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The Structure of Catena-μ-ethylenediaminecadmium(II) Tetracyanoniccolate(II) Dibenzene Clathrate: $Cd(en)Ni(CN)_4.2C_6H_6$[a]

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The crystal structure of $Cd(en)Ni(CN)_4\cdot 2C_6H_6$ *was determined by the single crystal X-ray diffraction method. The crystal belongs to the tetragonal system with space group of P4/m,* $a = 7.675\pm0.003$ *A,* $c = 8.056\pm0.010$ *A, and* $Z = 1$ ($D_m = 1.69$, $D_c = 1.72$). *The structure was solved by the Fourier method and refined by the block-diagonal least-squares method to an* R*-value of 0.089 for 619 reflection data. The cadmium atoms and the nickel atoms are linked cross-wise with the cyanide anions on the (001) plane to form the layers of the polymeric metal cyanide complex* $[CdNi(CN)_4]_\infty$*, and the layers are stacked along the c-axis. Each ethylenediamine molecule bridges between two cadmium atoms in the adjacent layers to make a three-dimensional host lattice. The benzene molecules are enclathrated in the cavities formed by the host lattice. The electron density for each nitrogen atom of the ethylenediamine molecule was found to be distributed over a torus about the Cd–Cd axis. This fact and the* ^{1}*H–NMR data support the rotation of the ethylenediamine molecule about the axis at room temperature.*

Introduction

In this laboratory, new benzene clathrates with the chemical formula of $Cd(en)M'(CN)_4\cdot 2C_6H_6$ (M' = Ni or Pd, en = ethylenediamine) have been prepared.[1] The infrared and the powder X-ray diffraction data have suggested that the ethylenediamine molecules in these compounds bridge between two cadmium atoms. Although ethylenediamine is known as a typical chelating ligand, its bridging behavior has also been reported in several coordination compounds. In most of them, the bridge structure was proposed from the infrared spectrum for which the selection rule suggested the trans conformation of en molecule about the C–C bond.[2-9] Recently, Iwamoto and Shriver[9a] have demonstrated the mutual exclusion of the Raman and infrared spectral bands for the en molecules in several $M(en)X_2$–type complexes. However, the structure of the bridging en has been determined, so far by the single crystal X-ray diffraction method, in only four compounds: $[Pt(CH_3)_3en]_2enI_2$,[10] $[Pt(CH_3)_3acac]_2$-en,[11] [Li(en)]enX (X = Cl, Br),[12] in which the bridging en molecules always hold the trans form. The powder X-ray diffraction pattern of $Hg(en)Cl_2$ also suggested an infinite bridge structure of $-(Hg-NH_2CH_2CH_2NH_2)-$.[2] In order to clarify the stereochemistry of the bridging en, more metal complexes must be studied by X-ray diffractometry.

The present paper deals with the single crystal structure analysis of $Cd(en)Ni(CN)_4\cdot 2C_6H_6$. The preliminary results have been reported previously.[13] The ^{1}H–NMR of the deuteriobenzene clathrate, $Cd(en)Ni(CN)_4\cdot 2C_6D_6$, was also examined with regard to the motion of the en molecule in the crystal, because the possibility of its rotation was suggested from the diffraction data.

Experimental Section

a) *X-ray Structure Analysis.* The single crystals of $Cd(en)Ni(CN)_4\cdot 2C_6H_6$ were prepared by leaving an aqueous solution of the mixture of $CdCl_2$, en and $K_2Ni(CN)_4$ in 1:3:1 ratio in contact with a layer of benzene for a few days. The crystals thus obtained were pale yellow and grew in prismatic form along the [001] axis.

