CHEMISTRY LETTERS, pp. 1387-1390, 1989.

Crystal Structure of catena-[catena-Bis-μ-(1,9-diaminononane)cadmium cis-di-μ-cyano-dicyanonickelate(II)]-(2,3-Xylidine)(1/2)

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The two-dimensional host metal complex of the title inclusion compound is built of one-dimensional extension of cadmium atoms bridged doubly by ambidentate 1,9-diaminononane ligands and cross-linking of tetracyanonickelate(II) between the cadmium atoms in adjacent doubly-bridged chains. The cavity formed in the two-dimensional network accommodates a pair of the guest molecules.

A series of the Hofmann-diam-type clathrates $Cd[NH_2(CH_2)_nNH_2]Ni(CN)_4 \cdot xG$ have been reported for those α,ω-diaminoalkanes (diam) of n = 4-9 with a variety of guest G molecules.[1] As has been demonstrated for a number of the representative members,[2-6] they have the crystal structures substantially similar to one another: two-dimensionally extended catena-[cadmium tetra-μ-cyanonickelate(II)] networks are bridged by ambidentate catena-μ-α,ω-diaminoalkane ligands to form a three-dimensional host structure accommodating guest G molecule in the diam-pillared interlayer space. The variation of x in the composition formula, from 0.5 to 1.5, has been interpreted in terms of the shape and size of the guest G molecule and the skeletal conformation of the diam ligand.

In the Hofmann-danon-type (danon = 1,9-diaminononane), the o-xylene clathrate $Cd(danon)Ni(CN)_4 \cdot 0.5[o\text{-}(CH_3)_2C_6H_4]$ has the least x = 0.5 owing to the twisted skeletal conformation of the danon ligand occupying three of the four cavity units,[6] whereas the maximum x = 2 is given in the prototype of the Hofmann-diam-type series, the Hofmann-en-type $Cd(en)Ni(CN)_4 \cdot 2G$,[7] whose host is comprised of the least bulky diam ligand so far demonstrated in the crystal structures, according to the full occupation of the possible cavity units by the guest molecules.[2] Some members of the Hofmann-danon-type, however, had been suggested to have x not smaller than 2 from the results of chemical analyses; e. g., the 2,3-, 2,4-, and 2,5-xylidine clathrates had been reported to have x = 3.[1] If so, the host structure should be substantially different from those of the previously known Hofmann-diam-type.

Although it has been difficult to obtain well-developed single crystals of the Hofmann-danon-type xylidine clathrates, a flaky crystal of the 2,3-xylidine clathrate, in the dimensions of 0.5×0.5×0.1 mm^3, was subjected to the single

