

THE CRYSTAL STRUCTURES OF α,ω -DIAMINOALKANECADMIUM(II) TETRACYANO-NICKELATE(II)-AROMATIC MOLECULE INCLUSION COMPOUNDS. II. 1,6-DIAMINO-HEXANECADMIUM(II) TETRACYANONICKELATE(II)-*o*-TOLUIDINE (1/1):
 $\text{Cd}(\text{NH}_2(\text{CH}_2)_6\text{NH}_2)\text{Ni}(\text{CN})_4 \cdot \text{o}-\text{CH}_3\text{C}_6\text{H}_4\text{NH}_2$

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ABSTRACT. The title inclusion compound crystallizes in monoclinic space group P2/m, with $a=9.541(2)$, $b=7.569(2)$, and $c=7.199(1)$ Å, $\beta=100.3(1)^\circ$, and $Z=1$. The structure has been refined to a conventional $R=0.036$ for 1973 independent reflections collected by counter method. The host metal complex has the structure similar to that of 1,4-diaminobutane-cadmium(II) tetracyanonickelate(II)-2,5-xylidine (1/1) with respect to the two-dimensionally extended wavy cyanometal complex sheets bridged by the α,ω -diaminoalkane ligands at the respective Cd atoms in adjacent sheets providing a channel-like cavity with the guest aromatic molecule. The guest *o*-toluidine molecule is surrounded by four 1,6-diaminohexane bridges taking an all-trans conformation of the aliphatic chain and show disorder in the orientation in the cavity.

1. INTRODUCTION

Davies and Maver reported on the preparation of $\text{Cd}(\text{NH}_2(\text{CH}_2)_6\text{NH}_2)\text{Ni}(\text{CN})_4$ host inclusion compounds of some disubstituted benzenes [1]. According to our investigation, a series of α,ω -diaminoalkanes, from 1,4-diaminobutane to 1,8-diaminooctane, also give novel hosts with $[\text{CdNi}(\text{CN})_4]_\infty$ network accommodating several aromatic molecules with bulky substituents [2]. The crystal structure of 1,4-diaminobutanecadmium(II) tetracyanonickelate(II)-2,5-xylidine (1/1) has been analyzed as a representative member of Hofmann-dahn-type series of inclusion compounds in the previous paper [3]. This paper describes the crystal structure of 1,6-diaminohexanecadmium(II) tetracyanonickelate(II)-*o*-toluidine (1/1) as a representative one of Hofmann-dahn-type series with a general formula $\text{Cd}(\text{dahxn})\text{Ni}(\text{CN})_4 \cdot n\text{G}$ ($\text{dahxn}=\text{NH}_2(\text{CH}_2)_6\text{NH}_2$).

2. EXPERIMENTAL

2.1. Preparation

Into 40 mL of water 0.91 g of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ and 1.04 g of $\text{K}_2[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$

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were dissolved. A creamy suspension was obtained by adding 0.93 g of 1,6-diaminohexane into the aqueous solution. Into the suspension 2.6 g of citric acid and 1.8 ml of 2-aminoethanol were added; the reading of pH in the suspension was 9.01. After the suspension was left overnight, a transparent golden yellow solution at pH 9.32 was obtained by filtration of the aqueous phase still remaining turbid with a milipore filter (0.45 μm). An organic phase of *o*-toluidine-mesitylene (1:6) was placed over the filtrate in a stoppered vessel, which was left under ambient temperature for a week to grow up single crystals at the interface. The single crystals were picked out and subjected to elemental analyses. Anal. Found: C, 40.6; H, 4.9; N, 19.7%. Calcd for $\text{C}_{17}\text{H}_{25}\text{N}_7\text{CdNi}$: C, 40.95; H, 5.05; N, 19.66%. When all the products at the interface and the bottom of the aqueous phase were collected by filtration, the specimens often gave Cd and Ni contents considerably higher than the calculated values: powdery products other than the well-grown crystals were probably impurities such as those of guest-poor inclusion compounds or metal complex without guest-accommodation.

