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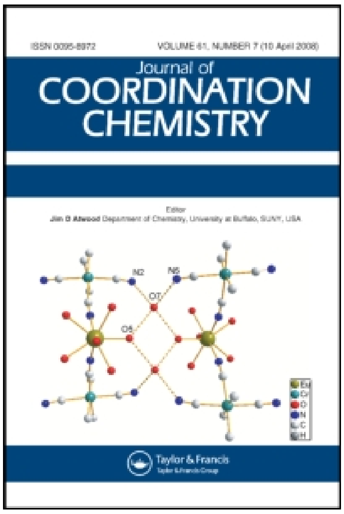

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Syntheses and Crystal Structures of Three-Dimensional Cyanocadmate Clathrates with Imidazole

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SYNTHESES AND CRYSTAL STRUCTURES OF THREE-DIMENSIONAL CYANOCADMATE CLATHRATES WITH IMIDAZOLE

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The crystal structures of two clathrates with imidazole (=imH), $[Cd_3(CN)_6(imH)_2]\cdot C_6H_{12}$, **I**, and $[Cd_3(CN)_6(imH)_2]\cdot C_6H_5Cl$, **II**, have been analyzed by single-crystal X-ray diffraction methods. Clathrate **I** crystallizes in the monoclinic system, space group $P2_1/n$ with $a = 13.416(2)$, $b = 14.140(2)$, $c = 14.151(1)$ Å, $\beta = 105.08(9)°$, $V = 2592.1(5)$ Å^3, $Z = 4$, $R_1 = 0.0360$, $wR_2 = 0.0850$ for 5931 independent reflections; **II**: monoclinic $P2_1/n$, $a = 12.369(2)$, $b = 14.313(2)$, $c = 14.416(4)$ Å, $\beta = 106.04(2)°$, $V = 2452.7(9)$ Å^3, $Z = 4$, $R_1 = 0.0398$, $wR_2 = 0.1105$ for 5642 independent reflections. The three-dimensional host structures of clathrates **I** and **II** are isostructural with each other. The host framework is built through cyanide bridges among two kinds of Cd ions, tetrahedral and octahedral, in a ratio of 2:1. The tetrahedral Cd(1) centre is linked to three octahedral Cd(3) atoms and one tetrahedral Cd(2) atom; the tetrahedral Cd(2) centre is ligated by one unidentate imidazole ligand and linked to one tetrahedral Cd(1) atom and two octahedral Cd(3) atoms; the octahedral Cd(3) centre is ligated by one unidentate imidazole ligand and linked to three tetrahedral Cd(1) atoms and two tetrahedral Cd(2) atoms. The novel host structure provides two types of channels, a large, elongated, rectangular channel and a small rectangular channel. The larger channel is occupied by imidazole ligands coordinated to tetrahedral Cd(2) and octahedral Cd(3). The smaller channel accommodates the guest molecules cyclohexane and chlorobenzene.

Keywords: Cyanocadmate clathrate; Imidazole; Cyclohexane; Chlorobenzene; Crystal structure

INTRODUCTION

Cadmium cyanide $[Cd(CN)_2]$ and polycyanopolycadmates $[Cd_x(CN)_y]^{2x-y}$ give a great variety of clathrate inclusion structures, as has been reported by the Iwamoto group [1–8] and others [9–17]. Except for the $Cd(CN)_2$ host structure that involves tetrahedral Cd only [1,2], then multidimensional hosts are constructed of CN linkages among

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tetrahedral Cd(t) and octahedral Cd(o) atoms. In some cases, trigonal bipyramidal, five-coordinate Cd(p) atoms are involved.

The presence or absence of a secondary ligand L at Cd(o) is one of the important factors for the host framework to provide cavities or channels appropriate in size and shape for guest molecules. For example, the host structures of both $[Cd(NH_3)_2Cd(CN)_4] \cdot 2G$ and $[Cd(en)Cd(CN)_4] \cdot 2G$ clathrates (en = ethylenediamine, $G = C_6H_6$, $C_6H_5NH_2$) [6,7] are topologically the same with respect to the three-dimensional (3D) lattice involving Cd(o) and Cd(t), although the latter is reinforced by an ethylenediamine bridge between Cd(o) atoms. However, the topologically related 3D lattice of $[Cd(py)_2Cd(CN)_4]$ (py = pyridine) [Cd(o) : Cd(t) = 1 : 1] has no ability to guest molecules [8]. A complicated 3D lattice in $[\{Cd(CN)(py)_2\}_3\{Cd_2(CN)_7\}]$ [Cd(o) : Cd(t) = 3 : 2] likewise cannot take up guests [8]. When the secondary ligand L is $C_6H_5NH_2$, the $[Cd(C_6H_5NH_2)_2Cd(CN)_4] \cdot 0.5C_6H_5NH_2$ clathrate has a different topology to the former clathrates.

