

The Twisted Skeleton of 1,9-Diaminononane in *catena*-[*catena*- μ -(1,9-Diaminononane)cadmium(II) Tetra- μ -cyanonickelate(II)]-*o*-Xylene(2/1)^a

MASATO HASHIMOTO, TAKAFUMI KITAZAWA, TAI HASEGAWA,¹ and TOSCHITAKE IWAMOTO*

Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro, Tokyo 153, Japan.

¹Department of Chemistry, Stanford University, Stanford, California 94305, U.S.A.

(Received: 4 December 1990; in final form: 16 May 1991)

Abstract. The Hofmann-danon-type *o*-xylene clathrate Cd[NH₂(CH₂)₉NH₂]Ni(CN)₄·0.5(CH₃)₂C₆H₄, crystallizes in the triclinic space group $P\bar{1}$ with $a = 15.118(3)$, $b = 14.048(4)$, $c = 7.325(1)$ Å, $\alpha = 91.50(2)$, $\beta = 131.66(3)$, and $\gamma = 107.50(2)^\circ$, $V = 1051(1)$ Å³ and $Z = 2$. The structure, refined to $R = 0.047$ using 2851 reflections, reveals a three-dimensional host framework built of the layers of a two-dimensional *catena*-[cadmium tetra- μ -cyanonickelate(II)] network and of the ambidentate 1,9-diaminononane (danon) bridging the Cd atoms in adjacent networks. The guest *o*-xylene molecule is accommodated in the cavity formed in the interlayer space similar to that in the Hofmann-daotn-type. The skeleton of the danon in the Cd—NC₉N—Cd linkage takes a (*gauche*)₂(*trans*)₈ conformation twisted at the (*gauche*)₂ part in contrast with the all-*trans* conformation of 1,8-diaminooctane in the Hofmann-daotn-type clathrate. The twisted (*gauche*)₂ part of the danon skeleton occupies the interlayer space to such an extent that void space available for the guest *o*-xylene molecule decreases to half that in the Hofmann-daotn-type clathrate Cd[NH₂(CH₂)₈NH₂]Ni(CN)₄·G.

Key words. Crystal structure, diaminononane, Hofmann-danon-type, *o*-xylene, tetracyanonickelate.

Supplementary Data relating to this article have been deposited with the British Library as Supplementary Publication No. SUP 82120 (31 pages).

1. Introduction

A number of representative crystal structures have been reported for the series of Hofmann-diam-type clathrates Cd[NH₂(CH₂)_{*n*}NH₂]Ni(CN)₄·*x* G ($n = 4, 5, 6$, or 8); G is the aromatic guest such as pyrrole, aniline, *o*-, *m*-, or *p*-toluidine, 2,4- or 2,5-xylidine, *N,N*-dimethylaniline, or the aliphatic 1-hexanol [1–6]. Among them, the host structures of the Hofmann-dahxn-type (dahxn = 1,6-diaminohexane; $n = 6$) and Hofmann-daotn-type (daotn = 1,8-diaminooctane; $n = 8$) are similar to each other with respect to the all-*trans* conformation of the ambidentate α,ω -diaminoalkane skeleton spanning adjacent puckered *catena*-[cadmium tetra- μ -cyanonickelate(II)] networks at the respective Cd atoms to give a general composition of the guest $x = 1$. This paper examines the conformation of the

^aThe Crystal Structures of α,ω -Diaminoalkanecadmium(II) Tetracyanonickelate(II) – Aromatic Molecule Inclusion Compounds. VI.

* Author for correspondence.

