= 단신 =

Piperazine 리간드를 가진 시아노카드뮴 호스트 착물의 방향족 게스트 분자에 대한 포접선택성

김종혁★ · 이석근

한국화학연구원 분석실

(2003. 7. 2. 접수, 2003. 8. 5 승인)

Inclusion Selectivity of the Cyanocadmate Host Complex with Piperazine Ligand for Aromatic Guest Molecules; Benzene, Toluene, Ethylbenzene and Xylene Isomers

Chong-Hyeak Kim★ and Sueg-Geun Lee

Chemical Analysis Laboratory, Korea Research Institute of Chemical Technology, P.O. Box 107, Yuseong, Daejeon 305-600, Korea

(Received Jul. 2, 2003, Accepted Aug. 5, 2003)

Abstract : Inclusion selectivity of a three-dimensional piperazine-ligated cyanocadmate host complex, $[Cd_x(CN)_{2x}\{HN(CH_2CH_2)_2NH\}_y] \cdot zG$, has been investigated for benzene (B), toluene (T), ethylbenzene (E), *o*- (O), *m*- (M), and *p*-xylene (P) isomers as the aromatic guest molecules. From the binary, ternary and quarternary guest mixtures of E and xylene isomer (X), the order of inclusion selectivity in the host complex is O > E > P > M. From the binary to quinary BTX mixtures, the order of preference in the complex is seen to be B > T > O ≫ P > M.

Key words : inclusion selectivity, cyanocadmate host complex, piperazine ligand, aromatic guest molecules

1. Introduction

The organic and inorganic supramolecular chemistry has been of great interest to chemists because of the potential applicabilities such as the media of molecular recognition, separation, topo-specific reaction, transport, self-assembly and self-organization, *etc*.[1] Especially, the application of molecular inclusion phenomena is one of the most important strategies to develop novel separation technologies. Examples of applications using the organic inclusion compounds derived from crown ethers, cryptands, cyclodextrins, cyclophanes, calixarenes, *etc*, have been reported by many investigators.[2,3] However, the use of artificially-designed multi-dimensional inorganic metal complexes has not yet been explored in detail in comparison with the application of designed organic macrocyclic hosts.

Recently, Iwamoto and co-workers have obtained a number of inclusion compounds using cadmium cyanide, $Cd(CN)_2$, or polycyanopolycadmate, $[Cd_x(CN)_y]^{2x-y}$, as host and several organic molecules as guests.[4-6] In general, the structures of host so far determined by single crystal X-ray diffraction experiments have been classified into three groups, cristobalite-like type, clay-like type, and zeolite-like type. Zeolites and clay

★ Corresponding author

Phone : +82-(0)42-860-7721   Fax : +82-(0)42-860-7794

E-mail : chkim@krict.re.kr

minerals attract wide interest both in academic and in industrial research since they are able to serve as ion exchangers, as molecular sieves, as shape-selective catalysts, etc. providing a great number of different applications.[7,8] Therefore, the host of zeolite-mimetic polycyanopolycadmate complexes applied to the studies concerning the inclusion selectivities of aromatic guest mixtures and some preliminary results have been reported previously.[9,10] Other investigations related to the zeolite-like adsorption properties of the cyanometallates with the general formular $M_x[M(CN)_6]_y$ have been reported.[11,12]

On the other hand, the separation of benzene, toluene, ethylbenzene and xylenes from the BTX mixture, which is obtained from crude petroleum, has long been an important subject of chemistry. That is the recovery of ethylbenzene for conversion to styrene monomer for the production of synthetic resin, the recovery of p-xylene for the preparation of terephthalic acid, the recovery of m-xylene for the production of isophthalic acid. However, we can predict that there are many problems in the separation of isomers, especially the boiling points of ethylbenzene (b.p. 136.2 ℃) and o-(b.p. 144.4 ℃), m-(b.p. 139.1 ℃), p-xylene(b.p. 138.4 ℃) isomers are too close to separate by distillation.

Our research aimed to investigate the inclusion selectivity of cyanometallate host complex and to develop novel materials with functions such as molecular recognition and separation. Recently, we have obtained a number of cyanometallate inclusion compounds using secondary ligand such as piperazine, imidazole, etc. As a continuation of this application research using molecular inclusion phenomena, we now report the relative inclusion selectivities of piperazine-ligated cyanocadmate host complex, $[Cd_x(CN)_{2x}\{HN(CH_2CH_2)_2NH\}_y] \cdot zG$, for aromatic guest molecules.

