

Angewandte **Chemie**

Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

© Wiley-VCH 2007

69451 Weinheim, Germany

Nanoporosity and Exceptional Negative Thermal Expansion in Single-Network Cadmium Cyanide

Anthony E. Phillips, Andrew L. Goodwin, Gregory J. Halder, Peter D. Southon, and Cameron J. Kepert*

1. Crystallographic details

The structure of $\text{Cd}(\text{CN})_2 \cdot \text{CCl}_4$ was solved and refined in the face-centered cubic space group $Fd\bar{3}m$. It has been shown by ^{113}Cd -NMR that in double-network $\text{Cd}(\text{CN})_2$ the cyanide bridges are almost statistically disordered;^[1] this same disorder is modeled in the present work by a glide plane in this space group which maps the cyanide C and N sites onto one another. The Cl atoms of the CCl_4 guests are disordered about the threefold axes, modeled by three equivalent sites each of occupancy $\frac{1}{3}$.

The samples used in this study were left to desolvate at 375 K under a nitrogen cryostream for periods of time ranging from 2 to 24 h, until the unit cell parameter became stable with time. Thermal expansion data were then collected on cooling: both variable temperature runs between 375 and 100 K and full structural determinations at selected temperatures were performed. Full structure determinations (see Fig. S1 for a depiction of the fully desolvated phase) were performed by collecting intensity data over a quadrant of the Ewald sphere in 360 frames spaced by intervals of 0.6° . The exposure time ranged from 10 to 20 s depending on the size and diffraction properties of the crystal. Variable temperature runs were performed by *in situ* collection of matrices typically containing 3×20 or 3×25 frames; the temperature assigned to each set of unit cell parameters was that recorded at the midpoint of the relevant matrix.

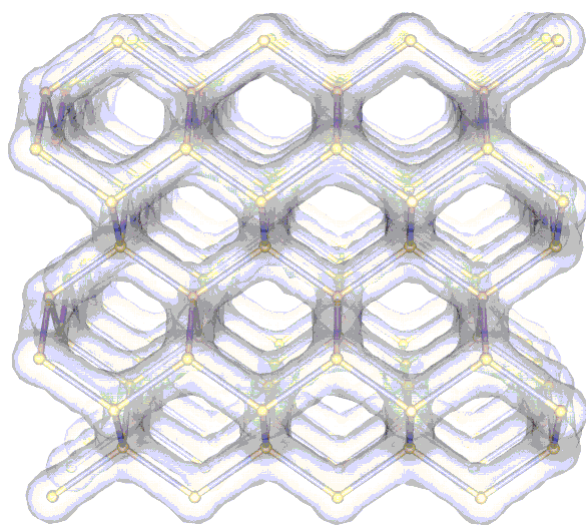


Figure S1: Crystal structure of single-network $\text{Cd}(\text{CN})_2$, indicating framework atoms (Cd atoms drawn as balls and cyanide atoms as sticks) and pore surface. The structure contains adamantane-type pores of diameter 9.6 \AA that are joined by windows of dimensions $7.4 \times 6.0 \text{ \AA}^2$. The void volume is calculated within PLATON to be 64% of crystal volume.

The CCl_4 occupancy was refined in the 300 K structural model using thermal parameters for the guest molecule obtained from a full structural model of the fully solvated structure; the occupancy was then fixed for refinements at other temperatures. The diffraction peaks for the partially loaded phases $x = 0.64$ and 0.75 were similar in sharpness to those of the fully solvated and desolvated phases. This suggests that the partially loaded phases display a high degree of crystal homogeneity, rather than being made up of domains of the fully solvated and desolvated structures. Full crystallographic details are given in Tables S1–5. All figures in these tables were obtained from full structural refinements, except those in Table S4 ($\text{Cd}(\text{CN})_2 \cdot 0.75\text{CCl}_4$), which were calculated from data collected as a single matrix from the variable-temperature run, and hence are obtained from fewer reflections; no absorption corrections were performed on these data.

The thermal expansion behaviour of the partially solvated clathrates (Table 1) is presented in Fig. S2.

