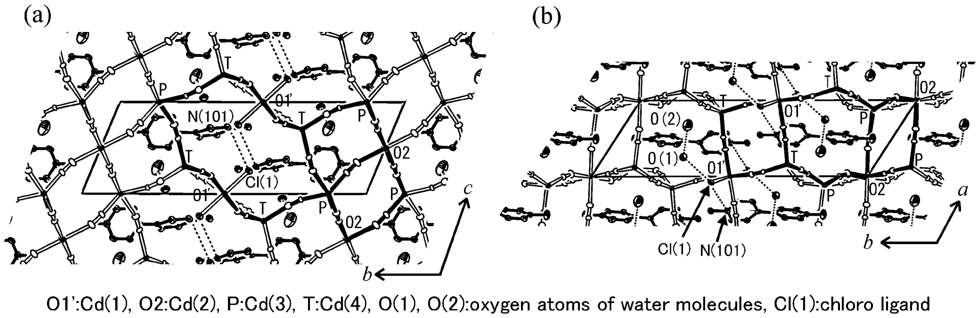

Fig. 6 Crystal structure of the Cd complex **IV-1**. (a) A projective view along the *a* axis. The thick bonds indicate an octagon (–P–T–O1′–T–P–T–O1′–T–) and two quadrangles (–O2–P–O2–P–) and (–O2–P–T–P–) in the 2-D network extending over the *bc* plane. (b) A projective view along the *c* axis. The thick bonds indicate a hexagon (–O1′–T–P–O2–P–T–), two quadrangles (–O1′–T–O1′–T–) and (–O2–P–O2–P–). The dotted lines indicate interactions between MV^{2+}(N(101)) and the chloro ligand (Cl(1)), between Cl(1) and a water molecule (O(1)) and between two water molecules (O(1) and O(2)).

IIa-1, 2.71(3) Å for **IIa-2**, 2.68(3) Å for **IIa-3**, 2.66(2) Å for **IIb-1** and 2.67(2) Å for **IIb-2**. The neutral guest is trapped in the IIB cavity, which has no symmetry elements. The shortest distance between MV^{2+} and the neutral guest is 3.654(9) Å for **IIa-1** and 2.51(4) Å for **IIa-2**. In the other Type II clathrates, the atoms of the neutral guests were not found clearly, so that the neutral guests were not included in the structure refinement. In these clathrates, due to the structural similarity of Type II clathrates, the distance between MV^{2+} and the neutral guest is considered to be similar to that of **IIa-2** and there is no short distance suggesting an interaction.

Type III: $[MV^{2+}][Cd_5(CN)_{12}]\cdot C_6H_6$ (III-1) and $[MV^{2+}][Cd_5(CN)_{12}]\cdot C_6H_5CH_3$ (III-2). In this type of host there are three independent Cd^{2+} ions, Cd(1)(O) at a $2/m$ symmetry site, Cd(2)(P) at a 2 symmetry site and Cd(3)(T) at a *m* symmetry site. Although the composition and the O : P : T ratio of the Type III host are the same as those of the Type I host, the network structures of Type I and III are different. In the Type III host there are channel-like cavities including MV^{2+} ions and neutral guests, and an empty cage-like cavities. The channel-like cavity is formed with four (–P–O–T–P–O–) pentagons, two (–O–P–T–P–) and four (–P–P–T–T–) quadrangles in a ratio of 2 : 1 : 2. Although the channel is one-dimensional, it runs in a zigzag fashion along the *c* axis of the crystal. This zigzag structure is shown in Fig. 5(a) and (b). Fig. 5(a) illustrates the crystal structure of **III-2** in the range $b = -0.17$ to $+0.67$ viewed along the *b* axis. Fig. 5(b) is a perspective view of the channel-like cavity. The zigzag structure arises from a mirror plane at $c = 0$ and its equivalent ones. The neutral guest toluene is on the mirror plane. MV^{2+} lies on a $2/m$ symmetry site, so that MV^{2+} is planar. The long molecular axis of MV^{2+} is parallel to the *b* axis, but the molecular planes of MV^{2+} and the neutral guest are not parallel with each other. The dihedral angle and the shortest distance between them is 37.1(4)°, 2.93(1) Å and 33.8(1)°, 3.004(4) Å for **III-1** and **III-2**, respectively. The nearest distance between MV^{2+} and the polycyano–polycadmate host is 2.86(1) Å for **III-1** and 2.876(5) Å for **III-2**. The empty cage-like cavity is a hexahedron $[4^25^4]$ with two (–O–P–T–P–) quadrangular faces and four (–P–O–T–P–O–) pentagonal faces. The cage-like cavities are arranged in the gap generated in the packing of the channel-like cavities. The cage-like cavity has the same topology of the IaC cavity of Type Ia and their shapes are very similar to each other.