2. Experimental

2.1. Preparation and identification

The single- and mixed-guest complexes were prepared by a method based on our previous papers.[9,10] An aqueous solution (30 ml) containing 1.14g (5 mmol) of $CdCl_2 \cdot 2.5H_2O$, 1.47g (5 mmol) of $K_2[Cd(CN)_4]$, and 0.43g (5 mmol) of piperazine (diethylenediamine) was adjusted to the pH 8 by adding of 2-aminoethanol and citric acid. The solutions containing the host moieties were respectively mixed with a layer of single-guest species or with the mixed-guest liquid phase of the feed mixture, one of the equimolar binary, ternary, quarternary, and quinary mixtures of benzene, toluene, ethylbenzene, o-xylene, m-xylene and/or p-xylene. This sample solution kept standing in a refrigerator at 5 ℃ for a few days to obtain crystalline products grown at the interface between the aqueous and the organic phases and/or the bottom of the aqueous phase. The colorless crystalline inclusion compounds of benzene, toluene, ethylbenzene, o-xylene, and p-xylene single-guest were obtained, but m-xylene single-guest itself never did give any inclusion compound under similar conditions: accommodation of m-xylene guest molecule was only possible when it was mixed with other guest species which could be enclathrated.

In order to identify compositions of the obtained complexes, infrared spectra of the products were recorded on a BioRad Digilab FTS-165 FT-IR spectrometer as the nujol mulls to prevent spontaneous liberation of guest molecules from the complexes. Bridging CN groups were ascertained from the strong peak at 2150 cm^{-1}, and guests were assigned by the characteristic bands of guest molecules. Carbon, hydrogen and nitrogen contents in single-guest complexes were determined by CE instruments EA-1110 elemental analyzer.

2.2. Gas chromatography and X-ray powder diffractometry

The qualitative and quantitative analyses of the aromatic guest species in the mixed-guest complexes were carried out on a gas chromatograph. Optimum separation and analysis conditions are as follows:

Gas chromatograph : Hewlett-Packard 5890 series II
Column : Nukol capillary (30 m × 0.25 mm)
Oven temp. : 50 ℃ (3 min) to 110 ℃ (5 min),

rate ; 6 ℃/min.
Detector : flame ionization detector (FID)
Injector temp. : 220 ℃
Detector temp. : 270 ℃.

Compositions of the guests in mixed-guest complexes were determined by gas chromatography through the following procedures. Fine crystals of the mixed-guest complexes were filtered out on a sintered glass, washed with small amounts of ethanol and acetone quickly, and air-dried for a short while. The washed crystals were immersed in a small amounts of carbon tetrachloride on an agate mortar, and powdered more finely to extract the aromatic guests at ambient temperature. The carbon tetrachloride solution containing the extracted aromatic species was filtered through the plastic membrane and subjected to the gas chromatographic measurement.

Although there is no guarantee of the complete extraction of the guest species from the complexes, the determined values were read as the mole fractions of the guests enclathrated assuming that the ratio had been kept unchanged. Reproducibilities of the results were within ±1% in a batch but *ca.* ±3% for a set of several batches of the mixed-guest complexes prepared under similar experimental conditions.

In order to assign the host structures of the obtained mixed-guest complexes, the powder X-ray diffraction patterns of the single-guest and mixed-guest complexes were obtained, and the patterns of the single-guest and mixed-guest complexes were compared. The powder X-ray diffraction patterns were measured at Rigaku D/MAX-IIIB diffractometer equipped with a graphite monochromator using nickel-filtered Cu-Kα radiation (λ = 1.54184 Å).

3. Results and Discussion

3.1. Inclusion selectivities for ethylbenzene and xylene isomer mixtures

The compositions of the guests in the formed mixed-guest complexes obtained from the feed mixtures and the feed mixtures with equimolar mixing ratio in mole fraction were compared to evaluate the inclusion selectivity; the results are shown in *Table* 1.

The enrichment factor Q in *Table* 1 is defined as $Q_X = N_X/n_X$ for guest X species where N_X and n_X are mole fractions of guest X in the complex and in the feed mixture, respectively. Although Q values are independent in a given feed mixture, they may be usable as relative figures.