The precession photographs of the crystal, 0.3 × 0.3 × 0.6 mm, mounted in a soft glass capillary for preventing the escape of benzene, were taken with Zr–filtered Mo Kα radiation. The reflection data were recorded about [110] and [100] axis up to the sixth and the second layer, respectively. The Laue group was found to be 4/m. The intensity of 619 independent reflections was measured with a flying-spot microdensitometer, Joyce and Loebl Co. Visual

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(1) Iwamoto, T., *Inorg. Chim. Acta, 2,* 269 (1968)
(2) Brodersen K., Z. *Anorg. Allg. Chem., 298,* 142 (1959).
(3) Powell D.B. and Sheppard N., *J. Chem. Soc.,* 3089 (1959).
(4) Newman G. and Powell D.B., *ibid.,* 477 (1961).
(5) Newman G. and Powell D.B., *ibid.,* 3447 (1962).
(6) Brodersen K. and Kahlert T., *Z. Anorg. Allg. Chem., 348,* 273 (1966).
(7) Krishnan K. and Plane R.A., *Inorg. Chem., 5,* 852 (1966).
(8) Kul'ba F. Ya., Barsukov A.V., and Varshavskii Yu. S., *Zh. Neorg. Khim., 13,* 457 (1968).
(9) Kong Pi-Chang and Theophanides T., *Can Spectrosc., 14,* 105 (1969).
(9a) Iwamoto T. and Shriver D.F., *Inorg. Chem. 10,* (1971).
(10) Truter M.R. and Cox E.G., *J. Chem. Soc.,* 948 (1956).
(11) Robson A. and Truter M.R., *ibid.,* 630 (1965).
(12) Durant F., Piret P., and Meerssche M.V., *Acta Cryst., 23,* 780 (1967).
(13) Miyoshi T., Iwamoto T., and Sasaki Y., *Inorg. Nucl. Chem. Letters, 6,* 21 (1970).

measurements were also taken on the very weak diffraction spots. Lorentz and polarization factors were applied, but no corrections for absorption were made. The unit-cell dimensions were derived by the least-squares refinement of the θ values; the θ angles were measured by a powder X-ray diffractometer with Cu Kα radiation and were calibrated with lines from silicon. The density of the crystal was measured by the flotation method in a K_2HgI_4 solution, but precise measurement was difficult owing to the rapid escape of benzene from samples. No piezoelectricity was observed.

Table I.