Type IV: $[MV^{2+}][Cd_3(CN)_7Cl]\cdot 2H_2O$ (IV-1). **IV-1** includes no neutral guest except water molecules. The host of **IV-1** consists of Cd^{2+} ions, CN^- bridges and unidentate chloro ligands. There are four independent Cd^{2+} ions: octahedral Cd(1)(O1′) and Cd(2)(O2), penta-coordinated Cd(3)(P), and tetrahedral Cd(4)(T) in a ratio of 1 : 1 : 2 : 2. The octahedral Cd^{2+} ions are at independent inversion centers and others are at general positions. Two chloro ligand are coordinated to the *trans* sites of Cd(1)(O1′), so that Cd(1) is acting as a planar 4-connecting center. The structure of **IV-1** is a 3-D network in which 2-D networks extending over the *bc* plane are stacked along the *a* axis and linked by CN^- bridges. The 2-D network is composed of three types of polygons: an octagon (–P–T–O1′–T–P–T–O1′–T–), a quadrangle (–O2–P–O2–P–) and a quadrangle (–O2–P–T–P–) in a 1 : 1 : 2 ratio. Fig. 6(a) and (b) show

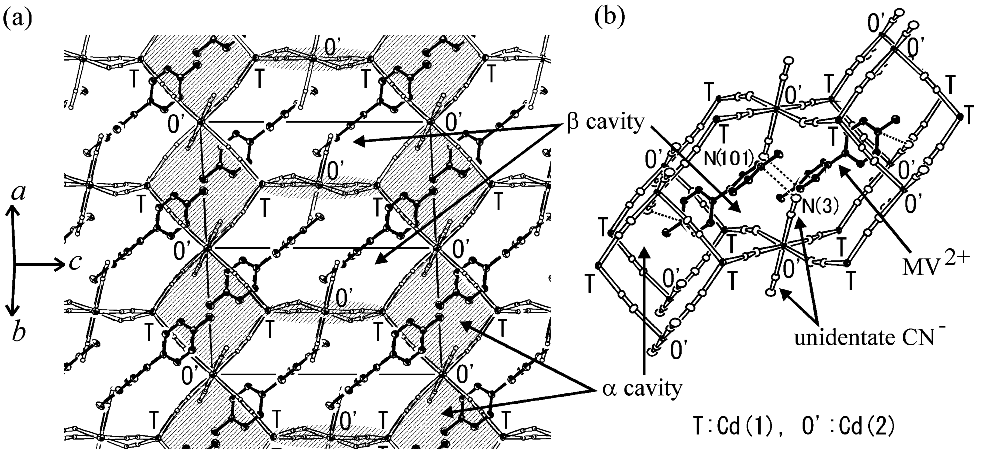

Fig. 7 Crystal structure of the Cd complex **V-1**. (a) A projective view along the [1 1 0] direction shows the 3-D network structure of **V-1** constructed by the linkage of (–O′–T–O′–T–) quadrangles (hatched areas). (b) Cavity structure of **V-1** and trapped MV^{2+} ions. The dotted lines indicate the shortest distance of 3.068(7) Å between the unidentate CN^- ligand and MV^{2+}.