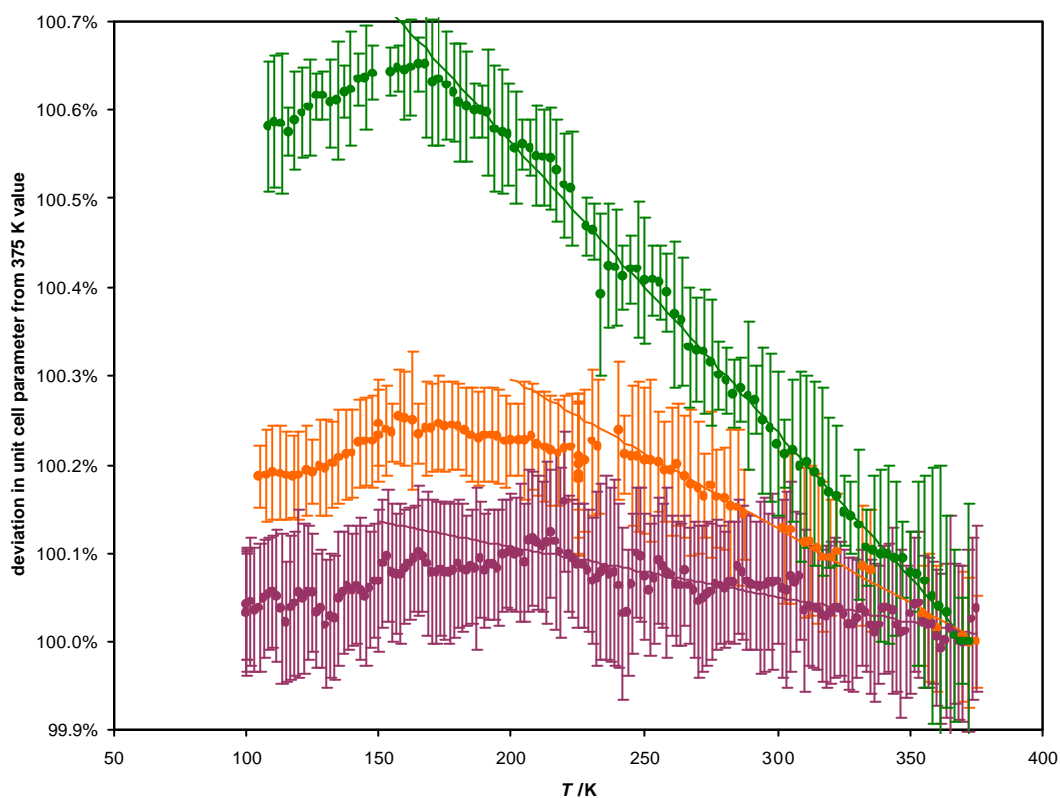


Figure S2: Thermal expansion behaviour of partially desolvated cadmium cyanide carbon tetrachloride clathrate: 0% CCl_4 occupancy (green points), 64% occupancy (orange points), and 75% occupancy (purple points). The three compounds do not have identical unit cell parameters at this temperature, so the unit cell parameters are expressed as percentage deviations from the respective values at 375 K for clarity.

Raman spectroscopy on $\text{Cd}(\text{CN})_2 \cdot \text{CCl}_4$ has revealed a phase transition between ordered and disordered CCl_4 molecules at 220 K.^[2] This is not apparent in the present work; indeed, within experimental error, the distance of the Cl atoms from the $\langle 111 \rangle$ axis was found to be constant with temperature. However, the present experiment was not designed to search for such a transition and its results should not be regarded as inconsistent with this previous work. We believe the minor step in the unit cell parameter of $\text{Cd}(\text{CN})_2 \cdot \text{CCl}_4$ observed at 240 K, which is within error, is unrelated to this transition.

For the fully desolvated framework, the PLATON SQUEEZE program was used to correct for the unmodeled electron density in the 105 K structure, attributed to N_2 sorption into 96% of the pore window sites, by subtracting this density from the raw data. The corrected data could then be modeled using the normal procedure, giving a more accurate solution which is also presented in Table S2.