2.2. Structure Determination

A single crystal of dimensions 0.15 \times 0.15 \times 0.08 mm was coated with epoxy resin in order to prevent spontaneous decomposition under ambient atmosphere and subjected to the intensity data collection on a Rigaku AFC-A6 automated four-circle diffractometer using $\text{MoK}\alpha$ radiation monochromatized with graphite ($\lambda=0.71073$ \AA) by 2θ - ω scan technique. Among 2452 independent reflections in the range $2^\circ < 2\theta < 70^\circ$, 1973 ones with intensities larger than three times their estimated standard deviations (e.s.d.'s) were used for the structure analysis; L_p -corrected but no absorption and extinction corrections. The crystal data are:

$\text{CdNiC}_{17}\text{H}_{25}\text{N}_7$, F.W.=498.55, monoclinic, $P2/m$, $a=9.541(2)$,
 $b=7.569(2)$, and $c=7.199(1)$ \AA , $\beta=100.3(1)^\circ$, $Z=1$, $U=511.5(2)$ \AA^3 ,
 $D_m=1.61(1)$ g/cm^3 , $D_x=1.62$ g/cm^3 , $\mu(\text{MoK}\alpha)=19.23/\text{cm}$.

No systematic absences.

The ordinary heavy-atom method was used for the structure refinement. All the calculations were carried out on a HITAC computer system M-280H/200H in the computation center of this University using the programs in UNICSIII [4] and their local versions. The atomic scattering factors used are those in the International Tables [5]. Among the three possible space groups, $P2/m$, Pm , and $P2$, the $P2/m$ was chosen from the observation of Harker's section on the Patterson map and assuming that the guest molecule should be distributed statistically in a cavity. The positions of Cd and Ni atoms were located at first on the Patterson map; other non-hydrogen atoms of the host moieties were located by the successive Fourier and difference Fourier syntheses and the block-diagonal least-squares calculations. After the least-squares refinement of the host structure by applying the anisotropic thermal parameters for the non-hydrogen atoms, the skeletal atoms of the guest molecule were found on the difference Fourier map. At the final stage of refinement, the anisotropic thermal parameters were applied for all the non-hydrogen atoms; the host hydrogen atoms were located at calculated positions with

Table I. Positional and equivalent-isotropic thermal parameters with estimated standard deviations in the least significant digits in parentheses

atom	weight	x/a	y/b	c/z	$B_{eq}/\text{\AA}^2$
Cd	0.250	0.0	0.0	0.0	1.94(2)
Ni	0.250	0.0	0.5	0.5	1.89(3)
N(1)	1.000	0.0636(5)	0.2211(5)	0.2313(5)	3.4(1)
N(2)	0.500	0.7692(6)	0.0	0.0594(7)	3.4(2)
C(1)	1.000	0.0418(4)	0.3268(5)	0.3350(5)	2.4(1)
C(2)	0.500	0.7477(7)	0.0	0.2595(9)	3.6(2)
C(3)	0.500	0.5932(7)	0.0	0.2786(8)	3.5(2)
C(4)	0.500	0.5758(7)	0.0	0.486(1)	4.3(3)
C(5)	0.500	0.5189(9)	0.5	0.161(1)	4.4(3)
C(6)*	0.500	0.7242(9)	0.5	0.028(1)	4.6(3)
C(7)	0.250	0.412(2)	0.5	0.012(2)	4.3(6)
C(8)	0.250	0.654(2)	0.5	0.196(2)	4.4(6)
C(9)	0.250	0.386(2)	0.5	0.143(2)	4.5(6)
C(10)	0.250	0.626(2)	0.5	0.319(2)	4.6(6)
					$B_{iso}/\text{\AA}^2$
H(1)**	1.000	0.28422	0.11610	0.00814	4.0
H(2)	1.000	0.20155	0.11610	0.66997	4.0
H(3)	1.000	0.45835	0.11610	0.79100	4.0
H(4)	1.000	0.37177	0.11610	0.44535	4.0

* C(6) is overlapped with "N(3)", the amino-nitrogen atom of *o*-toluidine molecule.