the structure of the 2-D network and the linkage of the 2-D networks, respectively. Two chloro ligands at different Cd(1)(O1′) ions in the (–P–T–O1′–T–P–T–O1′–T–) octagon lie on the octagonal face, so that the window of the octagon is closed by the chloro ligands. As a result, the 2-D network acts as a wall that partitions space. The linkage of the two 2-D networks along the *a* axis by CN^- bridges forms two quadrangles (–O1′–T–O1′–T–) and (–O2–P–O2–P–), a hexagon (–O2–P–O2–P–O2–P–) and two types of hexagons (–O1′–T–P–O2–P–T–). These polygons are almost perpendicular to the 2D network. The windows of these quadrangles are small, so that the quadrangles act as walls. However, the hexagons do not function as walls because of their large windows. A MV^{2+} ion penetrates one of the (–O1′–T–P–O2–P–T–) hexagons and the (–O2–P–O2–P–O2–P–) hexagon, and two water molecules lie in the window of another (–O1′–T–P–O2–P–T–) hexagon. Due to these structural situations, a clear definition of a cavity as made for Types I, II and III is difficult in **IV-1**. MV^{2+} lies at a general position of the crystal and has a non-planar structure with a dihedral angle of 59.9(4)°. All MV^{2+} ions in the crystal are related with inversion centers of the crystal, so that their long molecular axes are oriented to one direction, which almost coincides with the direction of the *b* axis. The shortest distance between two adjacent MV^{2+} ions is 4.03(2) Å. The chloro ligand Cl(1) is located at a distance of 3.491(6) Å from N(101) of MV^{2+}, (Fig. 6(a)). This distance suggests an interaction between MV^{2+} and the chloro ligand while a water molecule is positioned at the opposite site of N(101). A distance of 3.342(8) Å between Cl(1) and O(1) of the water molecule suggests a weak hydrogen bonding. Moreover, O(2) of another water molecule lies in a distance of 2.79(2) Å from O(1). (Fig. 6(b)).

Type V: $[MV^{2+}][Cd_2(CN)_6]$ (V-1). **V-1** includes neither neutral guest nor water molecule, and simply consists of MV^{2+} and a 3-D network of polycyano–polycadmate. The 3-D network is built of alternate linkage of tetrahedral Cd(1)(T) ions at 2 symmetry sites and octahedral Cd(2)(O′) ions at inversion centers by CN^- bridges. However, two cyano ligands at the *trans* sites of Cd(2)(O′) are not involved in the construction of the 3-D network structure, and Cd(2)(O′) acts as a planar 4-connecting center. The other four cyano ligands bridge between Cd(1)(T) and Cd(2)(O′) to form a (–O′–T–O′–T–) quadrangle. Each quadrangle is connected at its vertices with adjacent quadrangles. This linkage of the quadrangles makes up the 3-D network of **V-I**. Viewing the crystal structure along the *c* axis, the faces of the adjoining quadrangles are perpendicular to each other, but viewing it along the directions of [1 1 0] or [$\bar{1}$ 1 0], the faces are parallel to each other. Fig. 7(a) shows this structural scheme. 3-D networks similar to this network have been found in several polycyano–polycadmate related compounds.[18,19] For example, the host of the T_d-en-type clathrate $Cd(en)Cd(CN)_4 \cdot 2G$ (en =ethylenediamine) is considered to be a network of **V-1** in which the two unidentate cyano ligands are replaced with a bridging en ligand. In the network structure of **V-1**, clear definition of cavities is difficult. However, in $Cd(en)Cd(CN)_4 \cdot 2G$, this is possible because of the bridging en ligand and two types of cavities, α and β, are defined.[19] The α and β cavities are a $[4^6]$ rectangular box and a $[5^4]$ biprismatic cage, respectively, and each cavity includes one guest molecule. Because of a structural similarity between the network of **V-1** and that of the T_d-en-type, the same cavity description is helpful to understand the structure of the space for MV^{2+} in **V-1**. Fig. 7(b) illustrates the space in **V-1** corresponding to the α and β cavities. MV^{2+} is larger than the guest of the T_d-en-type clathrate, so that 3-D space generated by combining the α and β cavities is used for embracing MV^{2+} ions.