Table 1. Relative inclusion selectivities of the host complexes for the guest feed mixtures, ethylbenzene and xylene isomer

Mixed guest	Feed mixture				Complex				Enrichment factor			
	n_E	n_O	n_M	n_P	N_E	N_O	N_M	N_P	Q_E	Q_O	Q_M	Q_P
EO	0.50	0.50			0.38	0.62			0.76	1.24		
EM	0.50		0.50		0.70		0.30		1.40		0.60	
EP	0.50			0.50	0.52			0.48	1.04			0.96
OM		0.50	0.50			0.79	0.21			1.58	0.42	
OP		0.50		0.50		0.74		0.26		1.48		0.52
MP			0.50	0.50			0.29	0.71			0.58	1.42
EOM	0.34	0.33	0.33		0.35	0.53	0.12		1.06	1.58	0.36	
EOP	0.34	0.33		0.33	0.34	0.51		0.15	1.00	1.55		0.45
EMP	0.34		0.33	0.33	0.45		0.21	0.34	1.32		0.64	1.03
OMP		0.34	0.33	0.33		0.63	0.17	0.20		1.85	0.52	0.61
EOMP	0.25	0.25	0.25	0.25	0.32	0.42	0.11	0.15	1.28	1.68	0.44	0.60

[*] *n*, *N* and *Q* have been defined in text.

The results given in *Table* 1 showed that *o*-xylene guest molecule give the highest selectivity from the mixed feeds throughout the binary to quarternary mixtures; ethylbenzene was the second, and *p*-xylene in the third. For example, from the quarternary feed mixture of E-O-M-P, *o*-xylene is the most enriched with Q_O = 0.42/0.25 = 1.68, ethylbenzene is the second enriched with Q_E = 0.32/0.25 = 1.28, Q_P = 0.15/0.25 = 0.60, Q_M = 0.11/0.25 = 0.44; as for the binary E-O feed mixture, Q_E = 0.38/0.50 = 0.76, Q_O = 0.62/0.50 = 1.24. From those results, the order of the priority in the host complexes is O>E>P>M for the ethylbenzene and xylene isomer guest feed mixtures.

It is noticeable observation in comparison with earlier results;[13,14] in fact the priority of the *p*-xylene has been pointed out earlier paper dealing with the selectivity of aromatic isomers by inclusion into the bis (isothiocyanato)-tetrakis (4-methylpyridine)nickel(II) metal complex host. In previous papers[9,10] we reported that inclusion selectivity of the zeolite-mimetic polycyanopolycadmate complex, [onium · xG][Cd$_3$(CN)$_7$], were changed by onium cation guests; in case of $N(CH_3)_4^+$ onium, the selectivity order of aromatic guest is E>P>M>O; in case of $S(CH_3)_3^+$ onium and imidazole-ligated cyanocadmate complex,[15] the selectivity order of aromatic guest is P>E>M>O. In present work, cyanocadmate complex, $[Cd_x(CN)_{2x}\{HN(CH_2CH_2)_2NH\}_y] \cdot zG$, using piperazine ligand as a secondary ligand showed that the order of inclusion selectivity was O>E>P>M. It is surprising result that inclusion selectivity of guest molecules are changed by secondary ligands and/or onium ions.

In order to attempt to explain the results obtained we have looked in detail at a number of parameters: dimensions of guest molecules, vapor pressures, guest solubility, boiling points and calculated dipole moments of the guest obtained from molecular graphics. No correlation is found between the physical property and the experimentally observed inclusion selectivity. The variation of the inclusion selectivity suggests that inclusion process would be selective as regards the shape and size rather than the chemical properties of

molecules. Dimensions of guest molecules were obtained from molecular models of Fisher-Hirschfelder-Talor, are as fellows: For benzene 2.5×6.5×7.2 Å, for toluene 3.6×6.5×8.1 Å, for *o*-xylene 3.6×7.1×8.1 Å, for *m*-xylene 3.6×7.2×8.6 Å, for *p*-xylene 3.6×6.5×8.9 Å, for ethylbenzene 3.6×6.5×≒8.9 Å.

3.2. Inclusion selectivities for BTX mixtures

In order to evaluate inclusion selectivities of the piperazine-ligated host complexes for BTX guest mixtures, the enrichment factor Q is defined by the same method done in the previous section. The results of inclusion selectivities are listed in *Table* 2. As shown in results, benzene guest molecule is always the most enriched in the complex phase from the equimolar binary, ternary, quarternary and quinary BTX feed mixtures. Toluene has the second priority, and *o*-xylene the third. For example, from the quinary feed mixture of B-T-O-M-P, benzene is the most enriched with Q_B = 0.54/0.20 = 2.70, toluene is the second enriched with Q_T = 0.24/0.20 = 1.20, Q_O = 0.12/0.20 = 0.60, Q_P = 0.05/0.20 = 0.25, Q_M = 0.05/0.20 = 0.25. From those results, the order of the priority in the host complexes is B>T>O≫P>M for the BTX guest feed mixtures.