For the 64%-occupied framework at 105 K, peaks of unmodeled electron density also appeared in the pore windows. Refinement of a model in which highly disordered nitrogen molecules are explicitly present gave an approximate value of *ca.* 30% N_2 occupancy; however, the high correlation between the atomic displacement parameter and site occupancy limited the accuracy of this value to that of the (estimated) displacement parameter. This figure must therefore be regarded as a rough approximation only. Modeling of this system is further complicated by the disorder of the CCl_4 site occupancy: there are three possible window sites (between two occupied pores, between an occupied and an unoccupied pore, and between two unoccupied pores) which will have different N_2 occupancies but which are necessarily averaged by this model. For the 75%-occupied framework at 100 and 130 K, although the *R* value is somewhat higher than for the same structure at higher temperatures, no clearly defined peaks of unmodeled density could be detected. The difference electron density peaks attributed to N_2 sorption into the CCl_4 -free framework at 105 K are depicted in Fig. S3.

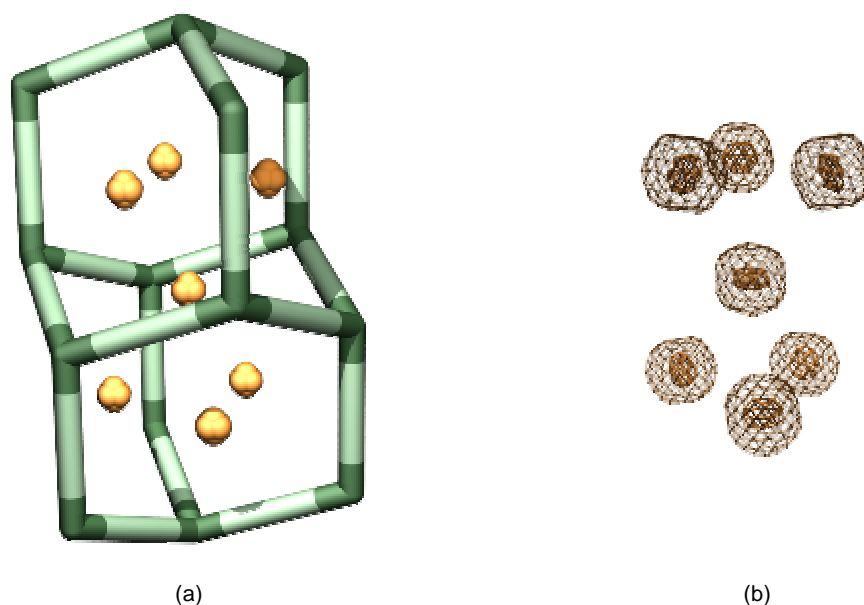


Figure S3: (a) Structural solution of single-network $\text{Cd}(\text{CN})_2$ at 105 K, showing the Q-peaks in the pore windows attributed to dinitrogen sorption; (b) Fourier difference map generated by MCE for the structure in the same orientation, showing the same electron density peaks.

Analysis of the 64%-solvated structure also shows that the C-Cl bond lengths do not change appreciably with temperature, so that it is valid to approximate the guest size as invariant to temperature changes, although experimental error in these bond lengths is comparatively high (1.4%) due to the structural disorder of the guests.

Further confirmation of the model for NTE used here comes from comparing the transverse and longitudinal atomic displacement parameters of the cyanide atoms (Fig. S4). It can be seen that the transverse vibrational modes are thermally populated more rapidly with increasing temperature than the longitudinal modes, consistent with these being the lowest energy modes and those responsible for the pronounced NTE.

