

X-ray crystal structure of two-dimensional bimetallic host clathrate with 2-aminoethanol, $[\text{Cd}\{\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}\}_2\text{Ni}(\text{CN})_4]\cdot 3\text{C}_6\text{H}_5\text{NH}_2\cdot\text{H}_2\text{O}$

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Abstract: A novel two-dimensional cadmium(II)-nickel(II) bimetallic host clathrate, $[\text{Cd}\{\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}\}_2\text{Ni}(\text{CN})_4]\cdot 3\text{C}_6\text{H}_5\text{NH}_2\cdot\text{H}_2\text{O}$, **1**, has been synthesized and structurally characterized by X-ray single crystallographic method. The clathrate **1** crystallizes in the monoclinic system, space group $P2_1/c$ with $a = 14.370(3)$, $b = 7.728(1)$, $c = 28.172(4)$ Å, $\beta = 97.58(1)^\circ$, $V = 3101.1(9)$ Å³, $Z = 4$. The host framework of the clathrate **1** is built of the cyanide bridges between octahedral Cd(II) atom and square planar Ni(II) atom. The octahedral Cd atoms ligated by two 2-aminoethanol molecules and four cyanide ligands bridged with square planar Ni atoms. The Ni atoms bridges to four Cd atoms *via* cyanides is made up of puckered quadrangles of composition $\{\text{CdNi}(\text{CN})_2\}_2$, all edges are shared. This cyanide bridges form an infinite two-dimensional host networks stacking along b axis. 2-Aminoethanol ligands bond to Cd atom through N atom as a monodentate ligand in the axial position and four cyanides take an equatorial plane with all in trans-configurations. The aniline guest molecules and water molecules are located in between the host layer sheets, respectively.

Key words : cadmium(II)-nickel(II) bimetallic clathrate, 2-aminoethanol ligand, aniline guest, crystal structure

1. Introduction

The development of inorganic-organic hybrid supra-molecular networks and coordination polymers have a considerable interest from scientists of different areas such as chemistry, solid-state physics and biology, because of their potential applications in material science, catalysis and metallo-biochemistry.¹⁻⁴ For designing inorganic-organic hybrid framework, we⁵⁻¹¹ and others^{12,13} have used various pseudohalide ions, such as CN^- , SCN^- , N_3^- , OCN^- , SeCN^- and CNO^- , and various complementary organic ligands.

The pseudohalide ions are known to build up one-, two-, and three-dimensional framework linking one metal atom M to another metal atom M' alternately.^{14,15} The complementary organic ligands such as aliphatic and aromatic amines are known to play an important role in stabilizing the multi-dimensional structures.

On the other hand, heteroatomic compounds such as imidazole, thiazole, morpholine, aminoethanol represent an important class of ligands in coordination chemistry. Especially, binding of imidazole derivatives to various metal complexes is a subject of great interest because of the frequent occurrence in

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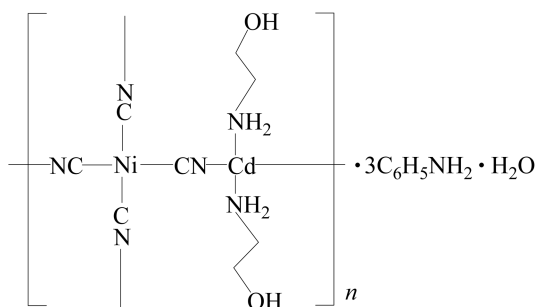


Fig. 1. Structural diagram of clathrate 1.

biologically important metal complexes. A number of metal complexes of various imidazole derivatives have been synthesized and characterized by X-ray single crystallography.¹⁶⁻²⁰ However, the frameworks of metal complexes containing aminoethanol derivatives have been considerably less investigated. In the case of 2-aminoethanol, the coordination behavior of the transition metal-(2-aminoethanol) complex is controversial. More specifically, the 2-aminoethanol acts as N-bonded monodentate ligand or as bidentate ligand via both N and O atoms.²¹ Therefore, as an extension of the study, we have introduced the cyanate ligand and 2-aminoethanol compound as a complementary ligand in order to develop novel multi-dimensional framework structure. We report herein the preparation and crystal structure of two-dimensional inorganic-organic hybrid coordination polymer of the title clathrate, $[\text{Cd}\{\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}\}_2\text{Ni}(\text{CN})_4] \cdot 3\text{C}_6\text{H}_5\text{NH}_2 \cdot \text{H}_2\text{O}$, **1** as shown in Fig. 1.