Zeolite-like 3D structures of $[Cd_3(CN)_7]^-$ with a Cd(o):Cd(t) ratio of 1:2 are obtained without secondary ligands for a number of organic cations and neutral guests as well as that of $[Cd_4(CN)_9]^-$ with 1:3 ratio [3,9]. A number of ether or alcohol clathrates $u\text{Cd(CN)}_2 \cdot v\text{H}_2\text{O} \cdot w\text{G}$ were reported to have CN-linked 3D host structures involving Cd(o) and Cd(t), where Cd(o) centres are coordinated with H_2O ligands at *trans* or *cis* positions: $3Cd(CN)_2 \cdot 2H_2O \cdot 2G$ ($G = Pr^n_2$–O [9], Pr^i–OH [10]; Cd(o): Cd(t) = 1 : 2); $3Cd(CN)_2 \cdot 2H_2O \cdot 3Bu^t$–OH (Cd(o):Cd(t) = 1:2) [13]; $4Cd(CN)_2 \cdot 3H_2O \cdot 3G$ ($G = Et_2O$, Pr^i_2–O; Cd(o):Cd(t) = 3:5) [9]; $5Cd(CN)_2 \cdot 2H_2O \cdot 6Pr^n$–OH (Cd(o): Cd(t) = 1:4) [10]; $5Cd(CN)_2 \cdot 4H_2O \cdot 4$*cyclo*-$C_6H_{11}OH$ (Cd(o):Cd(p) = 1:4) [15]. Clay-like layer structures are also possible for the $[Cd(o)Cd(t)_2(CN)_6L_2]$ hosts with cationic, neutral or anionic L ligands [4,5]. The host lattice of $Cd(CN)_2 \cdot G$ clathrates adopts silica-like polymorphous structures, *viz*, those of high- and low-temperature phases of cristobalite and the high-temperature phase tridymite, upon changing geometry of guest molecule [1,2].

Hence, selection of the secondary ligand is a key to crystal engineering in the polycyanopolycadmate systems. Here we report the syntheses and crystal structures of the cyanocadmate clathrates $[Cd_3(CN)_6(imH)_2] \cdot C_6H_{12}$, **I**, and $[Cd_3(CN)_6(imH)_2] \cdot C_6H_5Cl$, **II** with the imidazole ligand, a five-membered aromatic amine, as the secondary ligand (Fig. 1).

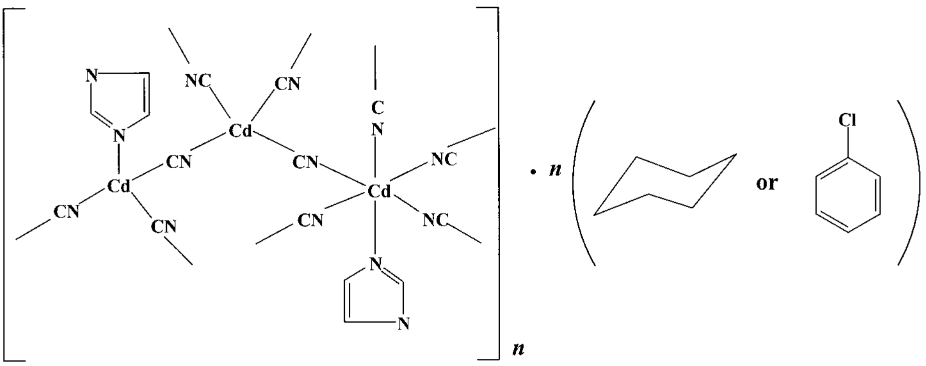

FIGURE 1 Structural chemical diagram for clathrates **I** and **II**.

EXPERIMENTAL

Preparation and Analysis of $[Cd_3(CN)_6(imH)_2]\cdot C_6H_{12}$, I

$CdCl_2 \cdot 2.5H_2O$ (2.28 g, 10 mmol) and $K_2[Cd(CN)_4]$ (2.94 g, 10 mmol) were dissolved in 40 ml of water; 10 ml of an aqueous solution of imidazole (1.0 g, 10 mmol) was added to this solution, dropwise, with stirring. A small amount of white precipitate was filtered off and *ca* 10 ml of cyclohexane was added. The resulting solution was allowed to stand in a refrigerator at 5°C. After a few weeks, pale yellow blocky crystals were obtained.

The IR spectrum of the crystal was recorded on a BioRad Digilab FTS-165 infrared spectrophotometer using the Nujol mull method. Imidazole and CN ligand were assigned by the relevant IR absorption bands [18]. An EDS spectrum obtained on a Philips XL-30S FEG scanning electron microscope/EDAX Phoenix energy dispersive X-ray spectrometer showed the presence of C, N, and Cd. Carbon, hydrogen and nitrogen were determined with a CE EA-1110 analyzer. Cd was determined using a Jobin-Yvon Ultima-C inductively coupled plasma emission spectrometer. The derived formula $[Cd_3(CN)_6(imH)_2]\cdot C_6H_{12}$ is consistent with results of single-crystal X-ray diffraction analysis. Yield: 75%. *Anal.* Calcd. for $C_{18}H_{20}N_{10}Cd_3$ (%): C, 30.29; H, 2.82; N. 19.63; Cd, 47.25. Found: C, 29.96; H, 2.67; N, 19.37; Cd, 47.5.