L	FO	FC
H,K= 7 -6		
0*	41	55
1*	67	62
2*	65	64
3*	54	56
4*	48	54
H,K= 8 -6		
0	152	167
1	157	155
2	145	150
3	142	152
4	143	135
5	116	122
H,K= 7 -5		
0	169	204
1	221	225
2	216	225
3	165	187
4	170	183
5	166	179
6	142	146
7	116	130
H,K= 8 -5		
0*	42	76
1*	53	63
2*	53	68
3*	47	69
4*	47	58
5*	38	59
6*	37	55
H,K= 9 -5		
0	147	175
1	153	165
2	156	176
3	139	151
4	131	142
5	109	145
6*	80	111
7*	75	109
H,K= 5 -4		
0	189	184
1	99	97
2	167	172
3	125	125
4	98	93
5	145	148
6*	83	76
7	97	104
8*	79	73
H,K= 6 -4		
0	295	298
1	247	249
2	257	257
3	275	260
4	214	210
5	198	201
6	198	186
7	136	159
8	122	124
H,K= 8 -4		
0	225	235
1	234	239
2	217	215
3	212	223
4	176	197
5	147	160
6	149	172
7	109	134
8	98	114
9	94	105
H,K= 10 -4		
0	128	159
1	135	159
2	126	144
3	131	150
4	110	136
5	98	115
H,K= 4 -3		
0*	52	51
1*	34	46
2*	50	53
3*	54	61
4*	45	55
5*	66	66
6*	41	63
7*	61	66
8*	40	56
9*	57	57
H,K= 5 -3		
0	297	287
1	309	306
2	351	339
3	259	248
4	247	247
5	268	268
6	160	179
7	176	182
8	147	157
9	128	125
H,K= 6 -3		
0	114	111
1	167	180
2	140	129
3	132	141
4	131	136
5	108	95
6	127	130
7*	71	82
8*	66	79
9*	64	77
H,K= 7 -3		
0	254	266
1	292	297
2	289	301
3	219	240
4	241	236
5	226	233
6	176	181
7	140	164
8	125	144
9	99	119
H,K= 9 -3		
0	196	216
1	192	203
2	200	223
3	162	182
4	157	172
5	144	181
6	104	131
7	102	130
H,K= 3 -2		
0	142	114
1	197	172
2	105	108
3	150	126
4	148	144
5*	86	100
7	103	101
8*	77	88
9*	71	73
H,K= 4 -2		
0	409	477
1	446	400
2	350	352
3	444	417
4	333	335
5	261	267
6	310	280
7	215	228
8	147	171
9	144	163
10	102	134
11*	77	95
H,K= 5 -2		
0*	85	90
2	92	105
3*	50	63
4*	66	59
5*	82	104
7*	70	80
8*	47	61
9*	47	58
H,K= 6 -2		
0	388	423
1	296	286
2	352	337
3	337	334
4	257	248
5	265	263
6	220	212
7	205	202
8	124	143
9	93	140
H,K= 7 -2		
0	129	136
1	116	124
2	137	157
3	106	112
4	96	102
5	114	130
6	87	83
H,K= 8 -2		
0	296	279
1	261	252
2	240	244
3	240	252
4	202	210
5	177	190
6	162	184
7	131	151
8	103	122
9	96	115
H,K= 2 -1		
0	615	516
1	106	147
2	219	194
3	227	179
4	111	101
5	193	190
6*	48	30
7	176	162
8	88	87
9*	63	69
10	90	87
11*	46	52
H,K= 3 -1		
0	531	504
1	481	455
2	566	531
3	389	367
4	443	385
5	403	403
6	214	220
7	303	274
8	218	221
9	144	154
10	149	145
11	102	114
H,K= 4 -1		
0	390	326
1*	58	36
2	220	190
3	159	164
4	94	88
5	183	175
7	137	136
9*	52	74
H,K= 5 -1		
0	417	368
1	540	513
2	496	456
3	383	358
4	391	376
5	349	330
6	282	267
7	241	225
8	218	208
9	148	157
10	111	131
11*	85	110
H,K= 6 -1		
5*	46	67
H,K= 7 -1		
8	130	154
9	98	124
10	88	101
H,K= 0 0		
1	476	617
2	705	1036
3	821	1064
4	609	636
5	702	656
6	442	366
7	521	478
8	290	273
9	263	232
H,K= 1 0		
1	99	123
3	177	155
4	193	170
5	94	103
6*	52	68
7	147	133
8*	85	98
9*	47	65
10*	77	75
11*	57	62
H,K= 2 0		
0	715	778
1	129	131
2	302	260
3	485	467
4	302	302
5	324	288
6	251	228
7	272	277
8	182	169
9	160	157
10	132	148
11*	74	95
H,K= 3 0		
1	382	337
2	97	87
3	194	156
4	254	219
5*	77	75
6	174	148
7	121	101
8	119	110
9*	80	82
10*	61	70
H,K= 4 0		
0	695	703
1	507	479
2	510	483
3	576	535
4	436	404
5	379	352
6	341	311
7	273	282
8	200	197
9	181	184
10	112	155
H,K= 5 0		
1	180	152
2	140	148
3	117	112
6*	85	94
7*	76	94
8*	60	83
H,K= 6 0		
0	517	514
1	330	311
2	408	396
3	393	384
4	287	277
5	333	309
6	247	229
7	228	233
8	136	157
9	137	154
10	115	134
H,K= 8 0		
0	265	267
1	213	220
2	216	226
3	233	234
4	173	187
H,K= -9 1		
0	207	203
1	213	209
2	215	221
3	175	178
4	173	173
5	172	179
6	125	133
H,K= -8 1		
0	96	110
2	96	85
3*	84	88
4*	69	60
5*	83	76
6*	85	65
7*	64	65
H,K= -7 1		