2. Experimental

2.1. Synthesis and analysis of clathrate 1

To a aqueous solution (30 cm³) containing of $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2.5\text{H}_2\text{O}$ (2.67 g, 10 mmol) and $\text{K}_2[\text{Ni}(\text{CN})_4]$ (2.4 g, 10 mmol), 2-aminoethanol (2.5 cm³, 40 mmol) was added dropwise with constant stirring. The pH of resulting solution was adjusted to 9 by adding 2-aminoethanol and citric acid.²² After the small amount of the precipitate was filtered off and the solution was covered with a layer of neat aniline. The mixture was allowed to stand in a

refrigerator at 278 K. After a few weeks, yellow stick-like crystals were obtained.

FT-IR spectrum of the crystal was recorded on a Bruker Equinox 55 infrared spectrometer using KBr wafer. EDS spectrum obtained on a EDAX Phoenix energy dispersive X-ray spectrometer with Philips XL-30S FEG scanning electron microscope. The contents of carbon, hydrogen, nitrogen and oxygen were determined by a CE EA-1110 elemental analyzer. The contents of Ni and Cd were determined by Jobin-Yvon Ultima-C inductively coupled plasma emission spectrometer. The composition of the crystal was deduced from the elemental analyses; the formula of $[\text{Cd}\{\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}\}_2\text{Ni}(\text{CN})_4] \cdot 3\text{C}_6\text{H}_5\text{NH}_2 \cdot \text{H}_2\text{O}$, **1**, is consistent with the results of single crystal X-ray diffraction analysis. Yield: ca 70%. *Calc. for* $\text{C}_{26}\text{H}_{37}\text{N}_9\text{O}_3\text{NiCd}$: C 44.95, H 5.37, N 18.14, O 6.91, Ni 8.45, Cd 16.18%. *Anal. Found*: C 44.43, H 5.14, N 18.16, O 6.45, Ni 8.19, Cd 15.92%.

2.2. X-ray Crystallography

A yellow stick-like crystal (0.30×0.40×0.40 mm) of the title clathrate was coated with epoxy glue in order to prevent spontaneous liberation of 2-aminoethanol, aniline and water molecule from the specimen under ambient conditions. And then the epoxy-coated crystal was mounted on an Siemens P4 four-circle X-ray diffractometer and the intensity data were collected in the θ -2 θ scan mode using graphite monochromated MoK radiation ($\lambda=0.71073$ Å) at 292±2 K. The unit cell parameters and an orientation matrix for clathrate were determined from the least-squares fit of 54 accurately centered reflections with θ range of 3.82~12.50°. Three standard reflections were monitored every 97 reflections; no remarkable decays were observed through data collection. Lorentz and polarization corrections were applied to the intensity data, and a semi-empirical absorption correction based on the psi-scans was applied.²³

All calculations in the structural solution and refinement were performed using the Siemens SHELXTL crystallographic software package.²⁴ Space groups were assigned based on the systematic