TABLE I Crystal data and structure refinement details for clathrates **I** and **II**

	I	**II**
Compound	$[Cd_3(CN)_6(imH)_2]\cdot(C_6H_{12})$	$[Cd_3(CN)_6(imH)_2]\cdot(C_6H_5Cl)$
Chemical formula	$C_{18}H_{20}Cd_3N_{10}$	$C_{18}H_{13}Cd_3ClN_{10}$
Formula weight	713.64	742.03
Temperature (K)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
Unit cell dimensions		
a (Å)	13.416(2)	12.369(2)
b (Å)	14.140(2)	14.313(2)
c (Å)	14.151(1)	14.416(4)
α (°)	90	90
β (°)	105.080(9)	106.04(2)
γ (°)	90	90
V (Å^3)	2592.1(5)	2452.7(9)
Z	4	4
Density (calculated) (g cm^{-3})	1.829	2.009
μ(MoKα) (mm^{-1})	2.462	2.712
F(000)	1368	1408
θ range for data collection (°)	1.9–27.5	1.9–27.5
Index range	$-1 \le h \le 17$, $-18 \le k \le 1$, $-18 \le l \le 17$	$-1 \le h \le 16$, $-1 \le k \le 18$, $-18 \le l \le 18$
Reflections measured	7225	6920
Independent reflections	5931 ($R_{int} = 0.0255$)	5642 ($R_{int} = 0.0389$)
Data/restraints/parameters	5931/0/281	5642/0/298
Goodness of fit on F^2	1.068	1.050
Final R indices [$I > 2\sigma(I)$]	0.0360, 0.0852	0.0398, 0.1108
R indices (all data)	0.0533, 0.0951	0.0507, 0.1194
Largest diff. peak and hole (eÅ^{-3})	0.515, -0.621	1.045, -1.041

Preparation and Analysis of $[Cd_3(CN)_6(imH)_2] \cdot C_6H_5Cl$, II

Use of the aqueous solution as above and neat chlorobenzene gave pale yellow blocky crystals after a few weeks. The formula $[Cd_3(CN)_6(imH)_2] \cdot C_6H_5Cl$ is consistent with results of single-crystal X-ray diffraction analysis. Yield: 70%. *Anal.* Calcd. for $C_{18}H_{13}N_{10}ClCd_3$ (%): C, 29.14; H, 1.77; N, 18.88; Cl, 4.76; Cd, 45.45. Found: C, 29.13; H, 1.73; N, 18.50; Cd, 45.1.

X-ray Crystallography

Pale yellow crystals were coated with epoxy glue in order to prevent spontaneous liberation of solvent guest molecules from the specimen under ambient conditions. An epoxy-coated crystal was mounted on an Siemens P4 four-circle X-ray diffractometer and intensity data were collected in the $\theta - 2\theta$ scan mode using graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å). Unit cell parameters and an orientation matrix for clathrates **I** and **II** were determined from a least-squares fit of 41 and 43 accurately centred reflections with a θ range of 4.57 – 12.51° and 3.31 – 12.54°, respectively. Three standard reflections were monitored every 97 reflections; little decay

TABLE II Atomic coordinates and equivalent thermal parameters for clathrate **I**

Atom	*x/a*	*y/b*	*z/c*	U_{eq} (Å^2)
Cd(1)	0.3459(1)	0.3283(1)	−0.1096(1)	0.048(1)
Cd(2)	0.3231(1)	0.0439(1)	0.1464(1)	0.053(1)
Cd(3)	0.2188(1)	0.6819(1)	−0.0087(1)	0.042(1)
C(1)	0.2704(4)	0.4573(3)	−0.0791(4)	0.051(1)
N(1)	0.2341(4)	0.5239(3)	−0.0591(3)	0.062(1)
C(2)	0.2973(4)	0.2710(4)	−0.2598(3)	0.052(1)
N(2)	0.2182(3)	0.7407(3)	−0.1640(3)	0.057(1)
C(3)	0.5158(4)	0.3219(4)	−0.0609(4)	0.054(1)
N(3)	0.3970(4)	0.6831(4)	0.0385(4)	0.066(1)
C(4)	0.2938(4)	0.1604(4)	0.0394(4)	0.057(1)
N(4)	0.2989(4)	0.2191(4)	−0.0140(4)	0.070(1)
C(5)	0.2579(4)	−0.0915(4)	0.0839(4)	0.054(1)
N(5)	0.2316(4)	0.8382(3)	0.0498(4)	0.063(1)
C(6)	0.3034(4)	0.0925(4)	0.2862(4)	0.058(1)
N(6)	0.2065(4)	0.6221(4)	0.1418(3)	0.068(1)
N(11)	0.4906(4)	0.0283(3)	0.1512(4)	0.064(1)
C(12)	0.5457(6)	0.0826(5)	0.1075(6)	0.087(2)
N(13)	0.6403(5)	0.0500(5)	0.1207(5)	0.102(2)
C(14)	0.6471(6)	−0.0313(6)	0.1758(6)	0.093(2)
C(15)	0.5563(6)	−0.0413(6)	0.1918(6)	0.099(2)
N(21)	0.0401(3)	0.6792(3)	−0.0616(4)	0.059(1)
C(22)	−0.0213(5)	0.6285(5)	−0.0237(6)	0.082(2)
N(23)	−0.1198(5)	0.6349(5)	−0.0742(6)	0.111(2)
C(24)	−0.1203(5)	0.6947(7)	−0.1505(7)	0.104(3)
C(25)	−0.0231(5)	0.7207(5)	−0.1415(5)	0.080(2)
C(31)	0.5208(16)	0.5622(12)	−0.1884(9)	0.229(10)
C(32)	0.4973(15)	0.4961(9)	−0.2653(12)	0.207(7)
C(33)	0.4710(20)	0.5295(15)	−0.3588(11)	0.288(14)
C(34)	0.4782(13)	0.6252(18)	−0.3815(11)	0.216(10)
C(35)	0.4930(20)	0.6872(11)	−0.3020(18)	0.263(13)
C(36)	0.5170(20)	0.6536(14)	−0.2123(14)	0.302(15)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE III Atomic coordinates and equivalent thermal parameters for clathrate **II**