In previous papers[9,10] we reported that inclusion selectivity of the zeolite-mimetic polycyanopolycadmate complexes, [onium · xG][Cd$_3$(CN)$_7$]; in case of $N(CH_3)_4^+$ onium, the selectivity order of aromatic guest is T>B>P>M>O; in case of $S(CH_3)_3^+$ onium, that is P>T>B>M>O; in case of imidazole-ligated cyanocadmate complex[15] is B>T>P>M>O. In present work, cyanocadmate complex, $[Cd_x(CN)_{2x}\{HN(CH_2CH_2)_2NH\}_y] \cdot zG$, using piperazine ligand as a secondary ligand showed that the order of inclusion selectivity was B>T>O≫P>M. In comparison with the previous results, inclusion selectivity of cyanocadmate complex for BTX guest mixtures were changed by onium cation guests and/or by secondary ligand.

Table 2. Relative inclusion selectivities of the host complexes for the guest feed mixtures, benzene, toluene and xylene isomer

Mixed guest	Feed mixture					Complex					Enrichment factor				
	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
BT	0.50	0.50				0.62	0.38				1.24	0.76			
BO	0.50		0.50			0.77		0.23			1.54		0.46		
BM	0.50			0.50		0.84			0.16		1.68			0.32	
BP	0.50				0.50	0.86				0.14	1.72				0.28
TO		0.50	0.50				0.75	0.25				1.50	0.50		
TM		0.50		0.50			0.90		0.10			1.80		0.20	
TP		0.50			0.50		0.86			0.14		1.72			0.28
OM			0.50	0.50				0.79	0.21				1.58	0.42	
OP			0.50		0.50			0.74		0.26			1.48		0.52
MP				0.50	0.50				0.29	0.71				0.58	1.42
BTO	0.34	0.33	0.33			0.60	0.27	0.13			1.76	0.82	0.39		
BTM	0.34	0.33		0.33		0.62	0.29		0.09		1.82	0.88		0.27	
BTP	0.34	0.33			0.33	0.60	0.31			0.09	1.76	0.94			0.27
BOM	0.34		0.33	0.33		0.75		0.17	0.08		2.21		0.52	0.24	
BOP	0.34		0.33		0.33	0.75		0.17		0.08	2.21		0.52		0.24
BMP	0.34			0.33	0.33	0.81			0.09	0.10	2.38			0.27	0.30
TOM		0.34	0.33	0.33			0.70	0.23	0.07			2.06	0.70	0.21	
TOP		0.34	0.33		0.33		0.70	0.21		0.09		2.06	0.64		0.27
TMP		0.34		0.33	0.33		0.79		0.09	0.12		2.32		0.27	0.36
OMP			0.34	0.33	0.33			0.63	0.17	0.20			1.85	0.52	0.61
BTOM	0.25	0.25	0.25	0.25		0.56	0.26	0.12	0.06		2.24	1.04	0.48	0.24	
BTOP	0.25	0.25	0.25		0.25	0.43	0.26	0.18		0.13	1.72	1.04	0.72		0.52
BTMP	0.25	0.25		0.25	0.25	0.60	0.26		0.07	0.07	2.40	1.04		0.28	0.28
BOMP	0.25		0.25	0.25	0.25	0.70		0.16	0.07	0.07	2.80		0.64	0.28	0.28
TOMP		0.25	0.25	0.25	0.25		0.67	0.20	0.06	0.07		2.68	0.80	0.24	0.28
BTOMP	0.20	0.20	0.20	0.20	0.20	0.54	0.24	0.12	0.05	0.05	2.70	1.20	0.60	0.25	0.25

[*] *n, N* and *Q* have been defined in text.