1,9-diaminononane skeleton with odd $n = 9$ when it spans adjacent cyanometal complex networks in the host structure analogous to those of the already known Hofmann-diam-type. It appears to be rather rare for danon to give a host structure analogous to the previously known Hofmann-diam-type ones. A number of clathrates, $\text{Cd}(\text{danon})_2\text{Ni}(\text{CN})_4 \cdot 2\text{G}$, have been obtained which are different in structure and composition from the present *o*-xylene one. We have reported the structures of *catena*-[*catena*-bis- μ -(1,9-diaminononane)cadmium *cis*-di- μ -cyano-dicyanonickelate(II)]-(2,3-xylylidine)(1/2) [7], and *catena*-[bis-*catena*- μ -(1,9-diaminononane)cadmium *cis*-di- μ -cyano-dicyanonickelate(II)]-(2,4-xylylidine)(1/2) [8]. The Cd atoms are doubly bridged with a pair of *catena*- μ -danon ligands in the former giving an extended one-dimensional linkage, whereas the —Cd—danon— linkage is single in the latter giving an extended two-dimensional network.

2. Experimental

2.1. PREPARATION OF SINGLE CRYSTALS

$\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ (9 g, 40 mmol) and $\text{K}_2[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$ (10.5 g, 40 mmol) were dissolved in 400 mL of water. A creamy suspension, formed by adding $\text{NH}_2(\text{CH}_2)_9\text{NH}_2$ (12 g, 80 mmol) to the solution, disappeared upon addition of citric acid (28 g) and 2-aminoethanol (30 mL) and stirring vigorously for a few hours. After filtration with a millipore membrane (pore size 0.45 μm) a golden yellowish solution was obtained at pH 9.66. A 20 mL portion of the filtrate was transferred into a screw-capped vial and layered with *ca.* 10 mL of neat *o*-xylene. The vial was kept standing at ambient temperature for one month. Yellowish, plate-like single crystals of $\text{Cd}[\text{NH}_2(\text{CH}_2)_9\text{NH}_2]\text{Ni}(\text{CN})_4 \cdot 0.5[o-(\text{CH}_3)_2\text{C}_6\text{H}_4]$ were formed at the interface of the two layers and the bottom of the vial. *Anal. Found*: C, 41.98; H, 5.35; N, 17.32; Cd, 22.8; Ni, 12.3%. *Calcd.* for $\text{CdNiC}_{17}\text{H}_{27}\text{N}_6$: C, 41.97; H, 5.59; N, 17.27; Cd, 23.10; Ni, 12.07%.

2.2. X-RAY EXPERIMENTS

A single crystal of dimensions 0.10 \times 0.35 \times 0.35 mm was coated with epoxy resin in order to prevent decomposition due to evaporation of the guest species. Data collection and refinement of unit cell parameters were carried out on a Rigaku AFC6A automated four-circle diffractometer. The crystal data and experimental conditions are as follows: $\text{Cd}[\text{NH}_2(\text{CH}_2)_9\text{NH}_2]\text{Ni}(\text{CN})_4 \cdot 0.5(\text{CH}_3)_2\text{C}_6\text{H}_4 = \text{C}_{17}\text{H}_{27}\text{N}_6\text{CdNi}$; formula mass = 486.54; yellow plate; triclinic $P\bar{1}$; $a/\text{\AA} = 15.118(3)$, $b/\text{\AA} = 14.048(4)$, $c/\text{\AA} = 7.325(1)$, $\alpha/^\circ = 91.50(2)$, $\beta/^\circ = 131.66(3)$, $\gamma/^\circ = 107.50(2)$, $V/\text{\AA}^3 = 1051(1)$, $Z = 2$; $D_m/\text{g cm}^{-3} = 1.53(1)$ (floatation method in bromoform–mesitylene mixture), $D_x/\text{g cm}^{-3} = 1.54$; MoK_α with graphite monochromatation ($\lambda = 0.70926 \text{\AA}$), $\mu(\text{cm}^{-1}) = 19.12$; ambient temperature, $2\theta - \omega$ scan mode for $2^\circ < 2\theta < 62^\circ$ scan range to collect reflections in $-18 \leq h \leq 18$, $-16 \leq k \leq 16$, $0 \leq l \leq 10$ with peak scan width $(1.50 + 0.45 \tan \theta)^\circ$; 4592 total reflections, 2851 ($=N_o$) used independent ones ($F_o > 3\sigma(F_o)$), 200 ($=N_p$) parameters refined; $R = \Sigma (||F_o| - |F_c||) / \Sigma |F_o| = 0.047$, $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w(F_o)^2]^{1/2} = 0.055$ ($w = 0.25$ for $|F_o| < 14$, $w = 1$ for $14 < |F_o| \leq 28$, and $w = 800/|F_o|^2$ for

$|F_o| > 28$), G.O.F. = $[\sum w(|F_o| - |F_c|)^2 / (N_o - N_p)]^{1/2} = 1.0153$. The crystal axes were chosen so as to facilitate comparison with the known Hofmann-diam-type structure.

