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FRACTIONAL ENCLATHRATION-CRYSTALLISATION BEHAVIOUR OF THE ZEOLITE-MIMETIC [ONIUM • *x*G] • $[Cd_3(CN)_7]$ 3D HOSTS FOR AROMATIC GUESTS BENZENE, TOLUENE, ETHYLBENZENE AND XYLENE ISOMERS

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Abstract Inclusion selectivity of [onium•*x*G]•$[Cd_3(CN)_7]$ (onium = NMe_4^+ or SMe_3^+) clathrates were investigated for C_6H_6 (B), PhMe (T), ortho (O), meta (M) and para (P) isomers of $C_6H_4Me_2$ (X) and PhEt (E) as G upon the enclathration-crystallisation processes of the respective mixed guest clathrates from the binary, ternary, quaternary and quinary mixtures of B, T, X and E. The order of preference in the NMe_4^+-host is T > B > P ≫ M > O and E > P ≫ M > O; in the SMe_3^+- host P > T > B ≫ M > O and P > E ≫ M > O.

INTRODUCTION

We have prepared and characterised a number of the zeolite-like 3D hosts of $[Cd_3(CN)_7]^-$ enclathrating organic onium cations and neutral organic molecules as the guests with the well-defined X-ray single crystal structures; the host structures have been classified into six types according to the structural features different in the array of the tetrahedral and octahedral Cd atoms linked by CN groups.[1] Among them our type Ⅲ host gives the clathrates of C_6H_6 and PhMe along with NMe_4^+ or SMe_3^+ cations: $[SMe_3 \cdot 2C_6H_6] \cdot [Cd_3(CN)_7]$, $[NMe_4 \cdot 1.5C_6H_6] \cdot [Cd_3(CN)_7]$ and $[NMe_4 \cdot PhMe] \cdot [Cd_3(CN)_7]$ isomorphous to one another with the space group *Pnam* and lattice parameters comparable with one another. This paper examines the inclusion selectivity of the $[Cd_3(CN)_7]^-$ host for typical aromatic guests such as C_6H_6 (B), PhMe (T), ortho (O), meta (M) and para (P) isomers of $C_6H_4Me_2$ (X), PhEt (E), upon the enclathration-crystallisation processes of the respective mixed guest clathrates; some preliminary results have been reported.[2] The results are interpreted in terms of the crystal structures of the respective mixed-

guest clathrates and seven single-guest clathrates determined anew in this work.

EXPERIMENTAL

Preparation

The mixed- and single-guest clathrates were prepared under similar conditions to those in literature.[1] Aqueous solutions containing the host moieties, $CdCl_2$, $K_2[Cd(CN)_4]$, and NMe_4Cl or SMe_3I were respectively covered with the organic phases of the equimolar binary, ternary, quaternary or quinary mixtures of B-T-O-M-P or E-O-M-P systems. Crystalline products obtained after a few days leaving at 5℃ were identified by IR, gas chromatography, and powder X-ray diffractometry. Single crystal specimens of the single-guest clathrates were prepared for $[NMe_4 \cdot xG] \cdot [Cd_3(CN)_7]$ (G = E, O, M, and P) and for $[SMe_3 \cdot xG] \cdot [Cd_3(CN)_7]$ (G = T, E, and P). Those clathrates with the onium guest NMe_4^+ and SMe_3^+ are denoted to N-series and S-series, respectively.

X-ray Diffraction

The powder X-ray diffraction patterns were recorded on a Rigaku RAD-C diffractometer using a graphite-monochromated Cu-K α radiation for the mixed- and single-guest clathrates. The single crystals coated with epoxy resin were subjected to the refinement of the unit cell parameters and the intensity data collection on a Rigaku AFC-5S four-circle diffractometer using a graphite-monochromated Mo-K α radiation. The structures were solved by our routine procedures;[1] their details will be reported elsewhere.

Gas Chromatography

Compositions of the guests in the mixed-guest clathrate and the feed mixtures were determined using a Shimadzu GC-8A gas chromatograph. The prepared mixed-guest clathrates were filtered out on a sintered glass, washed with small amounts of EtOH and then Me_2CO, and air-dried for a short while. The washed specimen was immersed in CCl_4 on an agate mortar, and finely powdered to extract the guests at ambient temperature. The CCl_4 solution was filtered through a plastic membrane and subjected to the gas chromatographic measurement.

RESULTS AND DISCUSSION

Structural Identification

Table 1 summarises the single crystal data of the single-guest clathrates including those of the previously reported ones relevant to this work. Among them, N-P and S-P are not isostructural with type Ⅲ (orthorhombic *Pnam*) but belong to the hexagonal $P6_3/mmc$ (isostructural to our type V) and pseudohexagonal *Pa* (monoclinic: β = 94.82(2)°) space groups, respectively. The powder diffraction patterns of the mixed-guest clathrates were compared with the orthorhombic and the hexagonal patterns of the respective single-guest clathrates to assign the host structures either of type Ⅲ or V.

