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catena-μ-(1,9-Diaminononane)cadmium(II) Array in the Crystal Structure of *catena*-[Bis-*catena*-μ-(1,9-diaminononane)cadmium(II) *cis*-Di-μ-cyano-dicyanonickelate(II)]-(2,4-Xylidine)(1/2) Different from That in the 2,3-Isomer Analog

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In a novel three-dimensional host framework of the title inclusion compound the ambidentate 1,9-diaminononane (danon) makes a two-dimensional *catena*-μ-network with Cd atoms in contrast with the *catena*-bis-μ-danon double-1D chain structure in the 2,3-xylidine analog. The 3D framework of the metal-complex host is accomplished by *catena*-μ-dicyano linkage of -NCNi(CN)$_2$CN- between adjacent networks.

In the previous communication,$^{1)}$ we have reported the crystal structure of *catena*-[*catena*-bis-μ-(1,9-diaminononane)cadmium(II) *cis*-di-μ-cyano-dicyanonickelate(II)]-(2,3-xylidine)(1/2). The title inclusion compound, *catena*-[bis-*catena*-μ-(1,9-diaminononane)cadmiumm *cis*-di-μ-cyano-dicyanonickelate(II)]-(2,4-xylidine)(1/2), is apparently different from the previous 2,3-xylidine inclusion compound only in the position of a substituted methyl group of the guest molecule. However, a novel three-dimensional host framework, different from the previous two-dimensional one, has been demonstrated in the crystal structure. The *catena*-μ-(1,9-diaminononane)-cadmium(II) linkage is two-dimensionally extended in the present one; the one-dimensional but doubled *catena*-bis-μ-(1,9-diaminononane)cadmium(II) linkage has been seen in the previous one. The difference in the way of linking between them exemplifies an isomerism involved in the coordination behavior of ambidentate ligands building up infinite polymeric structures. We have applied the namings, *catena*-bis-μ-(1,9-diaminononane)cadmium(II) for the double bridge in the 2,3-xylidine compound and bis-*catena*-μ-(1,9-diaminononane)cadmium(II) for the single bridge in the 2,4-xylidine one, to discriminate between them.

The 2,4-xylidine inclusion compound was prepared by the procedure as follows. Into the aqueous solution containing 2 mmol each of $CdCl_2$ and $K_2[Ni(CN)_4]$ in 10 cm^3 H_2O, 4 mmol of 1,9-diaminononane (danon) are added. The pH is adjusted at ca. 9.6 by adding citric acid and 2-hydroxyethylamine in the final volume of ca. 20 cm^3. The aqueous solution is covered with an organic mixture of 0.5 cm^3 of 2,4-xylidine and 10 cm^3 of hexane. Yellow flaky crystals appear at the interface between the aqueous and the organic phases by standing at room temperature for a week. Anal. Found: C, 53.05; H, 8.00; N, 16.16%. Calcd for $Cd[NH_2(CH_2)_9NH_2]Ni(CN)_4\cdot2[2,4-(CH_3)_2C_6H_3NH_2]$ (= $C_{38}H_{66}N_{10}CdNi$): C, 54.72; H, 7.989; N, 16.80%.

The crystal structure was analyzed by single crystal X-ray diffraction method. Crystallographic data are: FW = 834.11, monoclinic, C2/c, a = 28.59(1), b = 9.087(8), c = 17.239(7) Å, β = 106.08(4)°, V = 4304(4) $Å^3$, Z = 4, Dm = 1.29(1), Dx = 1.29 g cm^{-3}. The intensity data were collected for a 0.45×0.30×0.08 mm crystal on a Rigaku AFC-5R automated four-circle diffractometer at the Department of Chemistry, Faculty of Science, the University of Tokyo, with graphite-monochromated Mo Kα radiation (50 kV, 180 mA, λ = 0.71069 Å) at room temperature.[2)] Of total 10782 reflections collected assuming a primitive lattice, 3372 ones with $I>3.00\sigma(I)$ in the range $4° \leq 2\theta \leq 55°$ were used for the structure refinement with TEXSAN[3)] including ORTEP[4)] installed on the diffractometer system. Positions of Cd and Ni were determined by Patterson functions; C, N, and H atoms were located by successive Fourier and difference Fourier syntheses. Atomic scattering factors with real and imaginary dispersion corrections used were those from the International Tables.[5)] Absorption correction by DIFABS in TEXSAN was applied. All atoms including hydrogens were found: all non-H atoms were refined anisotropically and H atoms isotropically by full-matrix least-squares procedures to the final R = 0.033 and Rw = 0.039 (sigma weight).[6)]