2.3. STRUCTURE REFINEMENT

The heavy-atom method was used; all the calculations were carried out on a HITAC M68OH/682H computer at the Computer Center of the University of Tokyo using the programs in UNICSIII [9] including ORTEP [10] and their local versions. Atomic scattering factors, including real and imaginary dispersion corrections, were taken from the International Tables [11].

The skeletal atoms of the host moieties were located on the Patterson and the successive Fourier syntheses; the anisotropic refinement by block-diagonal least-squares procedure gave an $R = 0.065$. The difference Fourier synthesis at this stage gave the location of the guest *o*-xylene molecule and 14 of 22 crystallographically independent H atoms of danon. The refinement for the host atoms including all the host H atoms fixed at the calculated positions with the isotropic thermal parameters fixed at 6.0 \AA^2 gave a slight improvement in $R = 0.061$. The guest *o*-xylene molecule was treated as a rigid carbon skeleton distributed statistically about the inversion center at $1/2, 1/2, 1/2$ with an occupancy factor of 0.5 for each of the C atoms, since the molecule is not centrosymmetric. The most plausible position of the skeleton was located where the minimum R value was given. In the final stage the thermal parameters were isotropically refined for the guest skeleton fixed at the most plausible position; the host H atoms were also included in the structure factor calculation at the calculated positions with the fixed isotropic thermal parameter of 6.0 \AA^2 each; the final $R = 0.047$ was obtained. The atomic parameters obtained are listed in Table I. The tables of the structure factor, anisotropic thermal parameters and calculated positions of hydrogen atoms have been deposited as supplementary material.

3. Results and Discussion

The structure solved is shown in Figures 1 and 2; selected bond distances and angles are listed in Tables II. The host framework is similar to those observed for the known Hofmann-diam-type in principle: the ambidentate danon ligand bridges adjacent layers of the *catena*-[cadmium tetra- μ -cyanonickelate(II)] network to provide the cavity surrounded by the four danon bridges for the guest *o*-xylene molecule. However, the danon skeleton, taking a (*gauche*)₂(*trans*)₈ conformation along the Cd(1)—N(5)—[C(11)—(19)]—N(6)—Cd(2) span, is twisted at the —N(5)—C(11)—C(12)—*gauche* part so much that the cavity space collapses alternately along the *b*-axis (see Figure 2), leading to the stoichiometric number of the guest of 0.5 per formula unit of the host complex. The apparently large opening of the cavity along the *c*-axis (Figure 2) is comparable with those observed for the Hofmann-diam-type hosts; the guest *o*-xylene molecule is trapped in the compartmentalized cavity with a considerable steric hindrance for moving to the next cavity due to the van der Waals radii of the methylene group (*ca.* 2.25 Å) of the guest, and the π -electron cloud thickness (*ca.* 3.4 Å) of the danon phenyl ring and the host cyanide group.