Table 1. Crystal data and structure refinement for clathrate **1**

Formula	C ₂₆ H ₃₇ N ₆ O ₃ NiCd
Formula weight	694.76
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	14.370(3)
<i>b</i> (Å)	7.728(1)
<i>c</i> (Å)	28.172(4)
α (°)	90
β (°)	97.58(1)
γ (°)	90
<i>V</i> (Å ³)	3101.1(9)
<i>Z</i>	4
<i>D_c</i> (g/cm ³)	1.488
μ (Mo-K α) (mm ⁻¹)	1.335
<i>F</i> (000)	1424
θ range for data collection (°)	1.9~26.5
Index range	-1 ≤ <i>h</i> ≤ 18, -9 ≤ <i>k</i> ≤ 1, -35 ≤ <i>l</i> ≤ 35
Reflections collected	6728
Independent reflections	5079 [<i>R</i> _{int} = 0.0333]
Data/restraints/parameters	5079/0/371
Goodness-of-fit on <i>F</i> ²	1.101
Final <i>R</i> [*] indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0398, <i>wR</i> ₂ = 0.0935
<i>R</i> [*] indices (all data)	<i>R</i> ₁ = 0.0489, <i>wR</i> ₂ = 0.1006

$$^*R_1 = F_o - |F_c|/F_o, wR_2 = [\{w(F_o^2 - F_c^2)^2\} / \{w(F_o^2)^2\}]^{1/2}.$$

Table 2. Selected bond lengths (Å) and angles (°) for clathrate **1**

Cd-N(1)	2.349(4)	Cd-N(2)	2.424(4)
Cd-N(3)	2.430(4)	Cd-N(4)	2.343(4)
Cd-N(10)	2.283(3)	Cd-N(20)	2.278(4)
Ni(1)-C(1) ⁱⁱ	1.864(4)	Ni(1)-C(4)	1.862(4)
Ni(2)-C(2)	1.873(5)	Ni(2)-C(3) ^y	1.863(5)
C(1)-N(1)	1.147(6)	C(2)-N(2)	1.143(6)
C(3)-N(3)	1.154(6)	C(4)-N(4)	1.144(6)
C(11)-N(10)	1.466(5)	C(11)-C(12)	1.513(6)
C(12)-O(13)	1.421(6)	C(21)-N(20)	1.456(6)
C(21)-C(22)	1.520(7)	C(22)-O(23)	1.384(7)
C(31)-N(30)	1.388(7)	C(31)-C(32)	1.383(7)
C(32)-C(33)	1.383(9)	C(33)-C(34)	1.381(9)
C(34)-C(35)	1.372(9)	C(35)-C(36)	1.391(9)
C(36)-C(31)	1.388(8)	C(41)-N(40)	1.402(7)
C(41)-C(42)	1.389(7)	C(42)-C(43)	1.385(8)
C(43)-C(44)	1.399(8)	C(44)-C(45)	1.386(9)

absences and intensity statistics, and were confirmed by successful refinements. The structure was solved by the direct method²⁵ and refined by successive full-matrix least-squares method followed by difference Fourier maps. All the non-hydrogen atoms were refined anisotropically; all the hydrogen atoms were put into calculated positions with the isotropic thermal parameters. Final difference of electron density maps contained no significant features. Further details of the crystallographic and experimental data are given in Table 1.

3. Results and Discussion

The structural features of clathrate **1** was identified to the basis FT-IR, EDS, elemental analysis and ICP-AES analysis. The strong IR peak at 2150 cm⁻¹ was assigned to CN stretching vibration. The characteristic peaks of the 2-aminoethanol, aniline and water molecules were assigned by the relevant IR absorption bands, respectively.²⁶ The EDS spectrum showed the presence of C, N, O, Ni and Cd elements. The composition of the clathrate **1** was deduced from the elemental analysis and ICP-AES analysis; the formula of [Cd{NH₂CH₂CH₂OH}₂Ni(CN)₄]₃C₆H₅NH₂·H₂O, **1**, is consistent with the results of X-ray crystallographic analysis.