TABLE 1 Crystal data for [onium•xG]•[$Cd_3(CN)_7$]

Onium	NMe_4^+					
xG	1.5B[1]	T[1]	2/3O	2/3M	E	P
Space group			*Pnam*			$P6_3/mmc$
a/Å	21.628(3)	22.33(2)	22.230(2)	22.267(3)	22.461(2)	8.857(2)
b/Å	13.998(3)	13.297(6)	13.570(6)	13.498(5)	13.498(2)	= *a*
c/Å	8.945(1)	8.846(4)	8.873(2)	8.833(2)	8.859(1)	20.716(3)
Z			4			2
Onium	SMe_3^+					
xG	2B[1]	T			E	P
Space group			*Pnam*			*Pa*
a/Å	21.934(7)	21.862(5)			21.855(3)	15.026(5)
b/Å	13.483(2)	13.389(7)			13.511(4)	9.025(2)
c/Å	8.875(3)	8.996(3)			8.975(3)	19.832(4)
β/°			90			94.82(2)
Z			4			4

Selectivities

In order to evaluate inclusion selectivities an enrichment factor Q is defined as $Q_A = N_A / n_A$ for guest A where N_A and n_A are mole % of guest A in the clathrate and in the feed mixture, respectively. Although the Q values are independent in a given feed mixture, they may be usable as relative figures. The results are listed in Table 2 and 3, along with the assignments of the powder X-ray diffraction patterns either to Ⅲ (orthorhombic) or to V (hexagonal or pseudohexagonal).

In the N-series, T is always most enriched in the clathrate phase from the binary, ternary, quaternary and quinary BTX feed mixtures, B has second priority, and P the third.

TABLE 2 Fractional enclathration-crystallisation data for $[NMe_4 \cdot xG] \cdot [Cd_3(CN)_7]$

Mixed	Feed Mixture					Clathrate					Enrichment Factor					Host
Guest	n_B	n_T	n_O	n_M	n_P	N_B	N_T	N_O	N_M	N_P	Q_B	Q_T	Q_O	Q_M	Q_P	Type
BT	50	50				28	72				0.56	1.44				III
BO	50		50			99		1			1.98		0.02			III
BM	50			50		99			1		1.98			0.02		III
BP	50				50	78				22	1.56				0.44	III
TO		50	50				97	3				1.94	0.06			III
TM		50		50			87		13			1.74		0.26		III
TP		50			50		66			34		1.32			0.68	III
BTO	34	33	33			26	70	4			0.76	2.12	0.12			III
BTM	34	33		33		35	55		10		1.03	1.67		0.30		III
BTP	34	33			33	29	51			20	0.85	1.55			0.61	III
BOM	34		33	33		99		0	1		2.91		0.00	0.03		III
BOP	34		33		33	79		3		18	2.32		0.09		0.55	III
BMP	34			33	33	58			6	36	1.71			0.18	1.09	III
TOM		34	33	33			83	5	13			2.44	0.15	0.39		III
TOP		34	33		33		63	6		31		1.85	0.18		0.94	III
TMP		34		33	33		62		12	26		1.82		0.36	0.79	III
BTOM	25	25	25	25		41	48	2	9		1.64	1.92	0.08	0.36		III
BTOP	25	25	25		25	24	52	2		22	0.96	2.08	0.08		0.88	III
BTMP	25	25		25	25	25	45		8	22	1.00	1.80		0.32	0.88	III
BOMP	25		25	25	25	59		5	9	27	2.36		0.20	0.36	1.08	III
TOMP		25	25	25	25		59	3	10	28		2.36	0.12	0.40	1.12	III
BTOMP	20	20	20	20	20	32	40	3	9	16	1.60	2.00	0.15	0.45	0.80	III

Mixed	Feed Mixture				Clathrate				Enrichment Factor				Host
Guest	n_E	n_O	n_M	n_P	N_E	N_O	N_M	N_P	Q_E	Q_O	Q_M	Q_P	Type
EO	50	50			91	9			1.82	0.18			III
EM	50		50		84		16		1.68		0.32		III
EP	50			50	70			30	1.40			0.60	III
OM		50	50			24	76			0.48	1.52		III
OP		50		50		4		96		0.08		1.92	V
MP			50	50			19	81			0.38	1.62	V
EOM	34	33	33		77	6	17		2.26	0.18	0.52		III
EOP	34	33		33	65	3		32	1.91	0.09		0.97	III
EMP	34		33	33	55		13	32	1.62		0.39	0.97	III
OMP		34	33	33		10	26	64		0.29	0.79	1.94	V
EOMP	25	25	25	25	56	3	10	31	2.24	0.12	0.40	1.24	III