Table I. Atomic parameters.^a

Atom	x	y	z	$B_{\text{eq}}/\text{\AA}^2$
Cd(1)	1.0	1.0	1.0	2.73(5)
Cd(2)	0.0	0.5	1.0	2.70(5)
Ni	0.92284(9)	0.73270(6)	0.4065(2)	2.42(6)
N(1)	1.0164(8)	0.6364(5)	0.2301(15)	4.4(6)
N(2)	0.9364(7)	0.9000(5)	0.1718(14)	4.0(6)
N(3)	0.9170(7)	0.5707(5)	0.6632(14)	4.1(5)
N(4)	0.8659(7)	0.8514(5)	0.6349(14)	3.9(5)
N(5)	0.8188(7)	1.0388(6)	0.7377(14)	4.3(5)
N(6)	0.2118(7)	0.5980(6)	1.1897(14)	4.3(5)
C(1)	0.9798(8)	0.6719(5)	0.2954(15)	3.1(5)
C(2)	0.9313(7)	0.8372(5)	0.2625(15)	2.9(5)
C(3)	0.9162(7)	0.6297(5)	0.5589(15)	3.1(5)
C(4)	0.8794(7)	0.8018(5)	0.5353(14)	2.7(5)
C(11)	0.7945(9)	1.1112(7)	0.8320(18)	4.5(7)
C(12)	0.7748(8)	1.0705(6)	0.9971(17)	3.9(6)
C(13)	0.6498(9)	0.9725(7)	0.8566(17)	4.5(6)
C(14)	0.6356(9)	0.9414(7)	1.0344(18)	4.6(6)
C(15)	0.5094(9)	0.8462(8)	0.9043(19)	5.2(7)
C(16)	0.5002(9)	0.8148(8)	1.0889(19)	4.9(6)
C(17)	0.3739(9)	0.7245(7)	0.9607(18)	4.7(6)
C(18)	0.3624(9)	0.7013(7)	1.1509(19)	4.9(7)
C(19)	0.2321(9)	0.6185(8)	1.0220(20)	5.3(7)
C(21)	0.4880	0.4743	0.3770	8.5(7)
C(22)	0.6120	0.6257	0.8223	12.4(10)
C(23)	0.4363	0.4605	0.4822	9.8(8)
C(24)	0.6637	0.6395	0.7178	19.0(19)
C(25)	0.4984	0.5362	0.7045	16.3(15)
C(26)	0.6016	0.5638	0.4955	12.3(10)
C(31)	0.4210	0.3929	0.1379	13.1(11)
C(32)	0.3134	0.3618	0.3501	10.3(8)

^a Atoms C(21) through C(32) have been fixed at the positions with the occupancy of 0.5 deduced from one of the statistically-distributed rigid *o*-xylene molecules related to the inversion center at 1/2, 1/2, 1/2 (see text).
 $B_{\text{eq}} = 4[\sum_i \sum_j \beta_{ij} a_i a_j]/3$.

Although the (*gauche*)₂(*trans*)₈ conformation of the danon reduces the constraint due to the odd-membered skeleton spanning the cyanometal network arrayed in parallel, the effect appears in the bending of the network and the coordination sphere of Cd atoms. There are two kinds of octahedral Cd atoms, each of which holds the position on the inversion center: Cd(1) is axially coordinated with N(5) and another equivalent at the *gauche*-side of the danon, Cd(2) being with N(6) and the equivalent at the *trans*-side of the danon. The distortion from a regular octahedron is greater for the former than for the latter in the bond angles: the N(*i*)—Cd(1)—N(*j*) angles are 83.9(3)–96.1(3)°, whereas those for Cd(2) are 88.5(4)–91.5(4)°. The Ni(CN)₄ moiety is not greatly distorted from a square-planar structure, but the angles Cd(*i*)—N(*j*)—C(*j*) deviate considerably from 180°: from 22.0(9)° for Cd(2)—N(3)—C(3) to 42.8(8)° for Cd(1)—N(4)—C(4). Thus, the

Table II. Selected bond distances and angles.

