

Crystal structure of a polycyano–polycadmate host clathrate including a charge-transfer complex of methylviologen dication and mesitylene as a guest

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The crystal structure of a methylviologen dication (MV²⁺)–mesitylene clathrate, one of a newly synthesized polycyano–polycadmate host clathrates, including a charge-transfer complex of MV²⁺ and an aromatic molecule, has been revealed by X-ray diffraction.

As a trial to develop functional materials using a polycyano–polycadmate host, we previously synthesized a series of polycyano–polycadmate host clathrates including a methylviologen dication (MV²⁺ = 1,1'-dimethyl-4,4'-bipyridinium ion) as a guest.¹ MV²⁺ is widely used in the fields of photochemistry, electrochemistry, etc. owing to its strong electron accepting nature.^{2,3} MV²⁺ is easily reduced to become a monocation radical MV^{•+} whose color is blue, and forms a charge-transfer (CT) complex with a donor. Although some of our previous clathrates showed a color change from colorless to blue on UV irradiation, the formation of a CT complex in the clathrates was not confirmed clearly.¹ In this study we have newly synthesized nine polycyano–polycadmate host clathrates including a CT complex of MV²⁺ and an aromatic molecule, and have determined one crystal structure.

The polycyano–polycadmate host is a Cd cyano complex of chemical formula [Cd_x(CN)_y]^{2x-y-}. The cyano group links two Cd atoms to form a framework host structure. Two typical structure types of the host are known.⁴ One is a zeolite-like structure, which has a 3-D framework host while the other is a clay-like structure, which is a layered structure of 2-D Cd cyano complexes. Another important feature of the host complex is that it is anionic. Therefore, the polycyano–polycadmate host clathrate has a cationic guest that neutralizes the negative charge of the host, and a neutral guest that is an ordinary neutral organic molecule. Depending on the combination of the cationic guest and the neutral guest, the formation of a wide variation of clathrates is possible.⁵ In this study, we attempted to form a CT complex of MV²⁺ (a cationic guest) and a donor (a neutral guest) in a polycyano–polycadmate host.

The synthetic procedure was as follows: into water (50 cm³), K₂Cd(CN)₄ (5 mmol, 1.47 g), CdCl₂·2.5H₂O (5 mmol, 1.14 g) and methylviologen dichloride (2 mmol, 0.50 g) were dissolved. After the solution was filtered, a neutral guest solution was poured onto the filtrate. Various aromatic compounds were tried as neutral guests diluted 1–50 times with *n*-propylbenzene and the mixture left at 277 K. After several days, colored clathrates were obtained in a crystalline or a powdered state. The presence of a polycyano–polycadmate host, MV²⁺ and a neutral guest was confirmed by IR spectroscopy. The new clathrates and their absorption maximum wavelengths as determined from UV–VIS diffuse reflectance spectra are listed in Table 1.

Among the clathrates, the crystal structure of the MV²⁺–mesitylene clathrate **1** was determined by single crystal X-ray diffraction.⁶ The host Cd complex of **1**, [Cd₃(CN)₆Cl₂]²⁻, contains two chloride ions together with cyano groups. Each cyano group bridges Cd atoms to form a 3-D framework structure, and each chloride ion coordinates to each Cd atom

[Fig. 1(a)]. The host structure of **1** can be classified as a zeolite-like structure, but its framework structure is new. Although the host is a 3-D framework, the cavity formed within has a 1-D channel-like structure running along the *b* axis of the crystal. Each chloride ligand protrudes from the wall of the channel cavity into the inside of the cavity.