A two-fold axis parallel to the *b* axis is orthogonal to the center C–C bond of MV^{2+}, so that the molecular symmetry of MV^{2+} is 2 and MV^{2+} is non-planar with a dihedral angle of 52.3(2)°. Because all MV^{2+} ions in the crystal are related with inversion centers of the crystal, the orientation of all long molecular axes of MV^{2+} are fixed toward a direction near [3 0 2]. The nearest distance between adjacent MV^{2+} ions is 3.944(7) Å. The N end of the unidentate cyano ligand is positioned just above N(101) of MV^{2+} at a distance of 3.068(7) Å. Judging from this geometry and distance, presence of an interaction between MV^{2+} and the host is considered.

Structural features. MV^{2+} is the first dication and the largest guest that has been included in a polycyano–polycadmate host. These factors appear in a structural feature that many penta-coordinated Cd^{2+} ions take part in forming the 3-D networks of the new clathrates. Although a penta-coordinated form of Cd^{2+} was found in previous polycyano–polycadmate hosts, it was a minor case and the main coordination form was hexa- or tetra-coordination. In a clathrate accommodating MV^{2+}, its 3-D network needs more CN^- ligands to cancel the positive charge of a dication MV^{2+}. In addition, in order to include a bulky MV^{2+}, the 3-D network needs larger cavities. To achieve these structural demands, a hepta-coordinated form of Cd^{2+}, whose surrounding space is crowded, is not suitable as a connecting center. A penta-coordinated form, which is made by insertion of a CN^- ligand into a tetra-coordinated Cd^{2+}, is more advantageous than a hepta-coordinated form which is made by insertion of a CN^- ligand into a hexa-coordinated Cd^{2+}. Use of a penta-coordinated Cd^{2+} together with tetra- and hexa-coordinated Cd^{2+} ions in building a 3-D network structure expands the structural variations of the polycyano–

polycadmate host. More novel structures are expected in future preparative studies.

The formation of CT complexes between MV^{2+} and donors is well known.[20–25] However, such a CT complex formation between MV^{2+} and a neutral guest is not expected in the clathrates of this work. Although a reason is relatively high ionization energies of the neutral guests used in this work (Table 1), a more important factor is their zeolite-like structure network hosts. In Type I and II, MV^{2+} and a neutral guest are included in each cage-like cavity separately. This inclusion structure prevents the association of MV^{2+} and a neutral guest. In Type III, the zigzag structure of the channel-like cavity prevents MV^{2+} and a benzene or a toluene molecule from adopting a stacked structure, which is considered to be the most suitable geometry for CT interactions between planar donors and acceptors.[8] In the diffuse reflectance spectra of the ten clathrates, no bands suggesting CT interaction were observed.

Photo-induced reduction of MV^{2+}

As shown in Table 1, certain compounds showed a color change from colorless to blue on UV irradiation. **IIb-1** and the benzyl alcohol clathrate were especially sensitive. These compounds readily turned blue upon sunlight irradiation for several minutes. **IIa-3**, **IIb-1**, **III-1**, **III-2**, **IV-1** and **V-1** were blue after the X-ray diffraction experiment. On the other hand, there were also insensitive compounds, such as **Ia-2**, **Ib-1** and **IIa-2**. The degree of the color development seems to depend on the neutral guest. However, **IV-1** and **V-1**, which have no neutral guest, also showed the color change on UV irradiation. It is well known that MV^{2+} is easily reduced by UV light in the presence of electron donors and a reduced product, methylviologen radical cation $MV^{+\bullet}$, has an intense blue color. In our case the blue color was considered to arise from this $MV^{+\bullet}$. The diffuse reflectance spectra of the blue clathrates after UV irradiation had characteristic absorption bands at *ca.* 400 and *ca.* 600 nm as shown in Fig. 8. This spectral feature resembles that of $MV^{+\bullet}$ observed in solutions[26] and zeolite matrices.[27] Clear evidence showing that the characteristic bands arise from $MV^{+\bullet}$ trapped in the host was obtained from an absorption spectra measurement on a single crystalline sample of blue **IIb-1**. In this experiment dichroism was observed. When the electric field vector of a polarized incident ray was parallel to the *c* axis of the crystal of **IIb-1**, the transmitted light was blue. On the other hand, when perpendicular to the *c* axis, it was almost colorless. The absorption spectra for both cases are shown in Fig. 9(a).