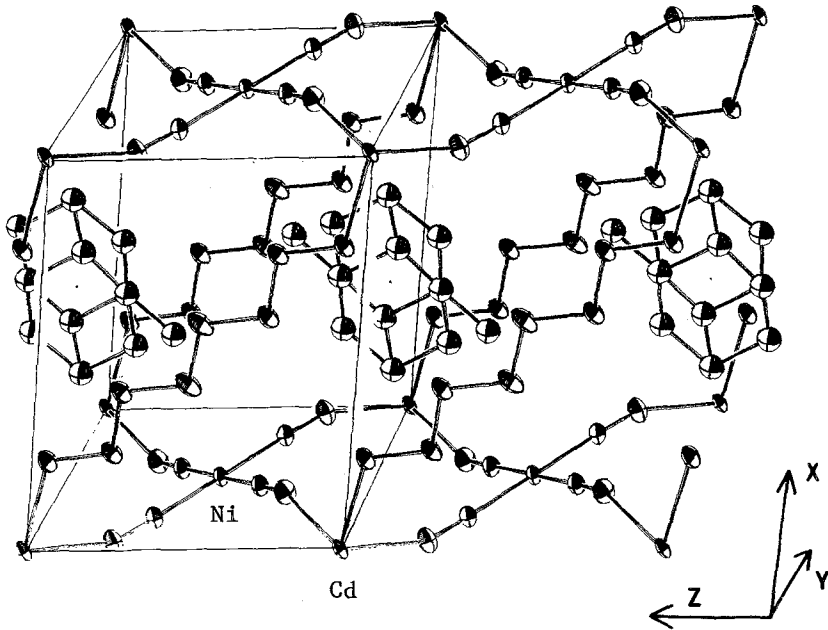
** H(1) at N(2), H(2) at C(2), H(3) at C(3), and H(4) at C(4).

the isotropic thermal parameters fixed at 4.0\AA^2 . According to the disorder in the orientation of the guest molecule, as mentioned later, all the skeletal atoms of the guest were treated as carbon atoms.

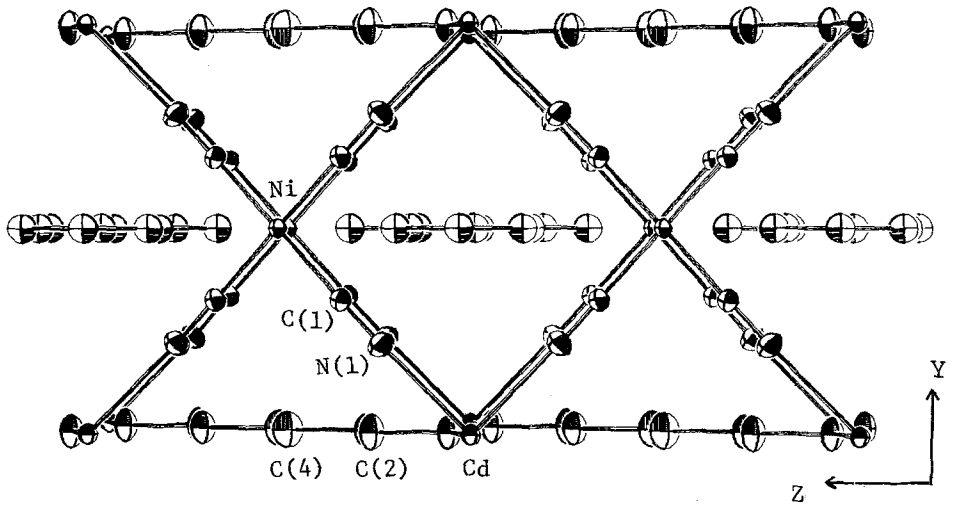
The parameters refined were the positional and anisotropic thermal ones for all the non-hydrogen atoms; the parameters for the hydrogen atoms were not adjusted but included in the calculation of F_c values. The weighting scheme used was: $w=(150/F_o)^2$ for $|F_o| \geq 150$, $w=1$ for $150 > |F_o| > 75$, and $w=0.25$ for $|F_o| \leq 75$. At the final cycle of least-squares calculation the shifts of the parameters were less than 10% of their e.s.d.'s for the non-hydrogen host atoms. Although some of the guest-skeletal atoms gave the shifts in their positional parameters comparable with their e.s.d.'s, the refinement was closed at this stage with $R=0.036$ and $R_w=0.033$, respectively [6].