One MV²⁺ and one mesitylene molecule are stacked to form a CT complex as shown in Fig. 1(b). The twist angle of the two rings of MV²⁺ is 0°. The molecular plane of MV²⁺ is almost parallel to that of the mesitylene molecule. The center of the aromatic ring of the mesitylene molecule is directed toward one of the N atoms of MV²⁺. This overlapping arrangement of MV²⁺ and the donor is typical for a π donor.^{2,7} The interspacing between MV²⁺ and the mesitylene molecule of 3.30(1) Å⁸ is apparently shorter than van der Waals contact of stacked aromatic rings. The diffuse reflectance spectrum of **1** and absorption spectrum of an acetonitrile solution of MV(PF₆)₂ and mesitylene are shown in Fig. 2. The CT absorption band of **1** was red-shifted compared with that of the solution. It is considered that the short interspacing contributes to the red-shift. The CT complex lies in the channel cavity, and is related to neighboring CT complexes by a two-fold screw axis parallel to the *b* axis. The molecular planes of MV²⁺ and the mesitylene molecule are parallel to the two-fold screw axis, so that the CT complexes are not stacked mutually. The two chloride ligands are located near the reverse side of the MV²⁺ molecular plane that is in contact with the mesitylene molecule. The distances between MV²⁺ and the chloride ligands are 3.256(5) Å for Cl(1) and 3.841(6) Å for Cl(2).⁹ This structural situation may suggest the existence of an interaction between MV²⁺ and the host Cd complex through the chloride ligands. The CT interaction between MV²⁺ and chloride ion in solution and in the solid state has been established,¹⁰ and the existence of a host–acceptor(MV²⁺)–donor triad interaction was recently shown for a zeolite including an MV²⁺ CT complex.¹¹

For *n*-propylbenzene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,2,4,5-tetramethylbenzene, pentamethylbenzene, hexamethylbenzene, naphthalene or anthracene as neutral guests, no clathrates was obtained. Considering their ionization

Table 1 Polycyano–polycadmate host clathrates including a MV²⁺-donor CT complex

Neutral guest(donor)	Color	λ _{max} /nm
Ethylbenzene	Slightly yellow	400
Mesitylene	Yellow	420
Anisole	Orange	446
Phenol	Yellow	411
<i>o</i> -Cresol	Orange	424
<i>m</i> -Cresol	Yellow	406
<i>p</i> -Cresol	Orange	424
Aniline	Red	443
Pyrole	Yellow	432

λ_{max} = wavelength at the maximum of diffuse reflectance spectrum.