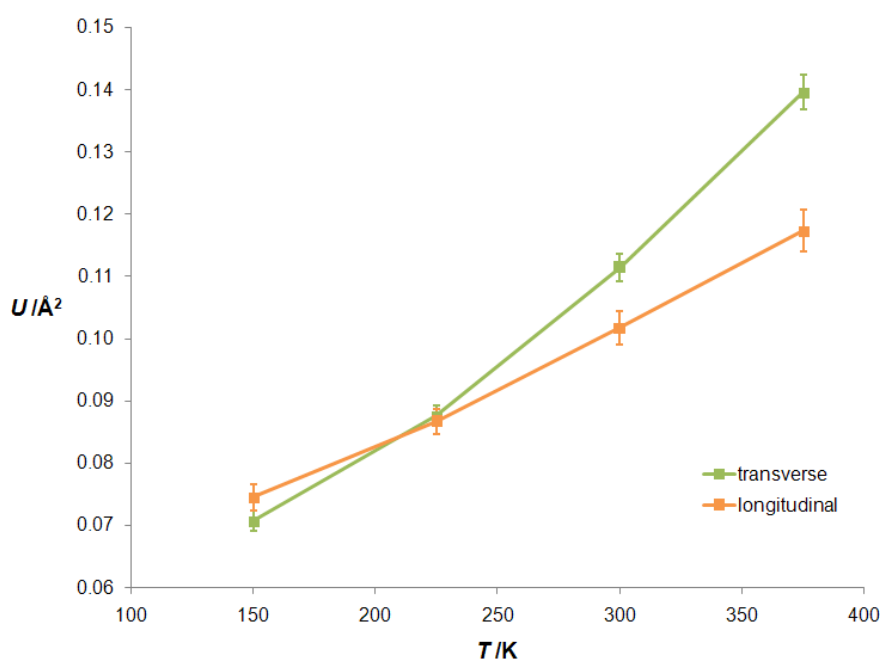


Figure S4: Transverse and longitudinal atomic displacement parameters of CN atoms in single-network Cd(CN)₂ as a function of temperature (data shown only from 150 K due to the occurrence of N₂ sorption at lower temperatures).

Data collection was carried out using the program SMART, integration of frame data performed using SAINT+, and corrections including the Lorentz, polarization, and absorption applied using SADABS.^[3] Structural solutions, refinement, and analyses were performed using SHELXS-97 and SHELXL-97 as implemented within SHELXTL, WinGX, and PLATON.^[4-8] For structures with unmodeled electron density due to dinitrogen sorption, the SQUEEZE module of PLATON was used to sum the residual electron density and to subtract it from the data; the residual peaks were visualized with MCE.^[9, 10] Crystallographic illustrations were produced with WebLab ViewerPro, Mercury, ORTEP, and POV-Ray.^[11-14]

Crystallographic information files (CIFs) for each of the structures presented in Tables S1–S3 and S5 can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. The data in Table S4 were obtained from partial reflection data and are hence insufficient to produce full CIFs.

Table S1: Crystallographic refinement details common to single-network cadmium cyanide data

Framework	Cd(CN) ₂	Cd(CN) ₂	Cd(CN) ₂	Cd(CN) ₂
Guest	∅	0.64(4)CCl ₄	0.75(4)CCl ₄	CCl ₄
<i>M</i> /g mol⁻¹	164.45	262.90	279.82	318.25
<i>Z</i>	8	8	8	8
<i>ρ</i> /g cm⁻³	1.074 (300 K)	1.713 (300 K)	1.814 (280 K)	2.064 (290 K)
Crystal size /mm	0.30 × 0.30 × 0.25	0.44 × 0.38 × 0.35	0.29 × 0.27 × 0.21	0.31 × 0.29 × 0.22
Crystal system	Cubic	Cubic	Cubic	Cubic
Space group	<i>Fd</i> $\bar{3}$ <i>m</i>	<i>Fd</i> $\bar{3}$ <i>m</i>	<i>Fd</i> $\bar{3}$ <i>m</i>	<i>Fd</i> $\bar{3}$ <i>m</i>
Number of restraints	0	0	0	0
Number of parameters	5	12	12	12

Table S2: Crystallographic refinement data for fully desolvated single-network cadmium cyanide