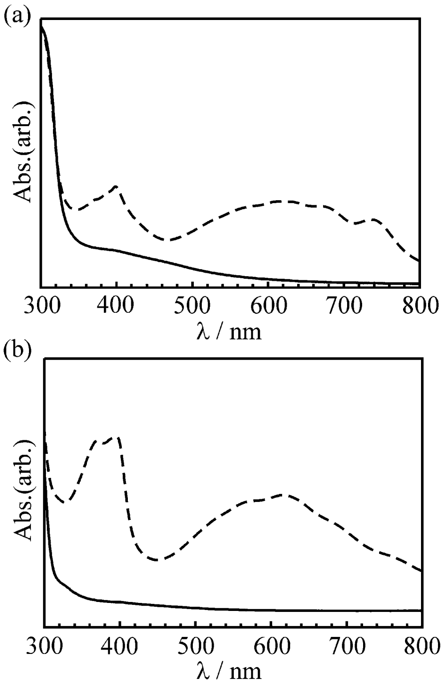

Fig. 8 UV–VIS diffuse reflectance spectra of the diethyl ether clathrate **IIb-1** (a) and the Cd complex **V-1** (b) before (—) and after (- - -) UV irradiation.

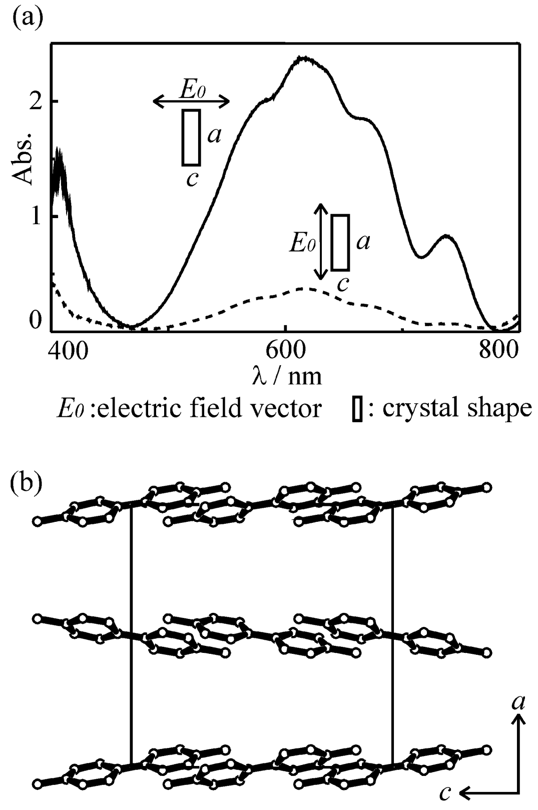

Fig. 9 (a) Absorption spectra of the diethyl ether clathrate **IIb-1** single crystal irradiated by UV light. The spectra were measured with the electric field vector (E_0) of a polarized incident ray parallel (—) or perpendicular (- - -) to the *c* axis of the crystal. (b) The arrangement of MV^{2+} in the crystal of **IIb-1** viewed along the *b* axis. The long molecular axes of all MV^{2+} ions are almost parallel to the *c* axis of the crystal.