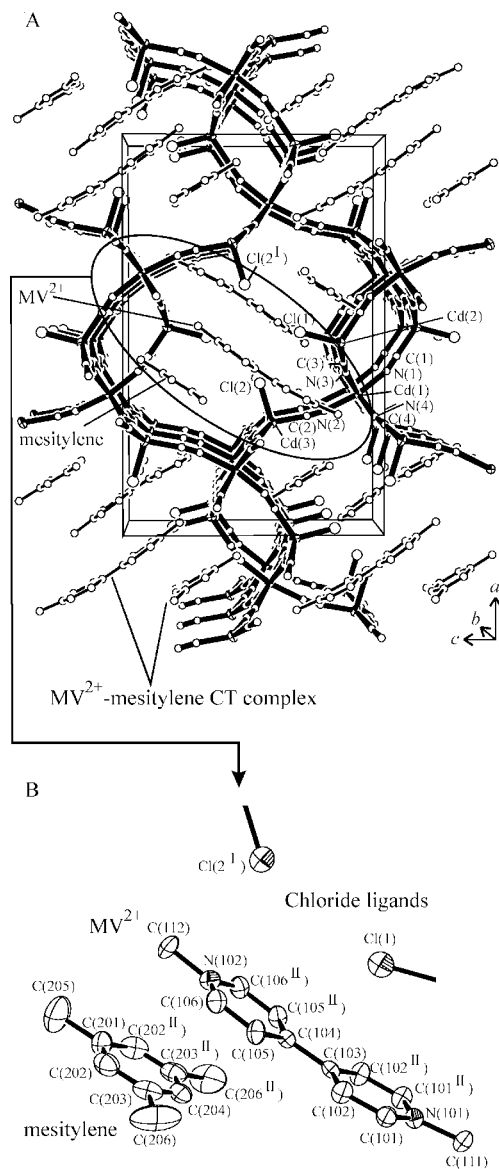


Fig. 1 (A) A perspective view of [MV²⁺][Cd₃(CN)₆Cl₂²⁻]·C₆H₃(CH₃)₃ **1** along the *b* axis. (B) Crystal structure around the MV²⁺-mesitylene CT complex of **1**. Selected interatomic distances (Å): Cl(1)···C(103) 3.37(1), Cl(1)···C(104) 3.51(1), Cl(2)^I···N(102) 3.79(1) (*I* = -*x* + 1, *y* - 1/2, -*z* + 1), Cl(2)^I···C(112) 3.77(1), N(102)···C(201) 3.84(1), N(102)···C(202) 3.78(1), N(102)···C(203) 3.59(1), N(102)···C(204) 3.47(2).

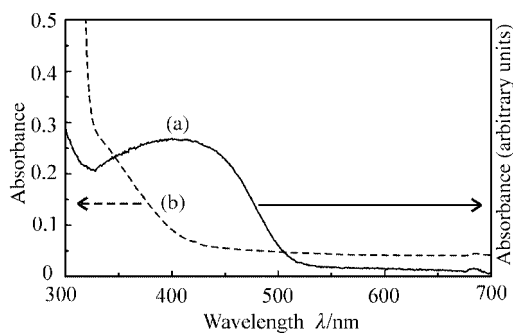


Fig. 2 Diffuse reflectance spectrum of **1** (a) and absorption spectrum of a MV(PF₆)₂ (0.03 M) and mesitylene (0.03 M) acetonitrile solution (b).

potentials relative to that for mesitylene, the formation of complexes might be expected for some of them. However, they are less symmetrical or larger than mesitylene. As such, crystal

packing and a limitation of inclusion ability of the polycyano-polycadmate host are considered. The cavity that the host must prepare for a CT complex with MV²⁺ and a neutral guest is very large. In our preparative experiments, mesitylene is the most symmetrical and largest clathrate forming molecule (Table 1).

In summary, it has been revealed that the polycyano-polycadmate host acts as a host for a MV²⁺ CT complex, and the presence of an interaction between MV²⁺ and the host is suggested. Considering the structural variety of the polycyano-polycadmate host clathrate,^{4,5} it is expected that the host structure of the new clathrates depends on the neutral guest. Structure determinations of the other clathrates are now in progress. At the same time, the preparation of single crystalline samples suitable for spectroscopic experiments are in progress. Although intensive studies of MV²⁺ CT complexes confined in a solid state matrix have been carried out,^{11,12} there have been few examples in which crystal structures have been clarified. Structural and spectroscopic data obtained from single crystals are useful for developing studies in this field. In this regard our clathrates have an advantage.

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- Crystal data for [MV²⁺][Cd₃(CN)₆Cl₂²⁻]·C₆H₃(CH₃)₃ **1**: C₂₇H₂₆N₈Cl₂Cd₃, *M* = 870.7, orthorhombic, space group *Pnma* (no. 62), *a* = 23.7905(7), *b* = 8.8535(2), *c* = 15.5522(4) Å, *U* = 3275.8(2) Å³, *T* = 293 K, *Z* = 4, *μ*(Mo-Kα) = 21.08 cm⁻¹, 21797 reflections measured, 3952 unique, *R*(*F*) = 0.0564 and *R*_w(*F*²) = 0.1133 for 2739 used reflections with *I* > 3σ(*I*). CCDC reference number 160670. See <http://www.rsc.org/suppdata/cc/b1/b102076p/> for crystallographic data in CIF or other electronic format.
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- The distance between the least squares mean plane of MV²⁺ [C(101), C(101^{II}), C(102), C(102^{II}), C(103), C(104), C(105), C(105^{II}), C(106), C(106^{II}), N(101), N(102), II = *x*, -*y* + 1/2, *z*] and the center of the aromatic ring of the mesitylene molecule.
- The distance between the least squares mean plane of MV²⁺ and the chloride ligand [Cl(1) or Cl(2)], I = -*x* + 1, *y* - 1/2, -*z* + 1].
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