The selected bond lengths and angles for clathrate

Table 2. Continued

C(45)-C(46)	1.384(9)	C(46)-C(41)	1.397(7)
C(51)-N(50)	1.384(7)	C(51)-C(52)	1.361(8)
C(52)-C(53)	1.37(1)	C(53)-C(54)	1.360(1)
C(54)-C(55)	1.36(1)	C(55)-C(56)	1.370(9)
C(56)-C(51)	1.391(8)		
N(1)-Cd-N(2)	89.8(1)	N(1)-Cd-N(3)	178.8(1)
N(1)-Cd-N(4)	94.5(1)	N(1)-Cd-N(10)	93.4(1)
N(1)-Cd-N(20)	87.7(2)	N(2)-Cd-N(3)	88.9(1)
N(2)-Cd-N(4)	175.1(1)	N(2)-Cd-N(10)	89.9(1)
N(3)-Cd-N(4)	86.7(1)	N(3)-Cd-N(10)	86.5(1)
N(3)-Cd-N(20)	92.2(1)	N(4)-Cd-N(10)	92.2(1)
N(4)-Cd-N(20)	93.8(1)	N(10)-Cd-N(20)	173.8(1)
C(1) ⁱⁱ -Ni(1)-C(1) ⁱⁱⁱ	180.0(2)	C(1) ⁱⁱ -Ni(1)-C(4)	90.6(1)
C(1) ⁱ -Ni(1)-C(4) ⁱ	89.4(2)	C(1) ⁱⁱⁱ -Ni(1)-C(4)	89.4(2)
C(1) ⁱⁱⁱ -Ni(1)-C(4) ⁱ	90.6(2)	C(4)-Ni(1)-C(4) ⁱ	180.0(2)
C(2)-Ni(2)-C(2) ^{vi}	180.0(2)	C(2)-Ni(2)-C(3) ^v	89.4(2)
C(2)-Ni(2)-C(3) ^{iv}	90.7(2)	C(2) ^{vi} -Ni(2)-C(3) ^v	90.7(2)
C(2) ^{vi} -Ni(2)-C(3) ^{iv}	89.4(2)	C(3) ⁱⁱⁱ -Ni(2)-C(3) ^{iv}	180.0
Cd-C(1)-N(1)	156.7(4)	Cd-C(2)-N(2)	169.9(4)
Cd-C(3)-N(3)	174.2(4)	Cd-C(4)-N(4)	159.4(4)
Cd-C(11)-N(10)	120.7(3)	Cd-C(21)-N(20)	123.8(3)
Ni(1)-N(4)-C(4)	178.1(4)	Ni(1) ^v -N(1)-C(1)	177.9(4)
Ni(2)-N(2)-C(2)	179.6(5)	Ni(2) ⁱⁱⁱ -N(3)-C(3)	176.8(4)
N(10)-C(11)-C(12)	111.6(4)	C(11)-C(12)-O(13)	113.3(4)
N(20)-C(21)-C(22)	112.2(5)	C(21)-C(22)-O(23)	113.1(5)
N(30)-C(31)-C(32)	120.4(5)	C(31)-C(32)-C(33)	121.1(6)
C(32)-C(33)-C(34)	120.0(6)	C(33)-C(34)-C(35)	119.0(6)
C(34)-C(35)-C(36)	121.6(6)	C(35)-C(36)-C(31)	119.2(5)
C(36)-C(31)-C(32)	119.1(5)	C(36)-N(30)-C(31)	120.5(5)
N(40)-C(41)-C(42)	120.3(5)	C(41)-C(42)-C(43)	120.8(5)
C(42)-C(43)-C(44)	119.7(5)	C(43)-C(44)-C(45)	119.3(6)
C(44)-C(45)-C(46)	121.1(6)	C(45)-C(46)-C(41)	119.6(5)
C(46)-C(41)-C(42)	119.4(5)	C(46)-C(41)-N(40)	120.3(5)
N(50)-C(51)-C(52)	120.9(6)	C(51)-C(52)-C(53)	119.8(6)
C(52)-C(53)-C(54)	121.0(7)	C(53)-C(54)-C(55)	119.8(7)
C(54)-C(55)-C(56)	120.0(6)	C(55)-C(56)-C(51)	120.1(6)
C(56)-C(51)-C(52)	119.2(6)	C(56)-C(51)-N(50)	119.8(6)

Symmetry transformations used to generate equivalent atoms: i) $-x+1, -y, -z+1$, ii) $x, y-1, z$, iii) $-x+1, -y+1, -z+1$, iv) $x, y+1, z, v) -x, -y+1, -z+1$, vi) $-x, -y+2, -z+1$.

