

Inclusion Selectivity of the Zeolite-Mimetic Host Clathrate $[\text{N}(\text{CH}_3)_4 \cdot x\text{G}][\text{Cd}_3(\text{CN})_7]$ for Aromatic C_8H_{10} ($= \text{G}$) Isomers, Ethylbenzene and Xylenes

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The anionic host $[\text{Cd}_3(\text{CN})_7]^-$ with the three-dimensional structure like zeolite shows the highest inclusion selectivity for ethylbenzene from the binary, ternary, and quarternary mixtures of ethylbenzene and three xylene isomers in the fractional enclathration-crystallization process; *p*-xylene is the second.

Among a number of the $\text{Cd}_x(\text{CN})_y$ mineralomimetic structures we have developed,^{1,4} the zeolite-like three-dimensional host structures built of $[\text{Cd}_3(\text{CN})_7]^-$ ^{1,2} are expected to exhibit guest selective functions in particular owing to their structural resemblance with the zeolite. Our zeolite-like series of the clathrates $[\text{Onium} \cdot x\text{G}][\text{Cd}_3(\text{CN})_7]$ have been characterized and classified into six types, type I to type VI, according to the structural features observed in their single crystal structures involving such onium cation as NMe_4^+ , SMe_3^+ , $\text{NH}_2(\text{CH}_2)_3\text{NMeH}_2^+$, etc. to neutralize the negative charge of the host and such organic guest molecule as SnMe_4 , $\text{CH}_2\text{ClCH}_2\text{Cl}$, C_6H_6 , $\text{C}_6\text{H}_5\text{Me}$, 1,3,5- $\text{C}_6\text{H}_3\text{Me}_3$, etc.¹ Since our type III clathrates $[\text{NMe}_4 \cdot x\text{G}][\text{Cd}_3(\text{CN})_7]$ of the orthorhombic space group $Pn\bar{a}m$ ($Z = 4$) were obtained for the guests 1.5 C_6H_6 , $\text{C}_6\text{H}_5\text{Me}$, and 0.67(1,3,5- $\text{C}_6\text{H}_3\text{Me}_3$) as $x\text{G}$,¹ we applied the system $\text{NMe}_4^+\text{-CdCl}_2\text{-}[\text{Cd}(\text{CN})_4]^{2-}$ to examine inclusion selectivity of the host for the aromatic mixtures of C_8H_{10} composition, i.e., those of ethylbenzene, and *o*-, *m*- and *p*-xylene isomers, upon the enclathration-crystallization process of the clathrate formation.

Mixed-guest clathrates were prepared under the conditions similar to those applied for the single-guest clathrates: the aqueous solution of the host moieties, containing NMe_4Cl , CdCl_2 , and $\text{K}_2[\text{Cd}(\text{CN})_4]$, was covered with the organic phase of the feed mixture, one of the equimolar binary, ternary, and quarternary mixtures of ethylbenzene (E), *o*-xylene (O), *m*-xylene (M), and/or *p*-xylene (P). The crystalline products obtained after a few days leaving of the two-phase specimens at 5°C were identified by infrared spectroscopy and powder X-ray diffractometry.⁵ For the identification of the crystal structures, single crystals of the single-guest clathrates were prepared for the four C_8H_{10} isomers; their single crystal structures will be reported elsewhere.⁶ The single-guest clathrates of E, O, and M are respectively isostructural to type III ($Pn\bar{a}m$, $Z = 4$),¹ but that of P is isostructural to our type V (hexagonal $P6_3/mmc$, $Z = 2$).¹

The composition of the enclathrated guests were determined by gas chromatography through the procedures as follows: the fine crystals of the mixed-guest clathrate were filtered out on a sintered glass, washed with small amounts of acetone, and air-dried for a short while; the washed crystals were powdered more finely in carbon tetrachloride to extract the aromatic guests at ambient temperature; the carbon tetrachloride solution of the guests was subjected to the gas chromatographic measurement.⁷

Table I summarizes the results where the enrichment factor Q has been defined as $Q_x = N_x / n_x$ for the mole fractions of X in the clathrate N_x and in the feed mixture n_x . From the binary, ternary and quarternary feed mixtures involving E, E is always most

enriched in the clathrate. For example, from the quarternary feed mixture of E-O-M-P, E is most enriched with $Q_E = 56 / 25 = 2.24$, and P is second enriched with $Q_P = 31 / 25 = 1.24$; as for the binary E-P feed mixture, $Q_E = 70 / 50 = 1.40$ and $Q_P = 30 / 50 = 0.60$. The second priority of P is also seen from the feed mixtures not involving E; M is the third.