TABLE 3 Fractional enclathration-crystallisation data for [SMe_3•xG]•[$Cd_3(CN)_7$]

Mixed	Feed Mixture					Clathrate					Enrichment Factor					Host
Guest	n_B	n_T	n_O	n_M	n_P	N_B	N_T	N_O	N_M	N_P	Q_B	Q_T	Q_O	Q_M	Q_P	Type
BT	50	50				27	73				0.54	1.46				III
BO	50		50			99		1			1.98		0.02			III
BM	50			50		99			1		1.98			0.02		III
BP	50				50	5				95	0.10				1.90	V
TO		50	50				95	5				1.90	0.10			III
TM		50		50			93		7			1.86		0.14		III
TP		50			50		9			91		0.18			1.82	V
BTO	34	33	33			23	66	11			0.68	2.00	0.33			III
BTM	34	33		33		24	61		15		0.71	1.85		0.45		III
BTP	34	33			33	4	8			88	0.12	0.24			2.67	V
BOM	34		33	33		98		1	1		2.88		0.03	0.03		III
BOP	34		33		33	27		5		68	0.79		0.15		2.06	V
BMP	34			33	33	4			7	89	0.12			0.21	2.70	V
TOM		34	33	33			86	7	7			2.53	0.21	0.21		III
TOP		34	33		33		8	3		89		0.24	0.09		2.70	V
TMP		34		33	33		8		7	85		0.24		0.21	2.58	V
BTOM	25	25	25	25		28	57	6	9		1.12	2.28	0.24	0.36		III
BTOP	25	25	25		25	2	6	2		90	0.08	0.24	0.08		3.60	V
BTMP	25	25		25	25	2	6		7	85	0.08	0.24		0.28	3.40	V
BOMP	25		25	25	25	1		2	6	90	0.04		0.08	0.24	3.60	V
TOMP		25	25	25	25		9	3	9	79		0.36	0.12	0.36	3.16	V
BTOMP	20	20	20	20	20	11	24	4	6	55	0.55	1.20	0.20	0.30	2.75	V

Mixed	Feed Mixture				Clathrate				Enrichment Factor				Host
Guest	n_E	n_O	n_M	n_P	N_E	N_O	N_M	N_P	Q_E	Q_O	Q_M	Q_P	Type
EO	50	50			94	6			1.88	0.12			III
EM	50		50		91		9		1.82		0.18		III
EP	50			50	32			68	0.64			1.36	V
OM		50	50			0	0			0	0		
OP		50		50		8		92		0.16		1.84	V
MP			50	50			8	92			0.16	1.84	V
EOM	34	33	33		87	5	8		2.56	0.15	0.24		III
EOP	34	33		33	27	4		69	0.79	0.12		2.09	V
EMP	34		33	33	24		10	66	0.71		0.30	2.00	V
OMP		34	33	33		0	19	81		0.00	0.58	2.45	V
EOMP	25	25	25	25	24	4	7	65	0.96	0.16	0.28	2.60	V

From the binary, ternary and quaternary EX mixtures, E is most enriched, P the second and M the third.

In the S-series the order of the priority is P > T > B ≫ M > O from the BTX feed mixtures in contrast with that in the N-series T > B > P ≫ M > O. Similarly the order is reversed at the top two for the EX feed mixtures P > E ≫ M > O from that in the N-series E > P ≫ M > O.

Structures of the Mixed-Guest Clathrates

The powder X-ray diffraction patterns observed for the mixed-guest clathrates are able to be assigned clearly to one of the two types, Ⅲ and Ⅴ, for both N- and S-series. Since the monoclinic host lattice of the S-P single-guest clathrate is distorted to such an extent with the monoclinic angle $\beta = 94.82(2)^\circ$ from a hexagonal one ($a \fallingdotseq b = 9.03$, $c \fallingdotseq 19.83$ Å in the pseudohexagonal lattice), its powder pattern shows a close similarity to those of the hexagonal type Ⅴ. All the mixed-guest clathrates most enriched in P showed type Ⅴ patterns, whereas the others did type Ⅲ.

The selectivities observed for the NMe_4^+-host T > B > P ≫ M > O and E > P ≫ M > O and for the SMe_3^+-host P > T > B ≫ M > O and P > E ≫ M > O can be interpreted in terms of the host structure, the number of methyl groups in the onium guest, and the position(s) of methyl group(s) in the aromatic guest. Since the channel-like and the cage-like characters in type Ⅲ host structure are respectively more and less than in type Ⅴ, the quaternary ammonium in Ⅲ reduces the space of neighbouring cavity in which the aromatic guest is accommodated in comparison with that in Ⅴ. On the other hand, the tertiary sulphonium is advantageous to the accommodation of itself and P in the cage-like cavities. The methyl groups at ortho and meta positions are unfavourable for accommodation in both host structures.

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