0	253	236
1	375	342
2	316	303
3	271	244
4	290	260
5	226	227
6	209	202
7	179	160
H,K= -6 1		
3*	77	83
9*	50	60
H,K= 1 1		
0	450	534
1	645	883
2	639	642
3	533	495
4	625	596
5	447	437
6	335	314
7	359	315
8	285	279
9	166	178
10	157	158
11	128	143
H,K= 2 1		
0	544	453
1*	77	17
2	208	177
3	225	180
4	127	123
5	189	173
6*	47	48
7	172	155
8	88	91
10	95	85
11*	46	55
H,K= 3 1		
0	581	542
1	483	414
2	582	542
3	411	365
4	423	369
5	410	416
6	214	206
7	308	280
8	217	218
9	139	152
10	135	146
11	107	112
H,K= 4 1		
0	331	296
1	84	61
2	210	180
3	167	161
4	101	98
5	171	164
6*	67	71
7	135	131
9*	47	75
10*	56	80
H,K= 5 1		
0	474	414
1	515	483
2	526	476
3	386	364
4	397	364
5	377	351
6	255	253
7	245	236
8	200	207
9	151	157
11*	80	107
H,K= 6 1		
2*	56	53
3*	71	74
4*	54	67
5*	41	51
8*	54	52
9*	50	58
H,K= 7 1		
0	259	253
1	367	332
2	325	311
4	275	256
5	236	235
6	201	197
7	157	165
8	135	153
9	95	124
10	69	102
H,K= 8 1		
0*	85	103
1	107	83
2	91	89
3	81	95
4*	71	75
5*	65	75
6*	87	78
7*	60	65
H,K= 9 1		
0	204	203
1	199	196
2	210	218
3	164	172
4	160	165
5	177	178
6	127	126
H,K= 2 2		
0	720	924
1	644	748
2	605	589
3	725	720
4	585	564
5	449	399
6	454	402
7	351	330
8	245	243
9	210	211
10	182	174
11	115	126
H,K= 3 2		
0	203	174
1	159	143
2	129	132
3	148	138
4	141	135
5	107	120
6	91	91
7	108	111
8*	75	87
9*	65	73
H,K= 4 2		
0	477	417
1	473	443
2	353	326
3	454	411
4	360	352
5	239	242
6	321	298
7	205	215
8	155	174
9	151	164
10	100	130
11*	79	98
H,K= 3 3		
0	695	724
1	520	494
2	678	672
3	493	474
4	469	408
5	526	495
6	266	246
7	351	319
8	208	234
9	147	175
10	147	164
11	91	114
H,K= -4 4		
0	494	439
1	493	451
2	417	383
3	455	410
4	404	351
5	267	273
6	326	295
7	211	219
H,K= -3 4		
0*	70	72
1*	24	39
2*	65	68
3*	52	64
4*	39	54
5*	74	78
6*	41	58
7*	64	72
8*	40	56
9*	59	57
H,K= -5 5		
0	347	324
1	397	370
2	387	362
3	317	296
4	286	286
5	305	274
H,K= -4 5		
0	156	155
1	146	137
2	167	161
3	134	132
4	119	114
5	134	131
6	102	98
7	107	97
8	90	78
H,K= -3 5		
0	316	309
1	275	284
2	367	346
3	237	248
4	240	235
5	301	278
6	156	169
7	182	187
8	159	155
9	106	123
H,K= -2 5		
0	100	100
2	99	103
3*	62	61
4*	54	49
5*	86	106
7*	70	81
8*	38	57
9*	47	57
H,K= -6 6		
0	324	321
1	270	257
2	284	280
H,K= -4 6		
0	301	304
1	246	235
2	257	258
3	263	255
4	206	203
5	181	204
6	170	178
7	137	161
8	122	121
H,K= -3 6		
0	101	110
1	188	181
2	148	131
3	142	139
4	137	136
5	115	97
6	132	129
7*	80	82
8*	73	80
9*	79	76
H,K= -2 6		
0	425	401
1	323	314
2	344	332
3	375	336
4	317	263
5	260	253
6	241	226
7	200	198
8	124	147
9	110	143
H,K= -6 7		
0*	47	67
1*	67	62
2*	69	70
3*	62	62
4*	39	56
H,K= -5 7		
0	151	182
1	229	240
2	202	214
3	158	185
4	163	190
5	157	166
6	150	155
7	127	124
H,K= -3 7		
0	250	261
1	307	302
2	309	298
3	242	242
4	241	238
5	233	229
6	191	185
7	153	162
8	131	145
9	98	119
H,K= -2 7		
0	150	162
1	86	103
2	144	166
3	102	115
4*	84	92
5	125	142
6*	54	72
H,K= -6 8		
0	162	174
1	152	145
2	155	153
3	156	151
4	135	129
5	124	127
H,K= -5 8		
0*	46	71
1*	71	61
2*	60	67
3*	54	65
4*	47	57
5*	47	58
6*	52	53
H,K= -4 8		
0	201	256
1	228	229
2	224	228
3	223	227
4	166	193
5	153	180
6	149	165
7	118	141
8*	80	115
9*	62	105
H,K= -2 8		
0	284	269
1	268	252
2	259	239
3	259	247
4	207	209
5	186	185
6	168	184
7	121	147
8	97	121
9	97	113
H,K= -5 9		
0	147	170
1	169	174
2	158	174
3	127	153
4	117	148
5	109	141
6*	80	117
7*	64	108
H,K= -3 9		
0	190	218
1	198	205
2	203	223
3	162	185
4	158	173
5	163	180
6	121	133
7	111	131
H,K= -4 10		
0	131	159
1	139	159
2	128	145
3	121	150
4	100	136
5	88	116