The spectrum in the former case showed similar characteristics to that observed in the diffuse reflectance spectrum of the blue powdered sample of **IIb-1** (Fig. 8(a)). This dichroism can be interpreted by the following. Fig. 9(b) demonstrates the arrangement of MV^{2+} in the crystal of **IIb-1** determined in the X-ray study. The long molecular axes of all MV^{2+} ions are almost parallel to the *c* axis of the crystal. Considering that $MV^{+\bullet}$ is expected to have a large transition moment along the long molecular axis, the crystal has a large absorption anisotropy, in which the absorption of the light polarized along the *c* axis is very high but that along the direction perpendicular to the *c* axis is very low. The observed dichroism is in accord with this structural situation. Therefore, it is supposed that MV^{2+} trapped in the host is reduced to $MV^{+\bullet}$ on UV irradiation and $MV^{+\bullet}$ shows its characteristic spectrum causing the blue color.

Another evidence for the production of $MV^{+\bullet}$ and its production yield were obtained from EPR measurements. All compounds were colorless and EPR silent before UV irradiation. However, the blue compounds irradiated by UV light showed a symmetric EPR signal. The *g* value of EPR signal observed in blue **IIb-1** was 2.0031. This EPR signal is similar to that of $MV^{+\bullet}$ confined in silica gel[28] and zeolite matrices.[27] The quantity of $MV^{+\bullet}$ in a single crystal of **IIb-1** was estimated by EPR spectroscopy. On irradiation the quantity of the radical increased monotonously, and after two hours the production of the radical was saturated. At this stage, the yield of $MV^{+\bullet}$ was estimated to be *ca.* 2% to all MV^{2+} ions in the crystal. Considering this result and large absorption coefficient of MV^{2+} in the UV region,[26] the generation of $MV^{+\bullet}$ is limited near the surface of the crystal.

The stability of $MV^{+\bullet}$ was examined. In a dark room and in the air, the blue compounds turned colorless and their EPR signal disappeared gradually. For a blue **IIb-1** crystal irradiated for 90 min, it took four days to turn completely colorless. The discolored compounds showed the color change from colorless to blue again on UV irradiation. On the other hand, in a dark room and in an atmosphere of nitrogen, the blue color remained for *ca.* six months. These findings suggest that the discoloration is a process of oxidation from $MV^{+\bullet}$ to MV^{2+} by O_2 such as observed in $MV^{+\bullet}$ trapped in zeolite matrices.[27] However, this discoloration is not a simple oxidation process. The coloration by the second UV irradiation was not so bright compared with that by the first one. After several repetitions of the UV irradiation and the discoloration, the clathrate became opaque, white–yellow and insensitive to UV irradiation. At this stage, decomposition of the clathrate was obvious. To detect changes of the clathrate during the coloration and the discoloration, microscopic IR spectra of **IIb-1** were measured before, during and after UV irradiation. Although clear signs suggesting change of the diethyl ether was not found, a new absorption band, which was assigned to $MV^{+\bullet}$, was observed at 1028 cm^{-1}.[29] This band grew during the irradiation, and disappeared gradually during the discoloration. Another change was observed in the region of C≡N bond stretching. This CN stretching band is a useful indicator to detect the change of cyano complexes.[30] A small shoulder appeared in a higher region of the CN stretching band after 5 minutes irradiation, and it became clearer after three hours irradiation. Moreover, after 14 days from the end of the irradiation the shoulder grew into a separated band at 2200 cm^{-1}. This observation indicates that the polycyano–polycadmate structure was damaged by $MV^{+\bullet}$ generated on UV irradiation. Apart from this decomposition, all clathrates prepared in this work collapsed due to spontaneous liberation of the neutral guest. This phenomenon is generally seen in many types of clathrates, especially, in clathrates including a guest with high vapor pressure.[31] In polycyano–polycadmate host clathrates this type of decomposition is generally accompanied by the decomposition of the 3-D network structure of the host.[2] In our case, this decomposition generated a new band at 2140 cm^{-1}, so that it was easy to confirm that both types of decompositions occur separately. It was also confirmed that the decomposed clathrate did not respond to UV light. Considering the above observations, the discoloration is a combination of the oxidation of $MV^{+\bullet}$ and the decomposition of the clathrate structure due to the damage from $MV^{+\bullet}$ and the spontaneous liberation of the neutral guest.