3. RESULTS AND DISCUSSION

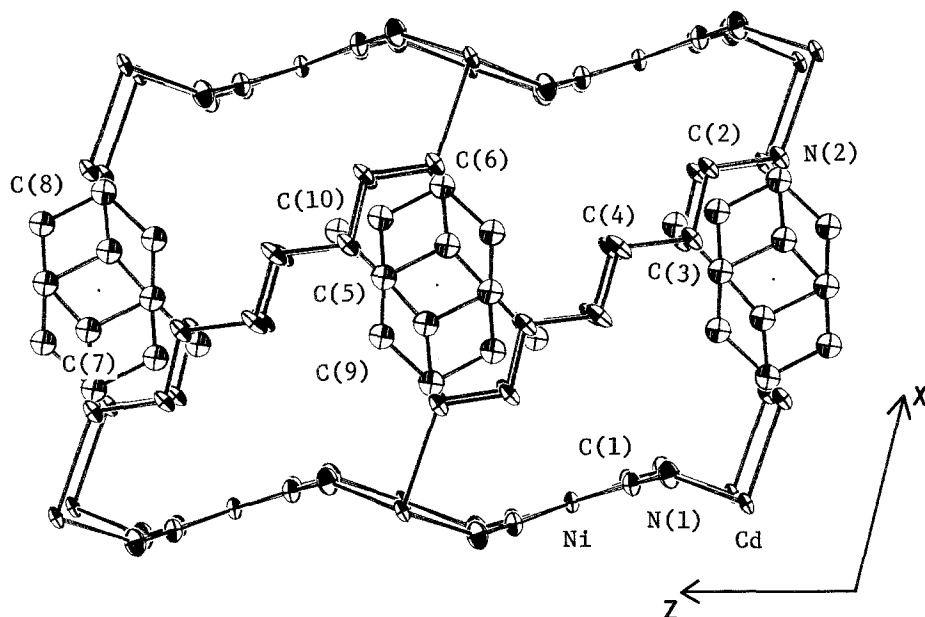
The structure solved is shown in Fig. 1 along with the atomic notations. The atomic parameters are listed in Table I; selected atomic distances and bond angles are in Table II.



(i)



(ii)



(iii)

Fig. 1. The structure of 1,6-diaminohexanecadmium(II) tetracyanonickelate(II)-*o*-toluidine (1/1). Hydrogen atoms are omitted; thermal ellipsoid with 30% probability; isotropic spheres of 4.0 \AA^2 for the atoms of guest molecule. (i) A perspective view of the unit cell. (ii) A perspective view along *a*-axis. (iii) A perspective view along *b*-axis. For the atomic notations see APPENDIX, too.

The host metal complex of $\text{Cd}(\text{dahxn})\text{Ni}(\text{CN})_4 \cdot \text{o-CH}_3\text{C}_6\text{H}_4\text{NH}_2$, I, has the structure substantially similar to that of $\text{Cd}(\text{dabn})\text{Ni}(\text{CN})_4 \cdot 2,5\text{-(CH}_3)_2\text{C}_6\text{H}_3\text{NH}_2$, II [3]. In the two-dimensionally extended cyanometal complex sheet, the Cd atoms are alternately linked with the square-planar $\text{Ni}(\text{CN})_4$ moieties at the N-ends; at each Cd-N junction the metal complex network bends to give a wavy structure of the sheet. 1,6-Diaminohexane bridges the respective Cd atoms in adjacent sheets to build up a three-dimensional host structure providing channel-like cavity with the guest *o*-toluidine molecule. The $[\text{N}(2)\text{-C}(2)\text{-C}(3)\text{-C}(4)]_2$ skeleton of dahxn takes an all-trans conformation on the mirror plane at $y=0$. The all-trans conformation makes the relative shift of adjacent cyanometal complex sheets so large that the *a*-dimension of unit cell, corresponding to the bridge length of the α,ω -diaminoalkane ligand between the sheets, becomes shorter (9.541 \AA) for the dahxn bridge in I than that (9.795 \AA) for the dabn one taking a cis-trans conformation in II.

The guest *o*-toluidine molecule accommodated between adjacent

Table II. Selected atomic distances in Å and bond angles in °.

distance					
Ni-C(1):	1.861(3);	C(1)-N(1):	1.142(5);	N(1)-Cd:	2.357(3)
Cd-N(2)* ¹ :	2.323(5);	N(2)-C(2):	1.504(8);	C(2)-C(3):	1.510(9)
C(3)-C(4):	1.54(1);	C(4)-C(4)* ³ :	1.50(1);	C(5)-C(7):	1.34(1)
C(7)* ² -C(5):	1.52(1);	C(5)-C(9):	1.26(1);	C(9)-C(6)* ² :	1.45(1)
C(6)-C(8):	1.48(1);	C(8)-C(5):	1.27(1);	C(5)-C(10):	1.37(1)
C(7)-C(6)* ² :	1.27(1);	N(2)···C(6) (= "N(3)"):	3.810(1)		
angle					
Ni-C(1)-N(1):	178.1(3);	C(1)-N(1)-Cd:	154.9(3)		
N(1)-Cd-N(2)* ¹ :	90.3(1);	Cd-N(2)* ¹ -C(2)* ¹ :	117.7(3)		
N(2)-C(2)-C(3):	112.0(5);	C(2)-C(3)-C(4):	110.5(5)		
C(3)-C(4)-C(4)* ³ :	112.8(6);	C(7)-C(5)-C(8):	140(1)		
C(7)* ² -C(5)-C(9):	118(1);	C(7)* ² -C(5)-C(10):	107(1)		
C(8)-C(6)-C(9)* ² :	109(1);	C(5)* ² -C(7)-C(5):	105(1)		
C(5)-C(7)-C(6)* ² :	112(1);	C(5)-C(8)-C(6):	114(1)		
C(5)-C(9)-C(6)* ² :	131(1)				