$Cd(NH_2CH_2CH_2NH_2)Ni(CN)_4 \cdot 2C_6H_6$ $M = 491.5$

tetragonal

$a = 7.675 \pm 0.003$ A, $c = 8.056 \pm 0.010$ A

space group P4/m — C_{4h}^1

$Z = 1$

$D_c = 1.72$, $D_m = 1.69$

b) *NMR Studies.* The ^{1}H–NMR spectra of the polycrystalline samples were recorded with a JEOL 30W spectrometer and a Varian Associate VF-16 spectrometer. The temperature of the sample was varied from room temperature to −120°C.

Structure Refinement. Since the unit cell contains only one unit of $Cd(en)Ni(CN)_4 \cdot 2C_6H_6$, the center of the en molecule must lie on the fourfold axis in order to satisfy the crystal symmetry. A certain amount of randomness must, therefore, be assumed. The positions of all the atoms except the hydrogen atoms were determined by three-dimensional Fourier syntheses, assuming that the cadmium atom is at 0,0,0 and that the nickel atom is at ½,½,0 as in the case of $Cd(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$.[14] The atomic parameters obtained gave a minus sign to only one structure factor, $F(2\bar{1}1)$, since the heaviest atom, cadmium, is situated at the point of origin. Some sections of the Fourier maps, calculated with the use of this sign, are presented in Figure 1. As Figure 1 shows, the electron density for the nitrogen atom of the en molecule is distributed uniformly over a torus about the Cd–Cd axis (fourfold axis), while that for the carbon atom exists on the axis with the shape of a distorted oblate-spheroid. This fact suggests that the en molecule is rotating about the Cd–Cd axis, or that each en moiecule is distributed in random orientations about the axis in the crystal. As will be described later, the NMR data support the rotation of the en molecule. The en molecule has three conformational isomers, *trans*, *cis* and *gauche*, depending on the change in the tortaional angel about the central C–C bond. In the present compound, however, the conformation of the en can not be determined by X-ray diffraction method, because any conformation gives the same features upon rotation.

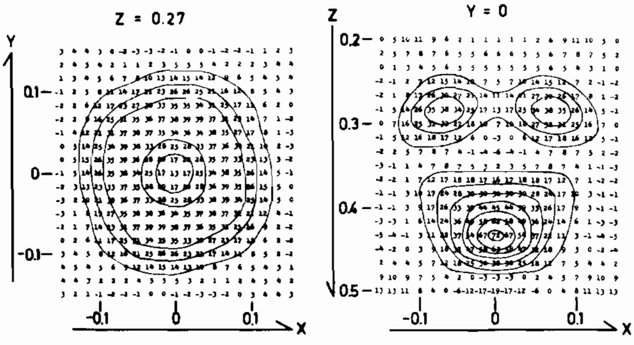

Figure 1. The Three-dimensional Fourier Maps (in an arbitrary scale). The section at $y = 0$ along the (010) plane and at $z = 0.27$ along the (001) plane, showing the electron densities for the nitrogen atom and the carbon atom of the ethylenediamine molecule.