Temperature /K	105 (raw)	105 (corrected for N ₂ sorption – see text)	150	225	300	375
<i>a</i> /Å	12.7208(14)	12.7208(14)	12.7343(11)	12.6830(13)	12.6683(13)	12.6308(14)
<i>V</i> /Å ³	2058.5(4)	2058.5(4)	2065.0(3)	2040.2(4)	2033.1(4)	2015.1(4)
Measured reflections	1984	1984	2010	1964	1978	1954
Unique reflections	147	147	147	146	108	108
<i>R</i> _{int}	0.0214	0.0214	0.0198	0.0192	0.0180	0.0197
<i>R</i> (<i>F</i> , <i>I</i> > 2 <i>s</i> (<i>I</i>))	0.0735	0.0201	0.0258	0.0160	0.0161	0.0205
<i>R</i> (<i>F</i> , all)	0.0846	0.0273	0.0321	0.0264	0.0218	0.0291
<i>wR</i> 2 (<i>F</i> ² , <i>I</i> > 2 <i>s</i> (<i>I</i>))	0.1907	0.0464	0.0678	0.0380	0.0444	0.0578
<i>wR</i> 2 (<i>F</i> ² , all)	0.2204	0.0493	0.0749	0.0459	0.0516	0.0685
<i>U</i> (Cd) /Å ²	0.0851	0.0830	0.0756	0.0861	0.1017	0.1199
<i>U</i> ₁ (C/N) /Å ²	0.0750	0.0677	0.0706	0.0876	0.1114	0.1395
<i>U</i> ₂ (C/N) /Å ²	0.0795	0.0878	0.0744	0.0866	0.1018	0.1172
<i>d</i> (Cd–C/N) /Å	2.185(12)	2.169(4)	2.179(5)	2.172(4)	2.167(5)	2.158(5)
CCDC reference number		CCDC 662058	CCDC 662059	CCDC 662060	CCDC 662061	CCDC 662068

Table S3: Crystallographic refinement data for 64% solvated single-network cadmium cyanide

Temperature /K	105	150	225	300	375
<i>a</i> /Å	12.6909(12)	12.7001(12)	12.6966(12)	12.6798(13)	12.6741(14)
<i>V</i> /Å³	2044.0(3)	2048.4(3)	2046.7(3)	2038.6(4)	2035.9(4)
Measured reflections	1935	1942	1960	1944	1946
Unique reflections	144	145	145	145	145
<i>R</i>_{int}	0.0179	0.0179	0.0190	0.0179	0.0213
<i>R</i> (<i>F</i>, <i>I</i> > 2<i>s</i>(<i>I</i>))	0.0845	0.0509	0.0487	0.0414	0.0395
<i>R</i> (<i>F</i>, all)	0.0898	0.0545	0.0522	0.0466	0.0493
<i>wR</i>2 (<i>F</i>², <i>I</i> > 2<i>s</i>(<i>I</i>))	0.2647	0.1534	0.1422	0.1200	0.0838
<i>wR</i>2 (<i>F</i>², all)	0.2760	0.1601	0.1497	0.1339	0.1050
<i>U</i> (Cd) /Å²	0.0876	0.0792	0.0810	0.0873	0.0937
<i>U</i>₁ (C/N) /Å²	0.0623	0.0689	0.0714	0.0858	0.1022
<i>U</i>₂ (C/N) /Å²	0.0859	0.0708	0.0828	0.0876	0.0918
<i>d</i> (Cd–C/N) /Å	2.146(17)	2.190(11)	2.160(10)	2.177(9)	2.193(8)
CCDC reference number	CCDC 662062	CCDC 662063	CCDC 662064	CCDC 662065	CCDC 662066

Table S4: Crystallographic refinement data for 75% solvated single-network cadmium cyanide

Temperature /K	100	130	180	230	280	330	375
<i>a</i> /Å	12.6946(12)	12.6939(11)	12.7023(11)	12.6990(12)	12.7010(13)	12.6965(12)	12.6931(13)
<i>V</i> /Å³	2045.8(3)	2045.4(3)	2049.5(3)	2047.9(3)	2048.9(4)	2046.7(3)	2045.0(4)
Measured reflections	245	247	246	249	250	251	254
Unique reflections	87	87	86	87	88	88	88
<i>R</i> (<i>F</i>, <i>I</i> > 2<i>s</i>(<i>I</i>))	0.0466	0.0394	0.0261	0.0272	0.0282	0.0331	0.0417
<i>R</i> (<i>F</i>, all)	0.0548	0.0485	0.0349	0.0341	0.0330	0.0396	0.0546
<i>wR</i>2 (<i>F</i>², <i>I</i> > 2<i>s</i>(<i>I</i>))	0.1103	0.0907	0.0516	0.0551	0.0687	0.0721	0.0883
<i>wR</i>2 (<i>F</i>², all)	0.1168	0.1002	0.0566	0.0574	0.0719	0.0767	0.1111
<i>U</i> (Cd) /Å²	0.0876	0.0843	0.0778	0.0763	0.0804	0.0833	0.0862
<i>U</i>_x (C/N) /Å²	0.0538	0.0535	0.0582	0.0659	0.0716	0.0838	0.0879
<i>U</i>_y (C/N) /Å²	0.0935	0.0851	0.0742	0.0766	0.0839	0.0855	0.0869
<i>d</i> (Cd–C/N) /Å	2.158(13)	2.158(11)	2.171(7)	2.180(8)	2.174(8)	2.171(9)	2.182(13)