1 are listed in Table 2. The ORTEP drawing and crystal packing diagram of clathrate **1** are shown in Figs. 2 and 3, respectively. As shown in Fig. 2, the two-dimensional host framework of the clathrate is built of the cyanide bridges between octahedral Cd(II) atom and square planar Ni(II) atom. The octahedral Cd atoms ligated by two 2-aminoethanol ligands and four cyanide ligands bridged with square

planar Ni atoms. 2-Aminoethanol ligands bond to cadmium through N as a monodentate ligand in the axial position and four cyanides take an equatorial plane with all in trans-configurations, respectively. The average bond length 2.387(4) Å of equatorial Cd-N_{CN} is longer than the average bond length 2.281(4) Å of axial Cd-N_{aminoethanol}. The average bond angles of N_{CN}-Cd-N_{aminoethanol} are 87.1(2)° and

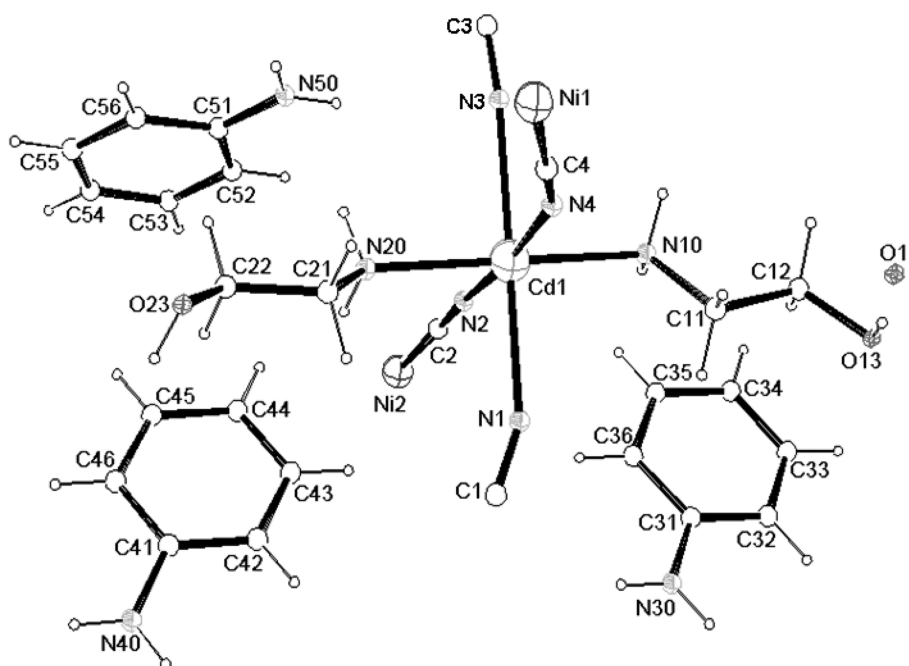


Fig. 2. ORTEP drawing of clathrate 1, with the atomic numbering. Thermal ellipsoids are drawn at the 30% probability level.