Atom	x/a	y/b	z/c	U_{eq} (Å^2)
Cd(1)	0.1842(1)	0.3144(1)	0.6180(1)	0.043(1)
Cd(2)	0.1835(1)	0.0371(1)	0.3536(1)	0.047(1)
Cd(3)	0.2096(1)	0.1771(1)	0.9917(1)	0.038(1)
C(1)	0.2178(4)	0.2634(4)	0.7670(4)	0.046(1)
N(1)	0.2211(4)	0.2345(3)	0.8414(3)	0.051(1)
C(2)	0.2469(4)	0.4499(3)	0.5828(4)	0.045(1)
N(2)	0.2280(4)	0.0198(3)	0.9404(3)	0.051(1)
C(3)	−0.0053(5)	0.3139(4)	0.5675(5)	0.056(1)
N(3)	0.4025(5)	0.1836(4)	1.0445(4)	0.062(1)
C(4)	0.2230(5)	0.1499(4)	0.4634(4)	0.051(1)
N(4)	0.2240(5)	0.2066(4)	0.5187(4)	0.061(1)
C(5)	0.1940(5)	0.0856(4)	0.2129(3)	0.048(1)
N(5)	0.1963(4)	0.1149(3)	1.1401(3)	0.057(1)
C(6)	0.2549(5)	−0.0972(4)	0.4148(4)	0.050(1)
N(6)	0.2181(5)	0.3321(3)	1.0513(4)	0.059(1)
N(11)	0.0012(4)	0.0238(3)	0.3540(3)	0.049(1)
C(12)	−0.0737(6)	−0.0403(5)	0.3052(5)	0.072(2)
N(13)	−0.1727(6)	−0.0257(7)	0.3241(6)	0.102(3)
C(14)	−0.1570(7)	0.0463(5)	0.3892(6)	0.074(2)
C(15)	−0.0554(7)	0.0731(5)	0.4032(5)	0.069(2)
N(21)	0.0172(4)	0.1742(3)	0.9262(3)	0.049(1)
C(22)	−0.0452(5)	0.2136(5)	0.8451(5)	0.066(2)
N(23)	−0.1536(5)	0.1860(6)	0.8277(5)	0.096(2)
C(24)	−0.1570(5)	0.1281(4)	0.9023(5)	0.054(1)
C(25)	−0.0534(5)	0.1231(4)	0.9585(5)	0.059(1)
C(31)	0.5009(8)	0.0298(10)	0.6743(7)	0.114(4)
C(32)	0.4899(8)	0.1205(11)	0.6510(7)	0.121(5)
C(33)	0.4901(8)	0.1828(10)	0.7251(8)	0.118(4)
C(34)	0.4988(10)	0.1535(12)	0.8169(8)	0.130(5)
C(35)	0.5098(10)	0.0556(14)	0.8375(9)	0.150(6)
C(36)	0.5148(10)	−0.0006(11)	0.7678(8)	0.132(5)
Cl(1a)	0.4971(7)	−0.0362(5)	0.5956(5)	0.146(3)
Cl(1b)	0.4689(4)	0.2825(3)	0.6992(3)	0.090(1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

was observed during data collection. Lorentz and polarization corrections were applied to the intensity data, and a semi-empirical absorption correction based on psi-scans was applied [19].

All calculations concerning structure solution and refinement were performed using the Siemens SHELXTL crystallographic software package [20]. Space groups were assigned based on systematic absences and intensity statistics, and were confirmed by successful refinements. The structures were solved by direct methods [21] and refined by successive full-matrix least-squares methods followed by difference Fourier maps. All non-hydrogen atoms were refined anisotropically; the hydrogen atoms were placed in calculated positions with isotropic thermal parameters. Final difference electron density maps contained no significant features. Further details are given in Table I.