The photo-induced reduction of MV^{2+} in the clathrates has been demonstrated above. However, the mechanism of this phenomenon is ambiguous. We here present two possibilities for the mechanism. In order to search for a species absorbing light, wavelengths causing the color change were checked using optical cut-off filters. On UV irradiation with a filter that cuts wavelength <330 nm, no color change occurred. When a filter to cut wavelength <290 nm was used the color change was observed. Therefore, the effective wavelength is at least <330 nm. At the same time, diffuse reflectance spectra of $Cd(CN)_2$ and $MV(PF_6)_2$ were measured. $Cd(CN)_2$, which is a primitive compound of the polycyano–polycadmate host clathrate, can be regarded as a typical 3-D network of polycyano–polycadmate hosts.[2] Absorption bands of $Cd(CN)_2$ were in the wavelength range of <250 nm and those of $MV(PF_6)_2$ were in the range 260–320 nm.[32] The diffuse reflectance spectra of **IIb-1** and **V-1** before UV irradiation showed large absorption bands below 330 nm. (Fig. 8) These bands are considered to arise from mainly MV^{2+} in the compounds. From these spectra, a scheme that MV^{2+} excited by UV light abstracts an electron from a donor is considered. The behavior of an excited MV^{2+} as a strong electron acceptor has been established in solutions[33] and in zeolite matrices.[34] In our case, however, the chemical species acting as an electron donor was uncertain. Although possible candidates are the neutral guest and the polycyano–polycadmate host, we could not obtain spectroscopic data directly. Alternatively, a mechanism in which $MV^{+\bullet}$ is generated from a MV^{2+}-donor CT complex excited by light is plausible. This scheme is firmly established in MV^{2+}–aromatic systems confined in zeolite matrices[21,35] and in many solutions.[36] In the clathrates presented here, CT interaction between MV^{2+} and a neutral guest cannot be considered from the results of the structural and spectroscopic studies. However, according to a recent suggestion that MV^{2+} has a CT interaction with its counter anions regardless of its donor strength, shape and valency,[32] it may be possible that MV^{2+} has CT interactions with a 3-D network anionic host surrounding MV^{2+}. In a CT complex $[BzV^{2+}]_3[Cu_9(CN)_{15}]\cdot H_2O$, which consists of a benzylviologen dication (BzV^{2+}) and a 3-D network of Cu(I) cyanide similar to the polycyano–polycadmate hosts, CT interactions between BzV^{2+} and CN^- bridges are proposed, while Cu(I) has also an electron-donating capability.[25] In our cases of Type I, II and III, the shortest distances between MV^{2+} and a CN^- bridge in a polycyano–polycadmate host are in the range of 2.66(2)–2.876(5) Å. Considering large thermal displacement factors of the MV^{2+} ions, the distances indicate rather short van der Waals contacts. Especially, in the cases of **IV-1** and **V-1**, this scheme is plausible. The polycyano–polycadmate 3-D networks of **IV-1** and **V-1** have a structural feature different from that of the clathrates with anionic unidentate ligands at a short distance from MV^{2+}: a chloride ligand for **IV-1** and a cyanide ligand for **V-1**. Both ligands may show CT interactions with MV^{2+}. However, in their diffuse reflectance spectra absorption bands suggesting such interactions were not confirmed clearly. In water, the maximum CT transition wavelengths between MV^{2+} and Cl^-, and MV^{2+} and CN^- are reported to be at 290 and 295 nm, respectively.[24] If CT bands exist in our cases, they overlap with large absorption bands of MV^{2+} and their detection is difficult. We consider the above spectroscopic observations not to exclude the possibility of CT interaction, but we could not obtain direct evidence suggesting this CT mechanism in the spectral data of **IV-1**, **V-1** and all clathrates. Moreover, the degree of the color development seems to depend on the neutral guest. Especially in Type-II clathrates a rough tendency that a clathrate of a neutral guest with lower ionization energy was more sensitive was recognized. (Table 1) This finding might suggest participation of the neutral guest in the photo-induced reduction. In this respect, a suggestive system, which is a donor(host)–acceptor–donor(guest) triad complex in zeolites, has been reported recently.[32,37] As other possible factors, participation of impurities and lattice defects are considered.[38] As shown in many examples of electron transfer, the donor after charge separation is expected to have a very short lifetime. In order to elucidate the donor and obtain more information about the photo-induced reduction, investigations using time-resolved spectroscopy may be necessary.