The atomic parameters were refined by least-squares methods, using the block-diagonal approximation, to an R value of 0.089. The calculated and the observed structure factors are listed in Table I. In calculating the structure factors of the nitrogen atom of the en, by assuming the rotational motion of the nitrogen atom about the [001] axis the following equation was used:[15]

$$F = f \cdot \exp[-B_{11}(h^2+k^2) - B_{33}l^2] \cdot J_0(2\pi \frac{r}{a}\sqrt{h^2+k^2}) \cdot \exp(2\pi i l \frac{z}{c})$$

where J_0 is the Bessel function of the zeroth order and where r is the radius of the circular electron density for the nitrogen atom. The carbon atoms of the en were assumed to be fixed on the [001] axis. The atomic parameters thus obtained by the least-squares refinement gave rise to the unusual bond distances and angles in the en molecule as follows: C–N = 1.33 A, C–C = 1.38 A, Cd–N–C = 136°, and N–C–C = 152°. As may be seen in Figure 1, the electron density for the carbon atom of the en has a considerably distorted shape, showing the motion of the en more complicated than that assumed. These chemically-unacceptable values appear to be caused from the assumption that the carbon atoms are fixed on the axis.* Therefore, the atomic parameters given in Table II can be referred approximately with regard to those values for the carbon atom C(2) of the en.

All the calculations were performed by the use of the Hitac 5020E computor in the computation center of the University of Tokyo. The LP corrections were carried out with the ACACA program, while the Fourier syntheses, the least-squares refinement, and the calculations of the bond lengths and angles were done with programs in UNICS.[16] The atomic scattering factors used were those listed in International Tables for X-ray Crystallography.[17] The $\Sigma w(|F_o| - |F_c|)^2$ function was minimized in the least-squares calculations, and the weight of the reflections was set 1 for $|F_o| > 8.6$, and 0.5 for $|F_o| \leqslant 8.6$ because of the low reliabilities of photometer-readings for the weak reflections. The least-squares refinements with the space groups of P4 and $P\bar{4}$ were also examined respectively, but the standard deviations of the atomic parameters bacame significantly larger. Therefore, it is unnecessary to consider the possibility of P4 or $P\bar{4}$.

Results and Discussion

a) *Description and Discussion of the Structure.* The structure obtained is shown in Figs. 2 and 3, while

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[14] Sasaki Y., *Bull. Chem. Soc. Japan*, *42*, 2412 (1969).

* The calculations of the least-squares refinement with another assumption that the both carbon and nitrogen atoms of the en move around the axis, gave, however, large standard deviations of the atomic parameters and did never converge into the model in which the electron density for the carbon atom is also distributed on a torus.

(15) Atoji M., Watanabe T., and Lipscomb W.N., *Acta Cryst.*, 6, 62 (1953).

(16) Crystallographic Society of Japan (1967) 5020 UNICS, The Universal Crystallographic Computation Program System.

(17) International Tables for X-ray Crystallography, Vol. III, P202, Kynoch Press, Birmingham (1962).

Table II. Atomic Coordinates of the Asymmetric Unit (×10⁴). (The numbers in parentheses are standard deviations in the last significant figures).

Atom	Wychoff's notation	x/a	y/b	z/c
Cd	a	0000(0)	0000(0)	0000(0)
Ni	c	5000(0)	5000(0)	0000(0)
C(1)	j	3306(26)	3263(27)	0000(0)
N(1)	j	2209(23)	2200(23)	0000(0)
C(2)	g	0000(0)	0000(0)	4145(39)
N(2)		$r=820(58)$*		2693(52)
C(3)	i	5000(0)	0000(0)	3188(33)
C(4)	l	4865(29)	1583(26)	4129(23)

* r is the radius of the torus of the electron density for the nitrogen atom of the en molecule.

Table III. Anisotropic Thermal Parameters (×10⁴). (The thermal parameters are of the form: $T=\exp\{-(B_{11}h^2+B_{22}k^2+B_{33}l^2+2B_{12}hk=2B_{13}hl+2B_{23}kl\})$.

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cd	59(3)	59(3)	60(3)	000(0)	000(0)	000(0)
Ni	43(6)	43(6)	89(8)	000(0)	000(0)	000(0)
C(1)	72(29)	87(31)	144(33)	—24(48)	000(0)	000(0)
N(1)	92(32)	104(34)	134(28)	16(45)	000(0)	000(0)
C(2)	315(104)	315(104)	52(47)	000(0)	000(0)	000(0)
N(2)	124(123)	124(123)	80(60)	000(0)	000(0)	000(0)
C(3)	343(84)	86(43)	158(41)	—13(95)	000(0)	000(0)
C(4)	161(39)	271(52)	181(34)	—5(69)	8(62)	0(69)

The numbers in parentheses are estimated standard deviations

Table IV. Interatomic Distances and Bond Angles with Their Estimate Standard Deviations (in Parentheses). (Those distances longer than 4.0 A are not presented).