Key to symmetry: normal, x,y,z; *¹, -1+x,y,z; *², 1-x,y,-z; *³, 1-x,y, 1-z.

cyanometal complex sheets is centered at 1/2,1/2,0 and surrounded by four dahxn bridges. Although the guest in II is clipped by a pair of dabn bridges with an inclination angle of the aromatic plane against the mirror plane of crystal in the space group P2₁/m, as shown in Fig. 2 of the preceding paper [3], the *o*-toluidine molecule in I is arranged on the mirror plane at y=1/2. As mentioned in 2.2., it is difficult to locate the skeletal atoms of the guest with great confidence owing to the disorder in the molecular orientations in the cavity. The tentatively assigned atomic positions are those of a pair of *o*-toluidine molecules related to the twofold axis and inversion center of crystal. The bottom C atom of one phenyl ring was just overlapped with the amino-N atom, "N(3)", attached to another phenyl ring; C(6) carbon atom can be seen overlapped with "N(3)". Although we have assigned the position of N(3) at the nearest from N(2), the amino-N of dahxn, the distance between N(2) and N(3) (=C(6)), 3.810(1) Å, appears to be too far for a hydrogen bond between both the amino groups. This is a remarkable difference in structure between I and II; in the latter the plausible distance, 3.28(1) Å, has been observed.

One of the problems to be solved for the formation trend of Hofmann-(long-carbon-chain α,ω -diaminoalkane)-type series of inclusion compounds is to interpret the reason why Hofmann-dahxn-type host cannot accommodate xylydines as guest, which Hofmann-dabn-type host can do even with the shorter carbon chain in the full length than dahxn. In order to solve the problem we need more information about the crystal structures of the series. The structure analyses of Hofmann-dahxn-type *m*- and *p*-toluidine inclusion compounds are in progress.

ACKNOWLEDGMENT

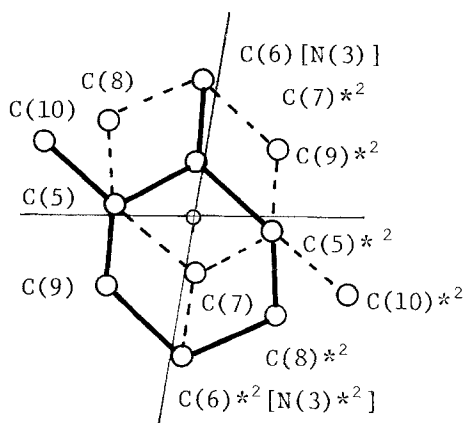
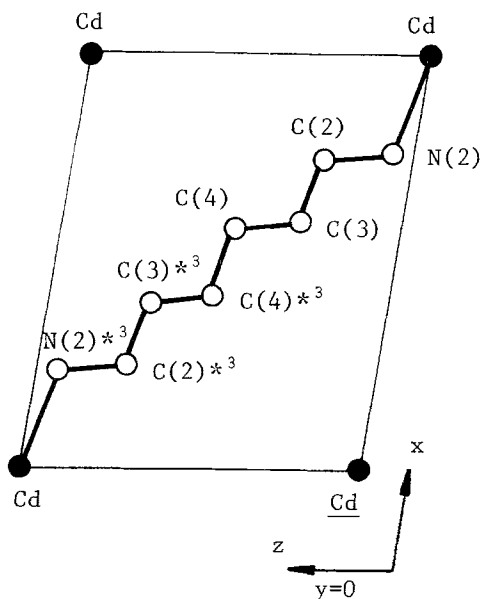
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6. Tables of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division under SUP. 82021 (21 pages).

APPENDIX

The atomic notations in detail for the dahxn and *o*-toluidine.



○ at 1/2,1/2,0.

One orientation is shown with solid lines and another with broken lines for the *o*-toluidine molecule.