RESULTS AND DISCUSSION

Refined atomic parameters are listed in Tables II and III for clathrates **I** and **II**, respectively. Selected bond lengths and angles are listed in Tables IV and V for clathrates

TABLE IV Selected bond lengths (Å) and angles (°) for clathrate **I**

Cd(1)–C(1)	2.182(5)	Cd(1)–C(2)	2.209(5)
Cd(1)–C(3)	2.205(5)	Cd(1)–N(4)	2.248(5)
Cd(2)–C(4)	2.203(5)	Cd(2)–C(5)	2.193(5)
Cd(2)–C(6)	2.174(5)	Cd(2)–N(11)	2.242(5)
Cd(3)–N(1)	2.370(4)	Cd(3)–N(2)	2.347(4)
Cd(3)–N(3)	2.310(5)	Cd(3)–N(5)	2.351(4)
Cd(3)–N(6)	2.338(4)	Cd(3)–N(21)	2.319(5)
C(1)–N(1)	1.131(6)	C(2)–N(2)^{i}	1.129(6)
C(3)–N(3)^{iii}	1.131(7)	C(4)–N(4)	1.137(7)
C(5)–N(5)^{iv}	1.121(6)	C(6)–N(6)^{vi}	1.141(6)
N(11)–C(12)	1.325(8)	C(12)–N(13)	1.316(9)
N(13)–C(14)	1.38(1)	C(14)–C(15)	1.30(1)
C(15)–N(11)	1.346(9)	N(21)–C(22)	1.307(7)
C(22)–N(23)	1.332(9)	N(23)–C(24)	1.37(1)
C(24)–C(25)	1.33(1)	C(25)–N(21)	1.358(8)
C(31)–C(32)	1.41(2)	C(32)–C(33)	1.36(2)
C(33)–C(34)	1.40(2)	C(34)–C(35)	1.40(2)
C(35)–C(36)	1.32(2)	C(36)–C(31)	1.33(2)
C(1)–Cd(1)–C(2)	117.5(2)	C(1)–Cd(1)–C(3)	117.9(2)
C(1)–Cd(1)–N(4)	103.8(2)	C(2)–Cd(1)–C(3)	108.0(2)
C(2)–Cd(1)–N(4)	105.5(2)	C(3)–Cd(1)–N(4)	102.3(2)
C(4)–Cd(2)–C(5)	113.2(2)	C(4)–Cd(2)–C(6)	110.3(2)
C(4)–Cd(2)–N(11)	95.3(2)	C(5)–Cd(2)–C(6)	120.9(2)
C(5)–Cd(2)–N(11)	102.6(2)	C(6)–Cd(2)–N(11)	111.2(2)
N(1)–Cd(3)–N(2)	91.8(2)	N(1)–Cd(3)–N(3)	86.0(2)
N(1)–Cd(3)–N(5)	171.1(2)	N(1)–Cd(3)–N(6)	88.0(2)
N(1)–Cd(3)–N(21)	92.9(2)	N(2)–Cd(3)–N(3)	91.1(2)
N(2)–Cd(3)–N(5)	88.8(2)	N(2)–Cd(3)–N(6)	175.9(2)
N(2)–Cd(3)–N(21)	87.3(2)	N(3)–Cd(3)–N(5)	85.2(2)
N(3)–Cd(3)–N(6)	93.0(2)	N(3)–Cd(3)–N(21)	178.0(2)
N(5)–Cd(3)–N(6)	92.0(2)	N(5)–Cd(3)–N(21)	96.0(2)
N(6)–Cd(3)–N(21)	88.6(2)	Cd(1)–C(1)–N(1)	176.9(5)
Cd(1)–C(2)–N(2)^{i}	173.6(5)	Cd(1)–C(3)–N(3)^{ii}	177.8(5)
Cd(1)–N(4)–C(4)	167.6(5)	Cd(2)–C(4)–N(4)	166.5(5)
Cd(2)–C(5)–N(5)^{iv}	174.6(5)	Cd(2)–C(6)–N(6)^{vi}	176.9(5)
Cd(2)–N(11)–C(12)	127.3(5)	Cd(2)–N(11)–C(15)	128.6(5)
Cd(3)–N(1)–C(1)	159.7(4)	Cd(3)–N(2)–C(2)^{ii}	169.8(4)
Cd(3)–N(3)–C(3)^{iii}	175.9(5)	Cd(3)–N(5)–C(5)^{v}	166.2(5)
Cd(3)–N(6)–C(6)^{vii}	177.5(5)	Cd(3)–N(21)–C(22)	125.9(5)
Cd(3)–N(21)–C(25)	129.1(4)	N(11)–C(12)–N(13)	111.4(7)
C(12)–N(13)–C(14)	106.9(6)	N(13)–C(14)–C(15)	105.2(7)
C(14)–C(15)–N(11)	112.6(7)	C(15)–N(11)–C(12)	103.9(6)
N(21)–C(22)–N(23)	112.7(7)	C(22)–N(23)–C(24)	105.4(6)
N(23)–C(24)–C(25)	107.0(7)	C(24)–C(25)–N(21)	110.2(7)
C(25)–N(21)–C(22)	104.8(6)	C(31)–C(32)–C(33)	118(1)
C(32)–C(33)–C(34)	123(1)	C(33)–C(34)–C(35)	115(1)
C(34)–C(35)–C(36)	120(2)	C(35)–C(36)–C(31)	125(2)
C(36)–C(31)–C(32)	118(1)		

Symmetry transformations used to generate equivalent atoms: (i) $-x+1/2$, $y-1/2$, $-z-1/2$; (ii) $-x+1/2$, $y+1/2$, $-z-1/2$; (iii) $-x+1$, $-y+1$, $-z$; (iv) x, $y-1$, z; (v) x, $y+1$, z; (vi) $-x+1/2$, $y-1/2$, $-z+1/2$; (vii) $-x+1/2$, $y+1/2$, $-z+1/2$.