Cd-N(1)	2.39(2) A	N(2)-N(1) [a]	2.80(4) A
Cd-N(2)	2.26(4)	C(3)-C(1)	3.85(2)
Ni-C(1)	1.86(2)	C(3)-N(1)	3.75(2)
C(1)-N(1)	1.17(3)	C(3)-C(2)	3.91(1)
C(2)-N(2)	1.33(5) [b]	C(3)-N(2) [a]	3.23(4)
C(2)-C(2′)	1.38(6) [b]	C(4)-C(1)	3.79(2)
C(3)-C(4)	1.44(2)	C(4)-C(1′)	3.83(2)
C(4)-C(4′)	1.40(4)	C(4)-N(1)	3.93(2)
		C(4)-C(2)	3.93(2)
N(2)-Cd-C(2)	16(1) °	C(4)-N(2) [a]	3.49(5)
Cd-N(2)-C(2)	136(3) [b]	C(4)-C(4″)	3.71(4)
N(2)-C(2)-C(2′)	152(2) [b]	C(4″)-N(2) [a]	3.68(5)
Ni-C(1)-N(1)	178(2)		
Cd-N(1)-C(1)	179(2)		
C(3)-C(4)-C(4′)	122(2)		

[a] The shortest distance attainable by the rotation of ethylenediamine molecule. [b] No great faith can be placed in these parameters. See text for further discussion.

the final coordinates of the asymmetric unit and the anisotropic thermal parameters are listed in Tables II and III respectively. The bond lengths and the bond angles are given in Table IV. As may be seen in Figs. 2 and 3, the cadmium atoms and the nickel atoms are at 0,0,0 and ½,½,0 respectively, and t hey are bridged together with the cyanide anions on the (001) plane to make a square-planar network. Moreover, the en molecules are along the [001] axis. Each of the en molecules links between two cadmium atoms in the neighboring networks, thus forming a three-dimensional host lattice of the polymeric metal complex structure. The guest benzene molecules are trapped in the cavities formed by the hast lattice with their ring planes vertical to the (001) plane. The en molecule is surronded by four planes of the benzene molecules, while the ring plane of the benzene molecule is placed between two en molecules in such an orientation as to avoid the steric repulsion from the en molecules. If the en molecule is replaced by two ammonica molecules, this structure is almost the same as that of $Cd(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$[14] .

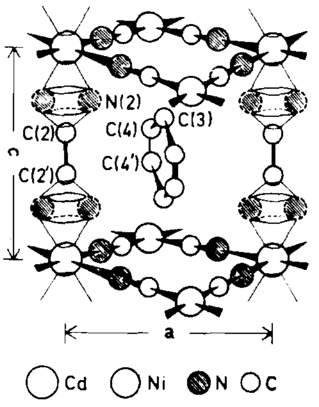

Figure 2. The Illustration of the Structure of $Cd(en)Ni(CN)_4 \cdot 2C_6H_6$.

The en molecule, with its center situated at 0,0,½, bridges between two cadmium atoms at 0,0,0 and 0,0,1. The nitrogen atoms of the en molecule are 0.6 A from the [001] axis, while the carbon atoms lie approximately on the axis. The angle between the axis and the direction of the Cd–N(en) bond is 16°. With regard to the orientation of the en molecule, the previous idea that was shown in Fig. 2 of ref. 1 should be corrected.

Table V. Bond Lengths and Angles in the Ethylenediamine Complexes.

Compound	C–N	C–C′	M–N	M–N–C	N–C–C′	M–M[a]
Present compound	1.33 A[b]	1.38 A[b]	2.26 A	136°[b]	152°[b]	8.06 A
$[Li(en)]enCl$[12]	1.48	1.50	2.07	122.2	109.4	6.39
$[Li(en)]enBr$[12]	1.47	1.53	2.06	122.1	109.7	6.37
$[Pt(CH_3)_3acac]_2en$[11]	1.38	1.70	2.31	111	104	7.68
$[Pt(CH_3)_3en]_2enI_2$[10]						7.79
$Hg(en)Cl_2$[2]						7.59
$[Co(en)_3]Cl_3 \cdot H_2O$[19]	1.50	1.51	1.98	108.3	105.7	—[c]

[a] The interatomic distance between the bridged metal atoms. [b] No great faith can be placed in these parameters. [c] The complex with chelating en molecules.