Table S5: Crystallographic refinement data for 100% solvated single-network cadmium cyanide

Temperature /K	300
<i>a</i> /Å	12.6993(18)
<i>V</i> /Å ³	2048.0(5)
Measured reflections	1798
Unique reflections	129
<i>R</i> _{int}	0.0223
<i>R</i> (<i>F</i> , <i>I</i> > 2 <i>s</i> (<i>I</i>))	0.0552
<i>R</i> (<i>F</i> , all)	0.0644
<i>wR</i> ² (<i>F</i> ² , <i>I</i> > 2 <i>s</i> (<i>I</i>))	0.1468
<i>wR</i> ² (<i>F</i> ² , all)	0.2058
<i>U</i> (Cd) /Å ²	0.0847
<i>U</i> ₁ (C/N) /Å ²	0.0854
<i>U</i> ₂ (C/N) /Å ²	0.0778
<i>d</i> (Cd–C/N) /Å	2.207(12)
CCDC reference number	CCDC 662067

2. Host-guest interactions and water sensitivity

When exposed simultaneously to air and water, crystals of $\text{Cd}(\text{CN})_2 \cdot x\text{CCl}_4$ decompose rapidly. When a wet crystal of the size used for single crystal diffraction measurements is removed from the mother liquor, it becomes cloudy and eventually opaque within 30–60 s. Examination of a decomposed crystal under a microscope showed that the white solid was no longer a single crystal but a mass of much smaller crystals, which have been identified by powder X-ray diffraction as double-network cadmium cyanide. If, on the other hand, the clathrate crystals are dried sufficiently quickly, they are kinetically stable in dry air for at least several days. This behaviour is attributed here to a catalytic effect of the water in inverting the tetrahedrally coordinated cadmium. A *tert*-butanol/water clathrate of cadmium cyanide is known in which a third of the cadmium atoms are octahedrally coordinated, with two axial water ligands;^[15] a similar configuration may represent a low-energy transition state between the metastable single network and the stable double network.

References

- [1] S.-I. Nishikiori, C. I. Ratcliffe, J. A. Ripmeester, *Can. J. Chem.* **1990**, *68*, 2270.
- [2] I. Kanesaka, T. Tamura, Y. Akizawa, *J. Raman Spectrosc.* **1999**, *30*, 69.
- [3] BrukerAXS, 5.060 ed., Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, **1997**.
- [4] G. M. Sheldrick, University of Göttingen, Germany, **1997**.
- [5] G. M. Sheldrick, University of Göttingen, Germany, **1997**.
- [6] BrukerAXS, 6.14 ed., Madison, Wisconsin, USA, **2000**.
- [7] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837.
- [8] A. L. Spek, *Acta Crystallogr., Sect. A* **1990**, *46*, C.
- [9] P. van der Sluis, A. L. Spek, *Acta Crystallogr., Sect. A* **1990**, *46*, 194.
- [10] M. Husák, B. Kratochvíl, *J. Appl. Crystallogr.* **2003**, *36*, 1104.
- [11] Molecular Simulations Inc., 3.7 ed., **2000**.
- [12] Cambridge Crystallographic Data Centre, 1.4.1 ed., **2001**.
- [13] C. K. Johnson, Oak Ridge National Laboratory, Oak Ridge, **1976**.
- [14] Persistence of Vision Team, 3.6.1c.icl8.win32 ed., **1991**.
- [15] B. F. Abrahams, B. F. Hoskins, R. Robson, *J. Chem. Soc., Chem. Commun.* **1990**, 60.