Table 1. Atomic parameters

atom	x/a	y/b	z/c	B/Å^2
Cd1	0	0	0	1.76(7)
Cd2	1/2	0	0	1.76(7)
Ni1	0	0.3355(6)	1/4	2.3(1)
Ni2	1/2	-0.3355(6)	1/4	2.3(1)
N1	0.0589(5)	0.185(2)	0.006(1)	2.3(3)
N2	0.4391(5)	0.163(2)	0.010(1)	2.5(3)
N11	0.0544(6)	-0.162(2)	0.087(1)	2.4(3)
N12	0.4438(6)	-0.178(2)	-0.076(1)	2.2(3)
N21	-0.0020(5)	0.110(2)	0.124(1)	1.9(3)
N22	0.4890(6)	-0.088(2)	0.123(1)	3.1(4)
N23	-0.0013(9)	0.564(3)	0.121(2)	5.1(6)
N24	0.4890(7)	-0.578(3)	0.125(1)	3.9(4)
N31	0.4334	0.1757	0.1891	8(1)
N41	0.0664	-0.1753	0.3111	7(1)
C1	0.0926(6)	0.242(2)	0.070(1)	1.3(3)
C2	0.1319(6)	0.335(2)	0.049(1)	2.2(3)
C3	0.1693(7)	0.234(3)	0.022(1)	2.8(4)
C4	0.2122(6)	0.320(2)	0.023(1)	2.0(3)
C5	0.249(2)	0.229(2)	-0.007(2)	3.4(3)
C6	0.291(1)	0.338(4)	-0.005(2)	5.4(7)
C7	0.3267(7)	0.225(3)	-0.044(1)	2.9(4)
C8	0.3620(7)	0.317(3)	-0.074(1)	3.3(4)
C9	0.405(1)	0.220(3)	-0.084(2)	4.9(7)
C11	0.0872(7)	-0.260(2)	0.044(1)	2.0(3)
C12	0.1265(6)	-0.177(2)	0.031(1)	1.5(3)
C13	0.1637(7)	-0.264(3)	0.003(1)	3.2(4)
C14	0.2059(7)	-0.169(3)	-0.001(1)	3.1(4)
C15	0.253(1)	-0.268(2)	0.013(1)	3.1(3)
C16	0.2880(8)	-0.177(3)	-0.021(1)	3.7(5)
C17	0.3306(7)	-0.269(2)	-0.030(1)	2.6(3)
C18	0.367(1)	-0.155(5)	-0.047(2)	6.6(8)
C19	0.4104(8)	-0.277(3)	-0.061(1)	3.3(5)
C21	-0.0091(7)	0.194(3)	0.168(1)	2.3(4)
C22	0.5016(6)	-0.189(2)	0.176(1)	1.6(3)
C23	0.9935(5)	0.481(2)	0.1690(8)	1.2(2)
C24	0.505(1)	-0.475(4)	0.182(2)	6.5(8)
C31	0.3907	0.1505	0.2035	6(1)
C32	0.3790	-0.0105	0.2097	7(1)
C33	0.3330	-0.0393	0.2256	11(2)
C34	0.3130	0.0773	0.2345	11(2)
C35	0.3184	0.2452	0.2270	12(2)
C36	0.3666	0.2631	0.2168	6(1)
C37	0.3751	0.4138	0.2075	9(2)
C38	0.2886	0.3378	0.2453	10(2)
C41	0.1092	-0.1485	0.2966	5.0(8)
C42	0.1214	-0.0080	0.2886	8(1)
C43	0.1665	0.0374	0.2736	11(2)
C44	0.1870	-0.0731	0.2650	10(2)
C45	0.1806	-0.2458	0.2728	5.9(9)
C46	0.1333	-0.2633	0.2830	6(1)
C47	0.1236	-0.4067	0.2934	7(1)
C48	0.2103	-0.3342	0.2541	13(2)

crystal experiments in order to solve the problem. The solved structure, and the results of the chemical analyses and the density measurement reexamined, support the composition $Cd(danon)_2$-$Ni(CN)_4 \cdot 2G$: $\underline{x}$ = 2 but a couple of danon ligands are contained in the metal complex host.

The compound was prepared by the procedure as follows. Into the aqueous solution containing cadmium chloride and potassium tetracyanonickelate(II) of the respective concentrations of 0.1 mol/dm^3, add 1,9-diaminononane (Aldrich; two times molar amounts that of $CdNi(CN)_4$). The precipitate once formed dissolves completely by adding citric acid and 2-hydroxyethylamine to keep the pH at 10. Place the organic mixture of 2,3-xylidine and hexane (1:20) over the resulting aqueous solution. Yellowish crystals appear at the interface between the aqueous and organic phases by standing at room temperature for a few days. Anal. Found: C, 53.8; H, 8.06; N, 16.61%. Calcd for $C_{38}H_{66}N_{10}CdNi$ (= $Cd[NH_2(CH_2)_9NH_2]_2Ni(CN)_4 \cdot 2[2,3\text{-}(CH_3)_2C_6H_3NH_2]$, F.W. = 834.12): C, 54.72; H, 7.98; N, 16.79%. Crystal data: monoclinic, P2/c, $\underline{a}$/Å = 29.170(2), $\underline{b}$/Å = 9.0513(5), $\underline{c}$/Å = 17.151(1), β/° = 107.935(6), $\underline{U}$/Å^3 = 4308(1), $\underline{Z}$ = 4; $\underline{D}_x$ = 1.29 g/cm^3, $\underline{D}_o$ = 1.29(1) g/cm^3; 2785 reflections used ($I > 5\sigma(I)$), $\underline{R}$ = 0.080. The intensity data were collected on a Rigaku AFC5R diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71069 Å). The structure was solved using the programs in TEXSAN installed in the diffractometer system.