<i>Distance, l/Å</i>					
Ni—C(1)	1.86(1);	Ni—C(2)	1.85(1);	Ni—C(3)	1.87(1);
Ni—C(4)	1.85(1);	C(1)—N(1)	1.14(2);	C(2)—N(2)	1.13(2);
C(2)—N(3)	1.14(2);	C(4)—N(4)	1.15(2);	Cd(1)—N(2)	2.32(1);
Cd(1)—N(4)	2.36(1);	Cd(1)—N(5)	2.33(1);	Cd(2)—N(1)	2.36(1);
Cd(2)—N(3)	2.33(1);	Cd(2)—N(6)	2.33(1);	N(5)—C(11)	1.47(2);
C(11)—C(12)	1.47(2);	C(12)—C(13)	1.52(2);	C(13)—C(14)	1.51(2);
C(14)—C(15)	1.52(2);	C(15)—C(16)	1.51(2);	C(16)—C(17)	1.50(2);
C(17)—C(18)	1.54(2);	C(18)—C(19)	1.49(2);	C(19)—N(6)	1.47(2).
<i>Angle, δ/°</i>					
C(1)—Ni—C(2)	89.2(4);	C(2)—Ni—C(4)	89.2(4);		
C(3)—Ni—C(4)	89.8(4);	C(1)—Ni—C(3)	91.8(5);		
C(1)—Ni—C(4)	175.4(4);	C(2)—Ni—C(3)	178.6(4);		
Ni—C(1)—N(1)	179(1);	Ni—C(2)—N(2)	178.8(9);		
Ni—C(3)—N(3)	177(1);	Ni—C(4)—N(4)	173.0(9);		
C(1)—N(1)—Cd(2)	153.7(9);	C(3)—N(3)—Cd(2)	158.0(9);		
C(2)—N(2)—Cd(1)	156.3(9);	C(4)—N(4)—Cd(1)	137.2(8);		
N(4)—Cd(1)—N(2)	89.9(3);	N(5)—Cd(1)—N(2)	96.1(3);		
N(5)—Cd(1)—N(4)	96.7(3);	N(3)—Cd(2)—N(1)	90.3(3);		
N(6)—Cd(2)—N(1)	88.8(3);	N(6)—Cd(2)—N(3)	89.4(3);		
Cd(1)—N(5)—C(11)	124.8(7);	N(5)—C(11)—C(12)	111(1);		
C(11)—C(12)—C(13)	116(1);	C(12)—C(13)—C(14)	112(1);		
C(13)—C(14)—C(15)	115(1);	C(14)—C(15)—C(16)	114(1);		
C(15)—C(16)—C(17)	114(1);	C(16)—C(17)—C(18)	112(1);		
C(17)—C(18)—C(19)	113(1);	C(18)—C(19)—N(6)	116(1);		
C(19)—N(6)—Cd(2)	118.6(7).				

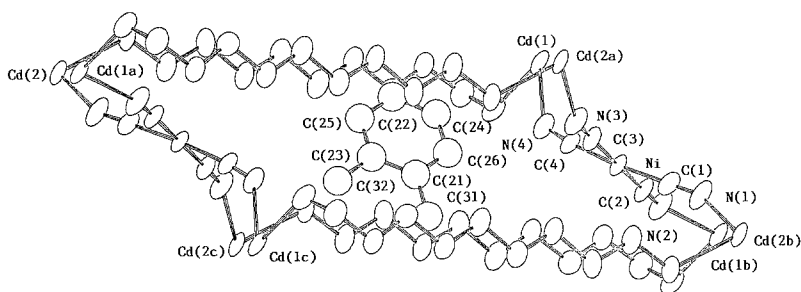


Fig. 1. ORTEP view of the cavity along the *b*-axis showing the guest *o*-xylene molecule taking one of the two orientations related to the inversion center coincident with the center of the cavity. Ellipsoids and spheres are each of 50% probability; hydrogen atoms are omitted; the skeletal atoms of the *o*-xylene molecule are shown as isotropic spheres of $B_{\text{iso}} = 6.0 \text{ \AA}^2$. Cd(1a), Cd(1b), and Cd(1c) are at (0, 0, 1), (1, 1, 0), and (0, 0, 0), and Cd(2a), Cd(2b), and Cd(2c) are at (1, 0.5, 1), (1, 1, 0), and (0, 0, 0.5), respectively; the danon linkage between Cd(1) and Cd(2): Cd(1)—N(5)—C(11)—C(12)—C(13)—C(14)—C(15)—C(16)—C(17)—C(18)—C(19)—N(6)—Cd(2).