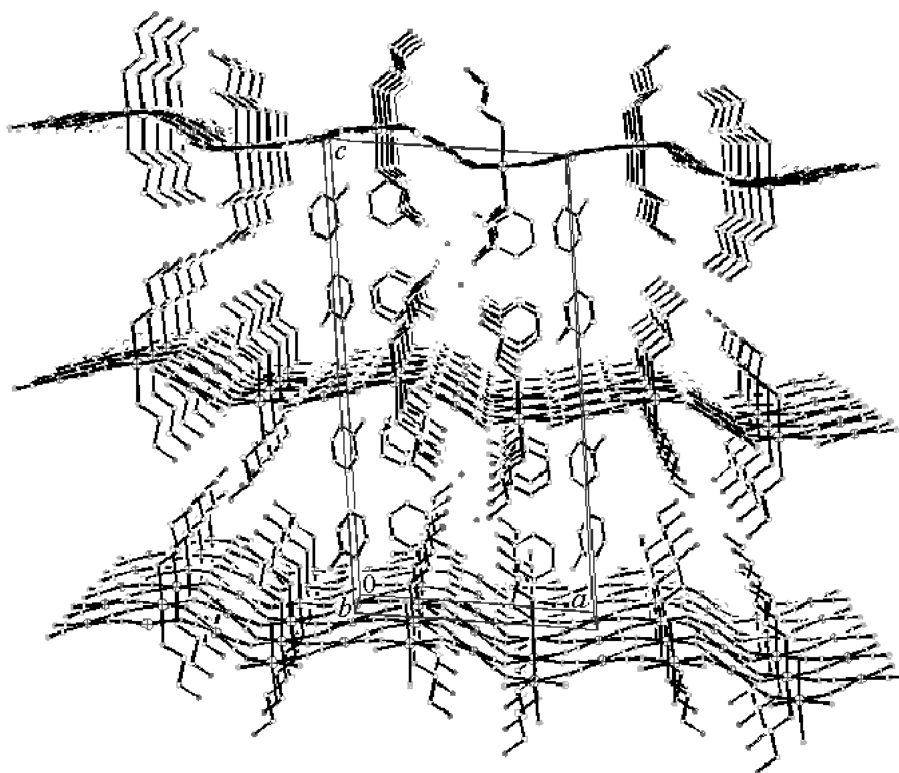


Fig. 3. Crystal packing diagram of clathrate 1, viewed along the *b* axis.

Table 3. Hydrogen bonding parameters (Å, °) for clathrate 1

D-H...A Interaction	H...A (Å)	D...A (Å)	D-H...A (°)
O(13)-H(13a)...Ow ^{vii}	1.86	2.680(5)	172.5
N(20)-H(20a)...N(50)	2.22	3.104(7)	166.7
O(23)-H(23a)...Ow ^{viii}	1.94	2.697(5)	154.0
N(30)-H(30a)...Ow ^{ix}	2.21	3.013(6)	154.8
N(40)-H(40b)...O(13) ^{viii}	2.40	3.137(6)	143.8
Ow-Hwa...O(23) ^x	2.01(7)	2.697(5)	162(7)
Ow-Hwb...O(13)	1.98(7)	2.753(5)	168(7)

Symmetry transformations used to generate equivalent atoms: vii) $-x+1, y-1/2, -z+3/2$, viii) $x, -y+3/2, z-1/2$, ix) $-x+1, y+1/2, -z+3/2, x$, x) $x, -y+3/2, z+1/2$.

92.9(1)°. The coordination environment of the central cadmium(II) atom adopts a slightly distorted octahedral geometry. The square planar Ni atoms, $\text{Ni}(\text{CN})_4^{2-}$, bridges to four Cd atoms *via* cyanides is made up of puckered quadrangles of composition $\{\text{CdNi}(\text{CN})_2\}_2$, all edges are shared. As shown in Fig. 3, this cyanide bridges form an infinite two-dimensional host networks stacking along *b* axis. The aniline guest molecules and water molecules are located in between the host layer sheets, respectively.

There are many inter- and intra-molecular O_2 -aminoethanol-H...O_{water}, N₂-aminoethanol-H...N_{aniline}, N_{aniline}-H...O_{water}, N_{aniline}-H...O₂-aminoethanol, O_{water}-H...O₂-aminoethanol hydrogen bonds between 2-aminoethanol, aniline and water molecules as listed in Table 3. These hydrogen bond interactions lead to self-assembled molecular conformation and contribute to stabilization of the crystal structure.

4. Supplementary Material

Crystallographic data of atomic coordinates, anisotropic displacement parameters, torsional angles, hydrogen atom coordinates, and structure factors for title clathrate are available.

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