I and **II**, respectively. The asymmetric units and perspective views of the host framework for clathrates **I** and **II** are shown in Figs. 2 and 3, respectively.

As shown in Figs. 1 and 3, the three-dimensional host structures of clathrates **I** and **II** are isostructural. The host framework is constructed by CN-linkages among tetrahedral Cd(1) and Cd(2) and octahedral Cd(3) atoms. As shown in Figs. 2a and 2b, the tetrahedral Cd(1) atom is linked to one tetrahedral Cd(2) atoms and

TABLE V Selected bond lengths (Å) and angles (°) for clathrate **II**

Cd(1)–C(1)	2.197(5)	Cd(1)–C(2)	2.200(5)
Cd(1)–C(3)	2.254(6)	Cd(1)–N(4)	2.249(5)
Cd(2)–C(4)	2.219(5)	Cd(2)–C(5)	2.181(5)
Cd(2)–C(6)	2.197(5)	Cd(2)–N(11)	2.264(5)
Cd(3)–N(1)	2.359(4)	Cd(3)–N(2)	2.398(4)
Cd(3)–N(3)	2.298(6)	Cd(3)–N(5)	2.364(4)
Cd(3)–N(6)	2.370(5)	Cd(3)–N(21)	2.304(5)
C(1)–N(1)	1.139(7)	C(2)–N(2)^{i}	1.128(7)
C(3)–N(3)^{iii}	1.096(9)	C(4)–N(4)	1.135(7)
C(5)–N(5)^{iv}	1.137(7)	C(6)–N(6)^{ii}	1.133(7)
N(11)–C(12)	1.354(8)	C(12)–N(13)	1.34(1)
N(13)–C(14)	1.37(1)	C(14)–C(15)	1.28(1)
C(15)–N(11)	1.33(7)	N(21)–C(22)	1.336(8)
C(22)–N(23)	1.353(9)	N(23)–C(24)	1.37(1)
C(24)–C(25)	1.316(9)	C(25)–N(21)	1.319(7)
C(31)–C(32)	1.34(2)	C(32)–C(33)	1.39(2)
C(33)–C(34)	1.36(1)	C(34)–C(35)	1.43(2)
C(35)–C(36)	1.30(2)	C(36)–C(31)	1.38(1)
C(31)–Cl(1a)	1.47(1)	C(33)–Cl(1b)	1.48(1)

C(1)–Cd(1)–C(2)	122.3(2)	C(1)–Cd(1)–C(3)	102.3(2)
C(1)–Cd(1)–N(4)	112.3(2)	C(2)–Cd(1)–C(3)	109.2(2)
C(2)–Cd(1)–N(4)	107.8(2)	C(3)–Cd(1)–N(4)	100.6(2)
C(4)–Cd(2)–C(5)	112.0(2)	C(4)–Cd(2)–C(6)	111.4(2)
C(4)–Cd(2)–N(11)	94.8(2)	C(5)–Cd(2)–C(6)	122.1(2)
C(5)–Cd(2)–N(11)	110.1(2)	C(6)–Cd(2)–N(11)	102.4(2)
N(1)–Cd(3)–N(2)	90.6(2)	N(1)–Cd(3)–N(3)	88.2(2)
N(1)–Cd(3)–N(5)	178.2(2)	N(1)–Cd(3)–N(6)	89.9(2)
N(1)–Cd(3)–N(21)	87.0(2)	N(2)–Cd(3)–N(3)	87.8(2)
N(2)–Cd(3)–N(5)	87.7(2)	N(2)–Cd(3)–N(6)	172.2(2)
N(2)–Cd(3)–N(21)	91.9(2)	N(3)–Cd(3)–N(5)	92.3(2)
N(3)–Cd(3)–N(6)	84.5(2)	N(3)–Cd(3)–N(21)	175.2(2)
N(5)–Cd(3)–N(6)	91.8(2)	N(5)–Cd(3)–N(21)	92.4(2)
N(6)–Cd(3)–N(21)	95.9(2)	Cd(1)–C(1)–N(1)	171.3(5)
Cd(1)–C(2)–N(2)^{i}	174.9(5)	Cd(1)–C(3)–N(3)^{iii}	177.6(6)
Cd(1)–N(4)–C(4)	167.2(5)	Cd(2)–C(4)–N(4)	168.1(5)
Cd(2)–C(5)–N(5)^{v}	176.4(5)	Cd(2)–C(6)–N(6)^{ii}	173.1(5)
Cd(2)–N(11)–C(12)	126.5(4)	Cd(2)–N(11)–C(15)	128.9(5)
Cd(3)–N(1)–C(1)	174.7(4)	Cd(3)–N(2)–C(2)^{ii}	169.3(5)
Cd(3)–N(3)–C(3)^{iv}	178.2(6)	Cd(3)–N(5)–C(5)^{vi}	177.6(5)
Cd(3)–N(6)–C(6)^{i}	166.0(5)	Cd(3)–N(21)–C(22)	129.3(4)
Cd(3)–N(21)–C(25)	125.1(4)	N(11)–C(12)–N(13)	108.8(7)
C(12)–N(13)–C(14)	106.9(7)	N(13)–C(14)–C(15)	106.3(7)
C(14)–C(15)–N(11)	113.4(7)	C(15)–N(11)–C(12)	104.5(6)
N(21)–C(22)–N(23)	110.0(7)	C(22)–N(23)–C(24)	106.1(6)
N(23)–C(24)–C(25)	106.3(5)	C(24)–C(25)–N(21)	112.3(6)
C(25)–N(21)–C(22)	105.3(5)	C(31)–C(32)–C(33)	116.7(9)
C(32)–C(33)–C(34)	122(1)	C(33)–C(34)–C(35)	119(1)
C(34)–C(35)–C(36)	118(1)	C(35)–C(36)–C(31)	123(2)
C(36)–C(31)–C(32)	122(1)	C(32)–C(31)–Cl(1a)	116.8(9)
C(36)–C(31)–Cl(1a)	121(1)	C(32)–C(33)–Cl(1b)	117.5(9)
C(34)–C(33)–Cl(1b)	120(1)		