3.3. Host structures for single-guest and mixed-guest complexes

In order to assign the host structures of the obtained mixed-guest complexes, the powder X-ray diffraction patterns of the single-guest and mixed-guest complexes were compared as shown in *Fig.* 1. According to the characteristic feature observed in the powder X-ray diffraction patterns, the host structures of the single guest complexes for benzene, toluene and *o*-xylene were identified as isostructural (B-, T- and O-type) with one another and to that of *p*-xylene and ethylbenzene were identified as P-type and E-type, respectively. X-ray diffraction pattern of *m*-xylene was not obtained, because *m*-xylene itself never did give any inclusion compound. However, the powder X-ray diffraction patterns of mixed-guest complexes give a remarkable difference compared with single-guest complexes as shown in *Fig.* 1. Therefore, syntheses of single crystals of the mixed-guest complexes with the stoichiometric compositions should be necessary to solve the relationship between inclusion selectivity of guest and host structure of the complex.
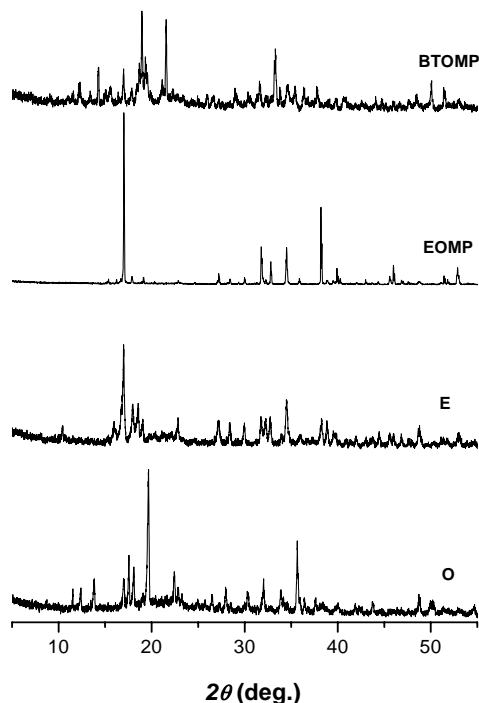
김종혁★·이석근

References

1. J. M. Lehn, ″Perspectives in Coordination Chemistry″, pp. 447-462, A. F. Williams, C. Floriani, A. E. Merbach, Eds., VCM, New York, 1992.
2. J. L. Atwood, J. E. D. Davies and D. D. MacNicol, ″Inclusion Compounds″, Vol. 1-3, Academic Press, London, 1984.
3. J. L. Atwood, J. E. D. Davies and D. D. MacNicol, ″Inclusion Compounds″, Vol. 4-5, Oxford University Press, Oxford, 1991.
4. T. Kitazawa, S. Nishikiori, R. Kuroda and T. Iwamoto, *J. Chem. Soc.*, *Dalton Trans.*, 1029 (1994).
5. T. Kitazawa, S. Nishikiori and T. Iwamoto, *Materials Science Forum*, **91-93**, 257 (1992).
6. T. Kitazawa, S. Nishikiori and T. Iwamoto, *J. Chem. Soc.*, *Dalton Trans.*, 3695 (1994).
7. A. Clearfield, *Chem. Rev.*, **88**, 125 (1988).
8. S. L. Suib, *Chem. Rev.*, **93**, 803 (1993).
9. C. H. Kim, S. Nishikiori and T. Iwamoto, *Chem. Lett.*, 409 (1995).
10. C. H. Kim, S. Nishikiori and T. Iwamoto, *Mol. Cryst. Liq. Cryst.*, **276**, 13 (1996).
11. G. Boxhoorn, J. Moolhuysen, J. G. F. Coolegem and R. A. van Santen, *J. Chem. Soc., Chem. Commun.*, 1305 (1985).
12. P. Cartraud, A. Cointot and A. Renaud, *J. Chem. Soc., Faraday Trans.*, **77**, 1561 (1981).
13. M. J. Minton and N. O. Smith, *J. Phys. Chem.*, **71**, 3618 (1967).
14. H. L. Wiener, L. Ilardi, P. Liberati, L. Dengler, S. A. Jeffas, S. Saba, and N. O. Smith, *J. Incl. Phenom.*, **4**, 415 (1986).
15. C. H. Kim, *Ph.D. Thesis,* The University of Tokyo, Japan, 1996.

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

4. Conclusion

The order of inclusion selectivities of the piperazine-ligated cyanocadmate host complexes, $[Cd_x(CN)_{2x}\{HN(CH_2CH_2)_2NH\}_y] \cdot zG$, for benzene, toluene, ethylbenzene and xylene isomer guests are $O > E > P > M$ and $B > T > O \gg P > M$. The present work may be very effective for the separation of isomers which have boiling points too close to separate by distillation such as ethylbenzene and *o*-, *m*-, *p*-xylene. Further studies, which will be the relationships between the selectivity for the aromatic guest molecules and the host structure, are in progress.