The positional and isotropic thermal parameters determined are listed in Table 1. The solved structure is shown in Fig. 1 as a view of the unit cell; the cavity structure is illustrated in Fig. 2. Owing to the flaky shape of the single

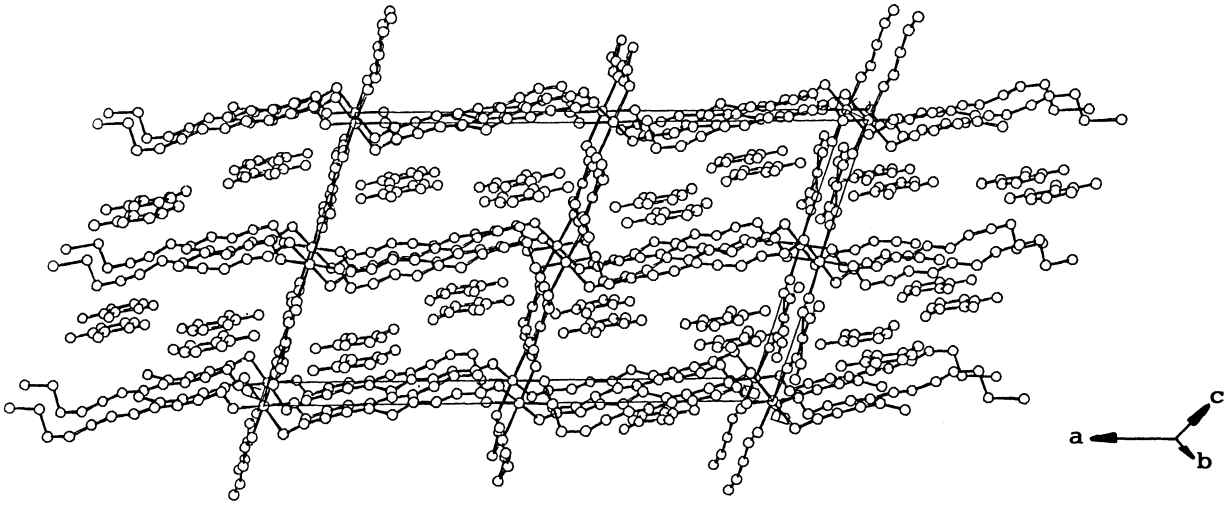

Fig. 1. Perspective view of the unit cell along the b-axis.