Symmetry transformations used to generate equivalent atoms: (i) $-x+1/2$, $y+1/2$, $-z+3/2$; (ii) $-x+1/2$, $y-1/2$, $-z+3/2$; (iii) $x-1/2$, $-y+1/2$, $z-1/2$; (iv) $x+1/2$, $-y+1/2$, $z+1/2$; (v) x, y, $z-1$; (vi) x, y, $z+1$.

three octahedral Cd(3) atoms; the tetrahedral Cd(2) atom is ligated by a unidentate imidazole ligand and linked to one tetrahedral Cd(1) atom and two octahedral Cd(3) atoms; the octahedral Cd(3) atom is ligated by another unidentate imidazole ligand and linked to three tetrahedral Cd(1) atoms and two tetrahedral Cd(2) atoms.

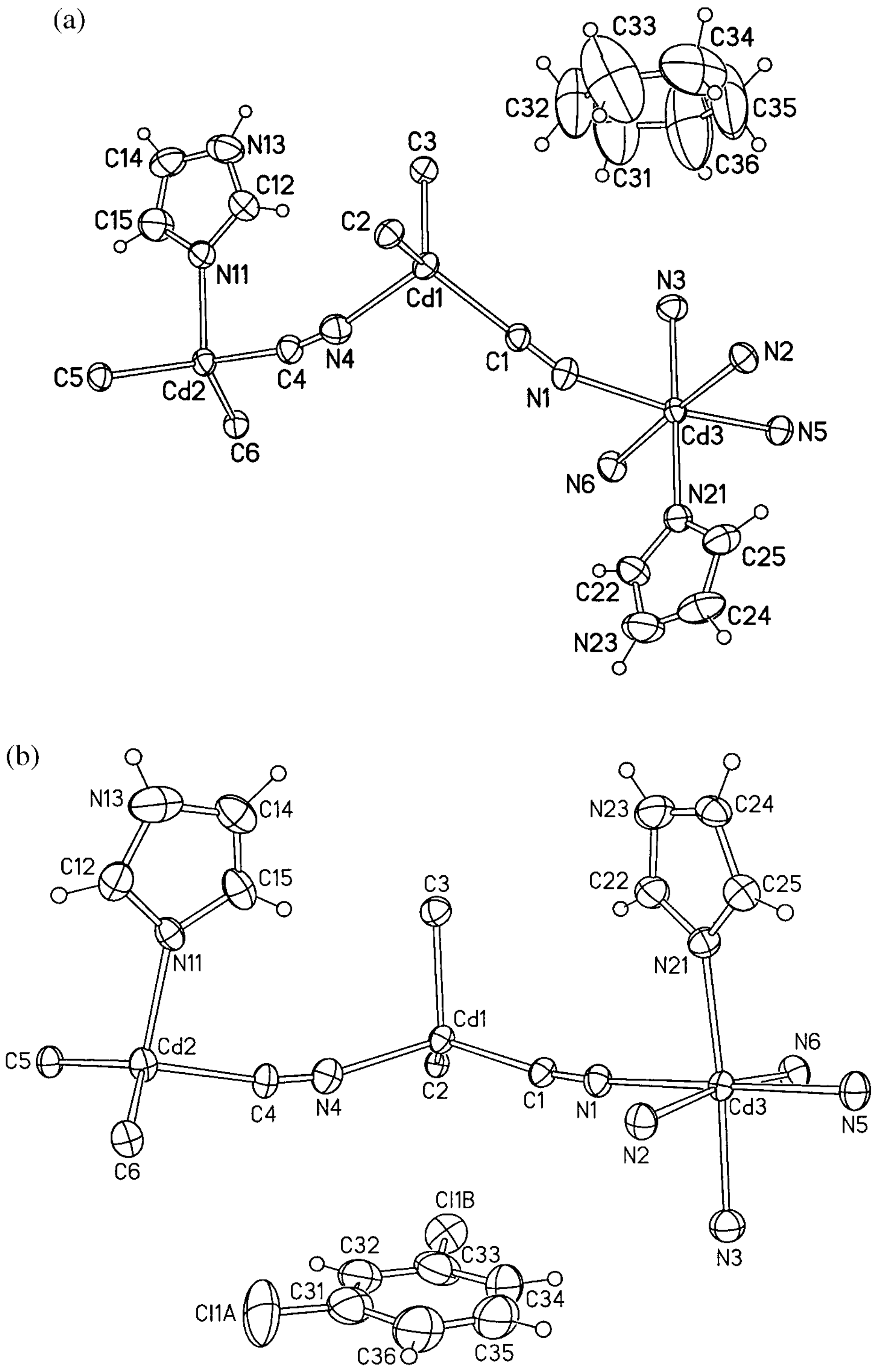

FIGURE 2 Asymmetric unit of clathrates **I** (a) and **II** (b) with thermal ellipsoids drawn at the 30% probability level.

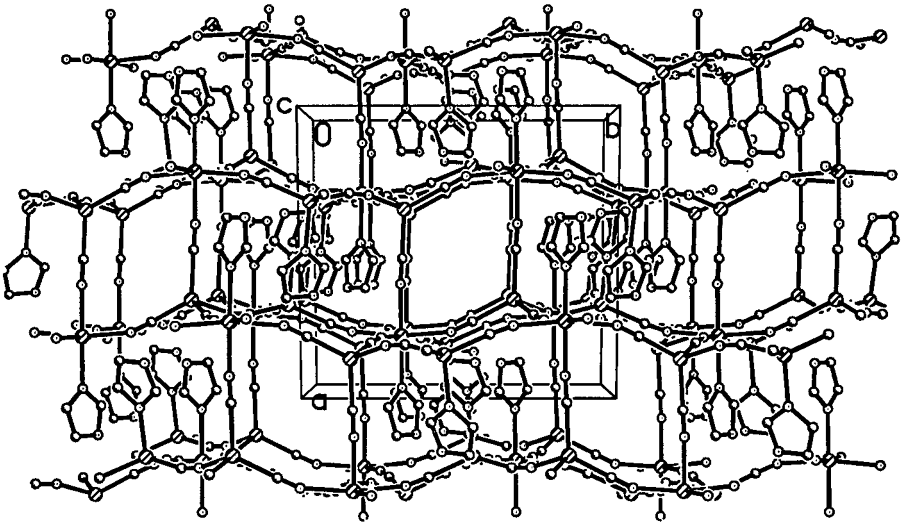

FIGURE 3 A perspective view of the host framework $[Cd_3(CN)_6(imH)_2]$ of clathrates **I** and **II** along the *c* axis. Guest molecules (C_6H_{12} or C_6H_5Cl) and H atoms have been omitted for clarity.

Although the coordination spheres about the Cd atoms are distorted from the regular octahedron and tetrahedron to some extent, bond distances and angles are not unusual; nor are the ring structures of the imidazole ligand (Tables IV and V). The tetrahedral Cd(1)–C and Cd(2)–C distances in clathrates **I** and **II** vary from 2.17 to 2.25 Å with associated angles of 109.5 ±13°; the octahedral Cd(3)–N distances are in the range of 2.31 to 2.40 Å with angles of 90 ± 6°. The octahedral Cd(3)–N(imH) distances are somewhat longer than the tetrahedral Cd(2)–N(imH) ones.