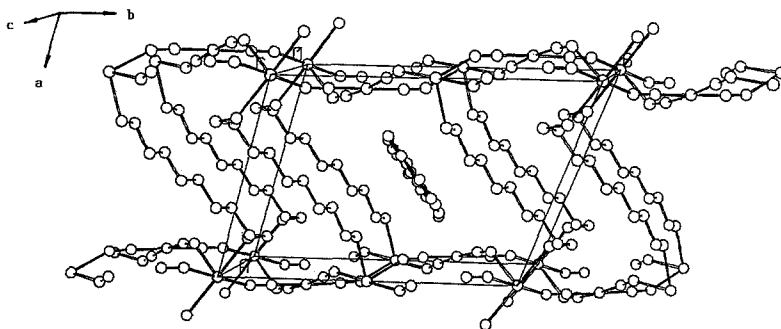


Fig. 2. A ball and stick view of the unit cell along the c -axis.

triclinic unit cell and the cavity structure are much distorted in comparison with the monoclinic structures of the Hofmann-dahxn-type and Hofmann-daotn-type *o*-toluidine clathrates. In the distorted cavity the guest *o*-xylene molecule appears not to be surrounded but clipped by the four danon bridges as shown in Figure 1. Although the skeletal atoms of the *o*-xylene in Figure 1 are depicted as the isotropic ($B_{\text{iso}} = 6.0 \text{ \AA}^2$) spheres for one of the two orientations related to the inversion center, the refined thermal amplitudes are considerably larger (see Table I). Since the thermal parameters for the danon skeleton are not unusual ($B_{\text{eq}} = \text{ca. } 4\text{--}5 \text{ \AA}^2$), the guest is seen to undergo thermal motions to a certain extent in the cavity formed in the rigid host framework.

The present *o*-xylene clathrate is the only example of a structure analogous to the known Hofmann-diam-type structures examined to date. 1,9-Diaminononane and 1,10-diaminodecane have given a series of inclusion compounds with the general formula $\text{Cd}(\text{diam})_2\text{Ni}(\text{CN})_4 \cdot 2\text{G}$ for a number of aromatic guest molecules under experimental conditions very similar to those applied to the present one. According to the preliminary structural data for more than twenty guest species, they have shown a variety of isomeric host structures with respect to the linkage of the diamine and the tetracyanonickelate(III). Hence, the present *o*-xylene compound gives an exceptional structure analogous to those of the Hofmann-diam-type with the α,ω -diaminoalkane whose skeletal carbon number is larger than 8.

References

1. S. Nishikiori and T. Iwamoto: *J. Incl. Phenom.* **2**, 341 (1984).
2. T. Hasegawa, S. Nishikiori, and T. Iwamoto: *J. Incl. Phenom.* **2**, 351 (1984).
3. S. Nishikiori and T. Iwamoto: *Inorg. Chem.* **25**, 788 (1986).
4. T. Hasegawa and T. Iwamoto: *J. Incl. Phenom.* **6**, 143 (1988).
5. T. Hasegawa and T. Iwamoto: *J. Incl. Phenom.* **6**, 549 (1988).
6. S. Nishikiori, T. Hasegawa, and T. Iwamoto: *J. Incl. Phenom.* **11**, 137 (1991).
7. M. Hashimoto, T. Hasegawa, H. Ichida, and T. Iwamoto: *Chem. Lett.* **1989**, 1387.
8. M. Hashimoto and T. Iwamoto: *Chem. Lett.* **1990**, 1501.
9. T. Sakurai and K. Kobayashi: *Rep. Inst. Phys. Chem. Res.* **55**, 69 (1979).
10. C. K. Johnson: ORTEP Report ORNL-3794, Oak Ridge National Laboratory, Tennessee, U.S.A. (1965).
11. *International Tables for X-Ray Crystallography*, Vol. IV, pp. 71–98, Kynoch Press (1974), Distr. Kluwer Academic Publishers Group, Dordrecht.