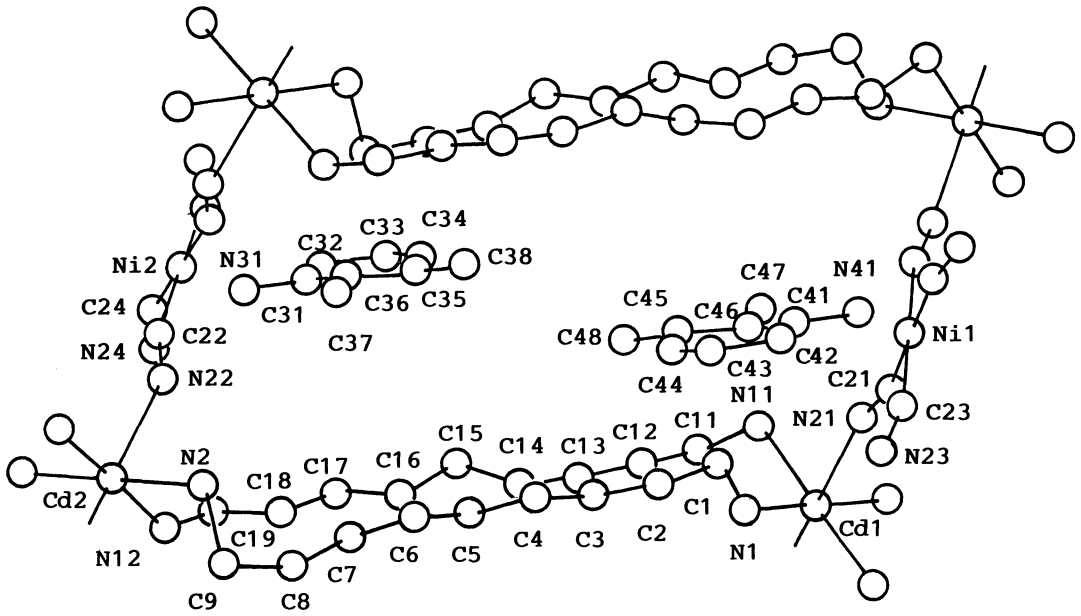

Fig. 2. Perspective view of the cavity accommodating a pair of the guests.

crystal used and to the sensitiveness of the compound against X-rays radiation, the results of the structure refinement are barely acceptable to determine the inclusion structure; absorption correction (DIFABS) was applied, but no improvement was attained by decay correction. At the final stage of the refinement, only the heavy atoms, two each of the crystallographically-independent Cd and Ni atoms, were refined anisotropically; other atoms in the host moieties were refined isotropically; the atomic coordinates of the guest molecules were fixed at the peak positions observed in the Fourier map but the thermal parameters were refined isotropically. All the hydrogen atoms were not included in the refinement.

The Cd and Ni atoms take CdN_6 six-coordination and $Ni(CN)_4$ square-planar coordination respectively, similar to those in the Hofmann-diam-type hosts.[8)]

However, the linking way among them is different from those observed previously for the Hofmann-diam-type. A couple of ambidentate danon ligands span Cd atoms successively to make up a double catena-μ-chain along the crystal a-axis. The chains are cross-linked at every Cd atom by a tetracyanonickelate(II) anion behaving ambidently to provide two cis-cyano-N atoms as the ligating atoms with the Cd atoms in adjacent double catena-μ-chains. The linking behavior of the tetracyanonickelate(II) may be called as cis-1D linkage; trans-1D linkage has been observed for a number of square-planar tetracyanometalate(II) complexes such as $Cd[NH_2(CH_2)_6NH_2][p\text{-}CH_3C_6H_4NH_2]_2Ni(CN)_4$,[5] $Ni(en)_2Pd(CN)_4$.[9] The cis-1D linkage is extended along the c-axis by taking a trans configuration against the Cd atom. Hence, the host consists of the stacking of the two-dimensional networks to form a layered structure along the b-axis. The cavity is formed in the layer itself, although layered hosts usually accommodate guest molecules in the interlayer space to give intercalation structures. As shown in Fig. 2, a pair of the guest 2,3-xylidine molecules are sandwiched between the double danon chains. No intermolecular atomic distances shorter than 3.4 Å have been observed for the 2,3-xylidine molecules: there is no evidence of hydrogen bond formation between the guests.

The features revealed in the present structure should be noted for the peculiar coordination and inclusion behavior as follows: the double-chain linkage of catena-μ-1,9-diaminononane ligands; the cis-1D -M-NC-M'$(CN)_2$-CN-M- linkage involving Cd as M and Ni as M'; the novel kind of cavity found out at first among the host structures of the Hofmann-type and related clathrates.[7] However, these features appear not to be limited only to the particular case of the present compound. Preliminary crystal data suggest that 2,4- and 2,5-xylidine form the respective clathrates isomorphic to the present one, although the structure refinements have not yet been accomplished.

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8) The CdN_6 octahedra are distorted from a regular octahedron to a small extent: the Cd-N bond lengths range from 2.34(2) Å to 2.38(2) Å and the N-Cd-N angles from 80.7(6)° to 99.3(6)°. The distortion in the $Ni(CN)_4$ moieties are little, too; the C-Ni-C angles deviate from a rectangle within 3° but the Ni-C distances (1.76(4) Å each) for the terminal CN groups in one $Ni(CN)_4$ moiety are significantly shorter than those for the bridging groups (1.85(2) Å each) and those in the other moiety (av. 1.87(3) Å).
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(Received May 10, 1989)