Table 1. Fractional enclathration-crystallization data: n , N , and Q have been defined in text

Feed mixture	$n \times 10^2$				$N \times 10^2$				Q			
	n_E	n_O	n_M	n_P	N_E	N_O	N_M	N_P	Q_E	Q_O	Q_M	Q_P
E-O	50	50			91	9			1.82	0.18		
E-M	50		50		84		16		1.68		0.32	
E-P	50			50	70			30	1.40			0.60
O-M		50	50			24	76			0.48	1.52	
O-P		50		50		17		83		0.34		1.66
M-P			50	50			19	81			0.38	1.62
E-O-M	34	33	33		77	6	17		2.26	0.18	0.52	
E-O-P	34	33		33	65	3		32	1.91	0.09		0.97
E-M-P	34		33	33	55		13	32	1.62		0.39	0.97
O-M-P		34	33	33		10	26	64		0.29	0.79	1.94
E-O-M-P	25	25	25	25	56	3	10	31	2.24	0.12	0.40	1.24

The powder X-ray diffraction patterns are able to be assigned to the orthorhombic phase of type III structure for the mixed-guest clathrates except for those of O-P, M-P, and O-M-P mixed ones in which P is most enriched. As shown in Figure 1, the patterns of the single-guest E, O, and M clathrates are similar to one another owing to the same space group $Pn\bar{a}m$ and the similar values of the unit cell parameters, to which patterns that of the E-O-M-P mixed one, as well as those of the E-enriched mixed ones, shows a close similarity. On the other hand, the pattern observed for P single-guest clathrate is less complicated owing to the hexagonal space group $P6_3/mmc$.⁸ The diffraction patterns observed for the three P-enriched mixed-guest clathrates are similar to that of P single-guest clathrate. There are three kinds of cavities in type III host structure, IIIA, IIIB and IIIC; type III benzene clathrate accommodates one each C_6H_6 in IIIA and IIIB respectively, and NMe_4^+ in IIIC, whereas toluene clathrate dose the phenyl ring of a $\text{C}_6\text{H}_5\text{Me}$ in IIIB and methyl group in IIIC, and the onium in IIIA.¹ Each of the E, O and M in the single-guest clathrates occupies cavities IIIB and IIIC similar to the $\text{C}_6\text{H}_5\text{Me}$. In the five single crystal structures obtained for type V, onium cation is accommodated in the smaller VA cavity but the aliphatic guests such as $\text{CH}_2\text{ClCH}_2\text{Cl}$, $\text{C}_2\text{H}_5\text{CN}$, are in the greater VB in pair,¹ the *p*-xylene guest in the single-guest clathrate is enclathrated in cavity VB in place of the couple of the aliphatic guests.

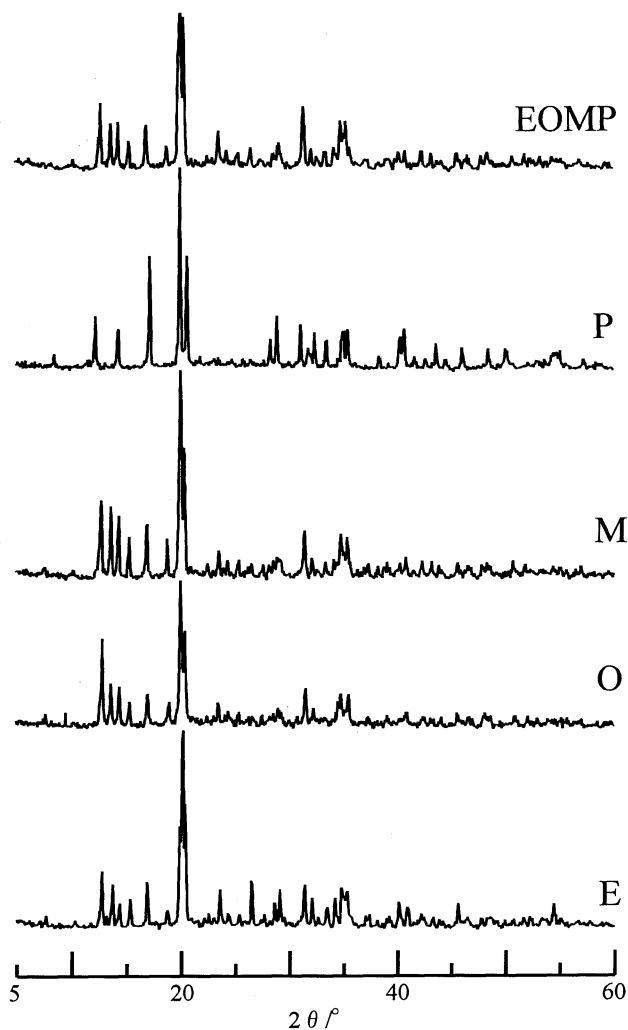


Figure 1. Powder X-ray diffraction patterns of the single-guest and the mixed-guest clathrates. Notations have been defined in text.

These structural features give a remarkable difference between the present system and an earlier example of aromatic guest clathrates of metal complex host $[\text{Ni}(\text{NCS})_2(4\text{-Mepy})_4] \cdot \text{G}$, in which P was more enriched than E, and O and M,⁹ although the host is comprised of the packing of the complex molecules. Limiting to di-substituted benzene derivatives, the present system is similar to the Ni-complex host clathrates in the tendency that *p*-isomer is generally preferable to *o*- and *m*-isomer. Well-defined crystal structures are necessary to discuss the inclusion behavior of host-guest systems in detail. Those details will be reported later.