The structure is illustrated in Fig. 1. Each Cd atom on the inversion center, 0,0,0 or the equivalent positions, is spanned with four ambidentate danon ligands to four Cd atoms so as to develop a two-dimensional network: for example, the Cd atom at 1/2,1/2,1/2 is linked to those at 0,0,0, 0,1,0, 1,0,1, and 1,1,1, respectively. The adjacent networks are crosslinked at the respective Cd atoms with the ambidentate $Ni(CN)_4$ moiety which forms a cis-1D linkage of $-Cd-NC-Ni(CN)_2-CN-Cd-$ chain, catetna-[cadmium(II) cis-di-μ-cyano-dicyanonickelate(II)], along the c-axis. The way of the crosslinking is in a trans configuration with respect to the Cd atom similar to that observed for the previous 2,3-xylidine compound. The way of danon-linking is, however, remarkably different from that in the previous one. A couple of danon ligands, one taking a gauche-$(trans)_8$-(gauche) skeletal configuration and the other trans-gauche-$(trans)_6$-gauche-trans, span the Cd atoms to form a doubly-bridged linear catena-bis-μ-danon-Cd chain in the

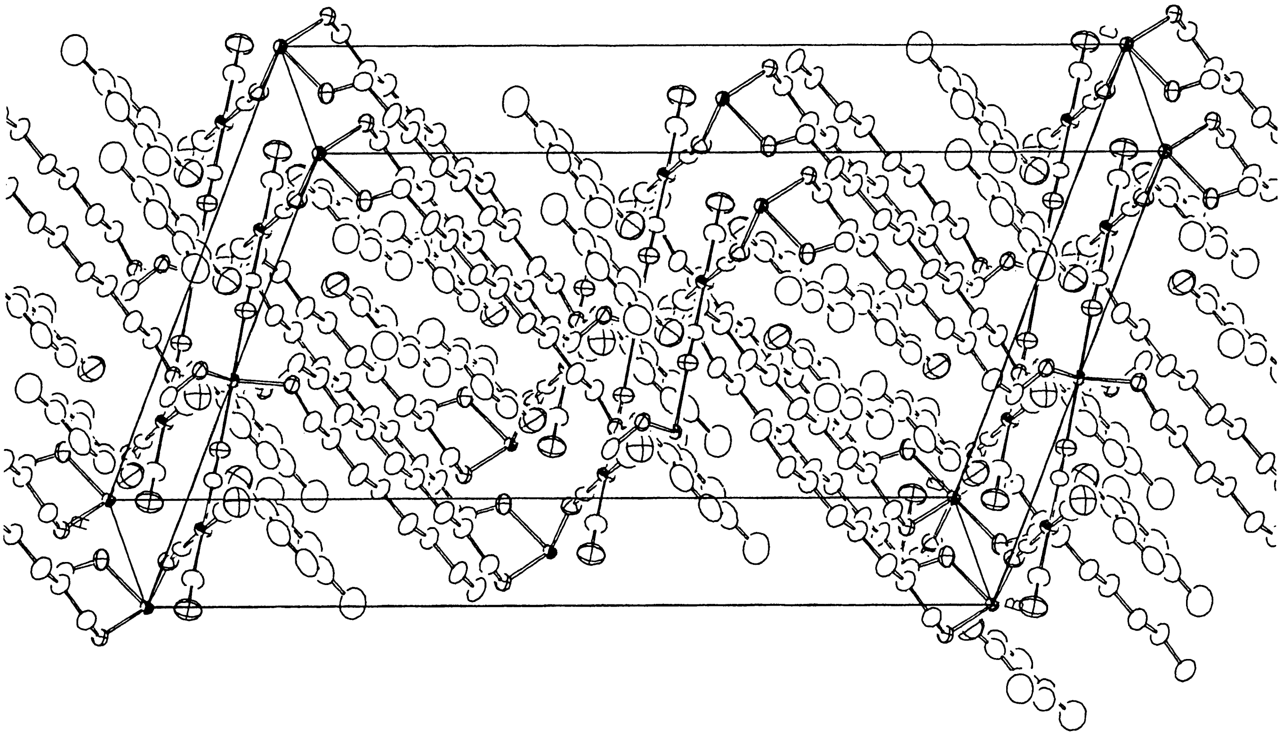

Fig. 1. A view of the unit cell.