The relation between the dihedral angle of the two pyridinium rings of MV^{2+} and the photo-induced reduction of MV^{2+} is an interesting feature. Our *ab initio* calculations using 6–31G** basis sets showed that the dihedral angle(ω) for the most stable geometry of a ground state MV^{2+} was 50° and the energy difference between MV^{2+} with $\omega = 50°$ and a planar MV^{2+}, which is the most unstable geometry, was 13.4 kJ mol^{-1}. According to the calculations performed by Wolkers *et al.* using 3–21G basis sets, these values are 60° and 19.3 kJ mol^{-1}, respectively.[39] Both values for the energy difference indicate that the dihedral angle is easily affected by surroundings and thermal motion.[13] Any dihedral angle could be possible for a ground state MV^{2+} in a crystal. The dihedral angles observed in this work were in the range of 0–76.5(4)° as listed in Table 1. Their deviations from the calculated value are considered to arise from crystal packing effects. The dihedral angle of $MV^{+•}$ in the most stable geometry was calculated to be 0° in our calculation, and the energy difference between a planar $MV^{+•}$ and $MV^{+•}$ with $\omega = 90°$, which is the most unstable geometry, was estimated to be 62.3 kJ mol^{-1}. Using 3–21G basis sets, Wolkers *et al.* calculated the energy difference between a planar $MV^{+•}$ and $MV^{+•}$ with $\omega = 15°$, which is the most stable geometry in their calculations, is 0.2 kJ mol^{-1}.[39] In general, high instability of non-planar $MV^{+•}$ is believed.[8,40] Observed ω values for $MV^{+•}$ in crystals are 6 and 11° for $[MV^{+•}][PF_6^-]$,[41] and 1.8 and 1.2° for $[MV^{+•}][Cl^-]\cdot 2H_2O$.[39] In these cases, the observed dihedral angles are in the range where the instability energy is estimated to be at most 1.3 kJ mol^{-1}. In our case, certain compounds showed the color development in spite of their large dihedral angles, such as **Ia-1**, **IV-1** and **V-1**, and a clear relation between the stability of $MV^{+•}$ and the dihedral angle was not observed. However, considering the following points: (i) the product yield of $MV^{+•}$ is at most 2%; (ii) the generation of $MV^{+•}$ is limited near the surface of the crystal; (iii) a possibility of partial decomposition of the crystal structure exists, it may be inadequate to use our results directly in the discussion about the molecular structure and the stability of $MV^{+•}$ trapped in the host. Although MV^{2+} in a CT complex is always said to be planar,[8] several CT complex crystals containing non-planar MV^{2+} have been known.[23,25] To re-examine the relation between the stability and the dihedral angle of $MV^{+•}$ is worth trying from the viewpoint of developing functionalized solid-state materials using redox of MV^{2+}.

Concluding remarks

A series of polycyano–polycadmate host clathrates accommodating MV^{2+} and a small organic molecule, and two polycyano–polycadmate complexes with MV^{2+}, have been prepared. The crystal structures of ten clathrates and the two Cd complexes have been determined by X-ray diffraction. The polycyano–polycadmates networks of the twelve compounds have new 3-D structures that belong to zeolite-structure, and are classified into five structure types. In some compounds photo-induced reduction of MV^{2+} has been observed. The degree of the reduction is different for each compound. This finding suggests that the clathrate structure influences the properties of MV^{2+} as an electron acceptor.

The compounds focused in this report are colorless and have no CT interaction between MV^{2+} and a neutral guest molecule. Recently, however, several colored clathrates have prepared,[11] and have an apparent CT interaction between MV^{2+} and a neutral guest. This is also an example that the properties of MV^{2+} are reserved in the polycyano–polycadmate host and further details of this will be reported somewhere.

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