References and Notes

- 1 T. Kitazawa, S. Nishikiori, and T. Iwamoto, *J. Chem. Soc., Dalton Trans.*, 3695 (1994).
- 2 T. Iwamoto, T. Kitazawa, S. Nishikiori, and R. Kuroda, *Chemical Physics of Intercalation II*, eds. P. Berneir, J. E. Fischer, S. Roth, and S. A. Solin, NATO ASI Series B, Vol. 305, Plenum, New York (1993), pp. 325-332; T. Iwamoto, *Chemistry of Microporous Crystals*, eds. T. Inui, S. Namba, and T. Tatsumi, Kodansha-Elsevier, Tokyo (1991), pp. 3-10; T. Iwamoto, *Inclusion Compounds*, Vol. 5, eds. J. L. Atwood, J. E. D. Davies, and D. D. MacNicol, Oxford University Press, Oxford (1991), pp. 177-212; T. Kitazawa, S. Nishikiori, R. Kuroda, and T. Iwamoto, *Chem. Lett.*, 459 (1988).
- 3 K. Kitazawa, S. Nishikiori, R. Kuroda, and T. Iwamoto, *J. Chem. Soc., Dalton Trans.*, 1029 (1994); S. Nishikiori, C. I. Ratcliffe, and J. A. Ripmeester, *J. Am. Chem. Soc.*, **114**, 8590 (1992); T. Kitazawa, S. Nishikiori, A. Yamagishi, R. Kuroda, and T. Iwamoto, *J. Chem. Soc., Chem. Commun.*, 413 (1992); T. Kitazawa, S. Nishikiori, R. Kuroda, and T. Iwamoto, *Chem. Lett.*, 1729 (1988).
- 4 T. Kitazawa, T. Kikuyama, M. Takahashi, and M. Takeda, *J. Chem. Soc., Dalton Trans.*, 2993 (1994); T. Kitazawa, H. Sugisawa, M. Takeda, and T. Iwamoto, *J. Chem. Soc., Chem. Commun.*, 1855 (1993); S. Nishikiori and T. Iwamoto, *J. Chem. Soc., Chem. Commun.*, 1555 (1993); T. Kitazawa, M. Akiyama, M. Takahashi, and M. Takeda, *J. Chem. Soc., Chem. Commun.*, 1112 (1993); T. Kitazawa and M. Takeda, *J. Chem. Soc., Chem. Commun.*, 309 (1993); T. Kitazawa, S. Nishikiori, and T. Iwamoto, *Mater. Sci. Forum*, **91-93**, 257 (1992).
- 5 A Rigaku RAD-C diffractometer equipped with a graphite-monochromated Cu-K α radiation.
- 6 $[\text{NMe}_4 \cdot \text{C}_6\text{H}_5\text{Et}][\text{Cd}_3(\text{CN})_7]$: orthorhombic *Pnam*, $a = 22.461(2)$, $b = 13.498(2)$, $c = 8.859(1)$, $Z = 4$;
 $[\text{NMe}_4 \cdot 0.67o\text{-C}_6\text{H}_4\text{Me}_2][\text{Cd}_3(\text{CN})_7]$: orthorhombic *Pnam*, $a = 22.230(2)$, $b = 13.570(6)$, $c = 8.873(2)$, $Z = 4$;
 $[\text{NMe}_4 \cdot 0.67m\text{-C}_6\text{H}_4\text{Me}_2][\text{Cd}_3(\text{CN})_7]$: orthorhombic *Pnam*, $a = 22.267(3)$, $b = 13.498(5)$, $c = 8.833(2)$, $Z = 4$;
 $[\text{NMe}_4 \cdot p\text{-C}_6\text{H}_4\text{Me}_2][\text{Cd}_3(\text{CN})_7]$: hexagonal *P6₃/mmc*, $a = 8.857(2)$, $c = 20.716(3)$, $Z = 2$.
- 7 A Shimadzu GC-8A gas chromatograph equipped with dual FID detectors; Bentone 34(5%) + DIDP(5%) liquid phase; 80 to 100 mesh Unipor KA solid phase; a glass column of 3 mm inner diameter and 4.2 m length; column temperature at 95°C; N₂ carrier gas at 60 cm³/min.
- 8 The unconventional orthorhombic lattice derived from the hexagonal system of the parameters *a* and *c* has the parameters *A*, *B*, and *C* as $A = c (20.716)$, $B = 2a \sin 60 (15.341)$ and $C = a (8.857)$ in comparison with the orthorhombic system of type III.
- 9 M. J. Minton and N. O. Smith, *J. Phys. Chem.*, **71**, 3618 (1967); W. D. Schaeffer, W. S. Dorsey, D. A. Skinner and C. G. Christian, *J. Am. Chem. Soc.*, **79**, 5870 (1957); F. V. Williams, *J. Am. Chem. Soc.*, **79**, 5876 (1957).