As shown in Fig. 3, a one-dimensional chain of –NC-Cd(3)–CN–Cd(2)–CN–Cd(1)– units run parallel to the *b* axis. According to the symmetry requirements of the $P2_1/n$ space group, the chain is linked through the CN-linkages between Cd(3) and Cd(1) to adjacent chains running almost parallel in the *ab* plane to give a two-dimensional network with hexagonal and tetragonal meshes. The networks are stacked along the *c* axis and pillared by the CN-linkage between Cd(1) and Cd(3), and between Cd(2) and Cd(3), to form the three-dimensional host structure.

The novel host structure provides two types of channels, a large elongated rectangular channel and a smaller rectangular channel (Fig. 3). The large channel formed by the Cd(3)–NC–Cd(2)–CN–Cd(1)–CN–Cd(3)–NC–Cd(2)–CN–Cd(1)–CN– unit is occupied by imidazole ligands coordinated to Cd(2) and Cd(3). The smaller channel formed by the Cd(1)–CN–Cd(3)–NC–Cd(1)–CN–Cd(3)–CN– unit is occupied by the guest molecules cyclohexane (Fig. 2a) and chlorobenzene (Fig. 2b), respectively. The guest molecules cyclohexane and chlorobenzene are accommodated in the channel with their rings almost parallel to the *ac* plane, as shown in Fig. 3.

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Supplementary Material

Full lists of crystallographic data are available from the authors upon request.

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