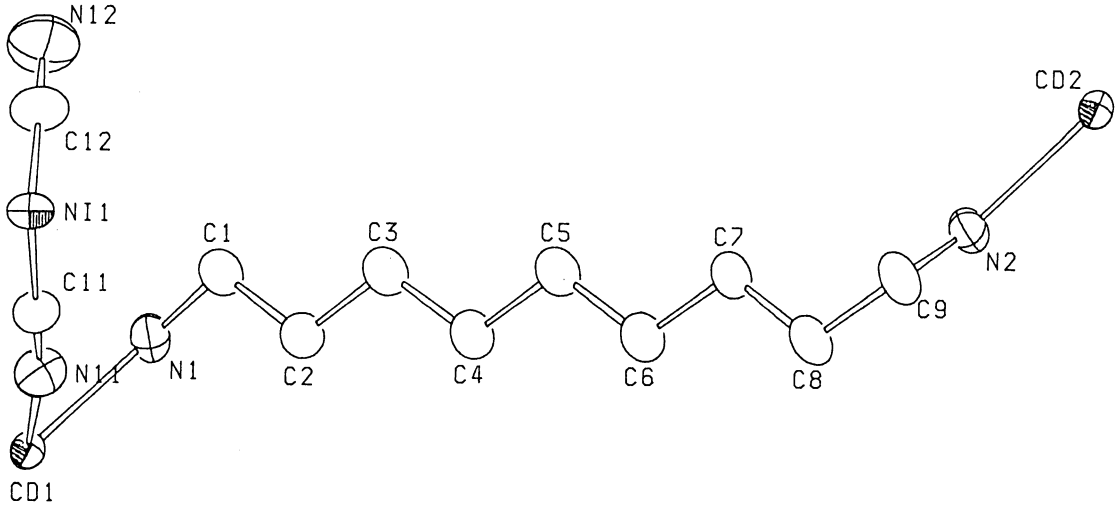

Fig. 2. Skeletal configuration of 1,9-diaminononane in catena-[bis-catena-μ-(1,9-diaminononane)cadmium(II) cis-di-μ-cyano-dicyanonickelate(II)]-(2,4-xylidine)(1/2): from left to right gauche-$(\text{trans})_7$-gauche-trans; CD1 at 0,0,0 and CD2 at 1/2,1/2,1/2.

2,3-isomer compound. In the present 2,4-xylidine one, the *catena*-μ-danon-Cd chain is single to form a bias-meshed two-dimenisional network, taking a gauche-$(\text{trans})_7$-gauche-trans skeletal configuration (see Fig. 2).

The guest 2,4-xylidine molecule is sandwitched with the four halves of the danon ligands two each of which are coordinated to one of a couple of the Cd atoms spanned with a tetracyanonickelate(II) moiety. The aromatic plane of the guest is almost parallel to the Cd-danon network which runs on the ac-diagonal plane of the base-centered unit cell. In the host coordination structure, the distortion is not so much for the Cd atom from the regular octahedon with the N-Cd-N angles of $90\pm4°$, Cd-N(danon) bond lengths of 2.355(3) and 2.358(3) Å, and Cd-N(CN) of 2.394(3) Å; the Ni(CN)_4 moiety is little distorted from the square-planar configuration. The bond angles in the danon ligand are neither so much deviated from the tetrahedral angle respectively. The related crystal structures will be reported later in detail. At the present stage, the guests 2,5-xylidine and *o*-toluidine appear to give the host structures similar to the present one, but 2-chloro-6-nitrotoluene similar to the previous one.

References

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2) The authors are indebted to Dr. Hikaru Ichida of the Department of Chemistry, Faculty of Science, for his kind suggestion and discussion in the structure refinement.

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5) International Tables for X-Ray Crystallography, Vol. IV, Kynoch Press, Birmingham (1974).

6) The authors have deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained on request from The Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK.

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