As the four cyanide anions around the cadmium atom are fixed on the (001) plane, the cadmium atom has the ligand configuration of a considerably distorted octahedron in this compound. Although the bond angles around the six-coordinated metal atoms seldom deviate so greatly from 90°, an angle of 68° has been reported for the N–Cd–O angle $Cd(NH_2NHCO_2)_2 \cdot H_2O$[18] Ligand arrangements around the d^{10} ions may be distorted rather easily from a regular octahedron, since the ligand-field energy does not affect the symmetry of the arrangement in the d^{10} complexes.

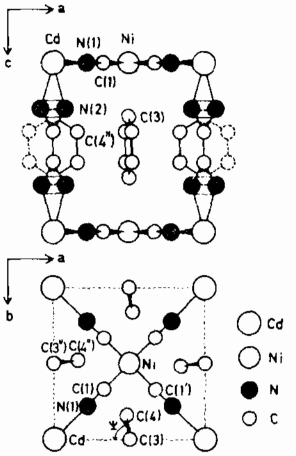

Figure 3. The Projection of the Strutcure on the (010) and the (001) Planes. The en molecules are not presented in the projection on the (001) plane.

The structures of the bridging en - metal systems in the present compound, in $[Pt(CH_3)_3acac]_2en$[11], and in [Li(en)] enX (X = Cl, Br)[12] are illustrated in Fig. 4, and the structural data concerned are listed in Table V along with that for an en chelate complex (+)-$[Co(en)_3]Cl_3 \cdot H_2O$[19]. All the bridging en molecules so far studied are in the trans conformation about the central C–C bond. On the other hand, considering the M–N–C–C set of chemical bonds in the complexes with bridging en molecules, there is another conformational isomerism about the N–C– bond. As Fig. 4 shows, the present compound, as like the platinum complex, has a trans conformation about the N–C bond, while a cis one is observed in the lithium complexes. The difference in the conformation affects the interatomic distance between the bridged metal atoms (the M–M distance in Table V). Indeed, very short M–M distances are reported in the lithium complexes with the cis conformation. That of the present compound, 8.06 A, is significantly longer than those of the other complexes with the trans conformation. The longer M-M distance can be caused from the smaller angle formed between the line combining the two M atoms and the direction of the C–C bond of the en molecule. In the present compound, the guest benzene molecule rules the lower limit of the Cd–Cd distance, and moreover, the steric repulsion between the guest molecule and the host lattice may make the C–C bond of the en molecule be approximately on the [001] axis. Accordingly, the observed distance, 8.06 A, is shorter than that, 8.32 A, in $Cd(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$[14] owing to the en-bridging structure, but is longer than those M–M distances, observed for the other en-bridged metal complexes in Table V.

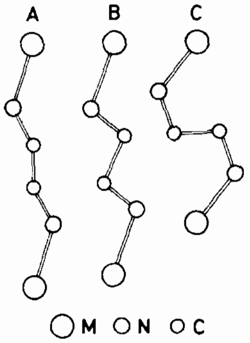

Figure 4. The Structure of the Bridging en Molecules.
A: $Cd(en)Ni(CN)_4 \cdot 2C_6H_6$
B: $[Pt(CH_3)_3acac]_2en$
C: [Li(en)]enCl or [Li(en)]enBr

As Table V shows, the interatomic distances between the benzene molecule and the networks, or those between the benzene molecules, are 3.7 A or more, except those of C(3)–N(2) (3.23 A) and C(4)–N(2) (3.49 A). Since the latter two are the shortest distances at the closest approach of the en to the benzene molecule, even they become longer with the rotation of the en molecule. It can be concluded, therefore, that no direct bonds exist between the guest benzene and its surroundings. The benzene molecule is en-

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(18) Braibanti A., Lanfredi A.M.M., Tiripicchio A., and Bigoli F., *Acta Cryst.*, *B25*, 100 (1969).
(19) Iwata M., Nakatsu K., and Saito Y., *ibid.*, *B25*, 2562 (1969).

clathrated in the three-dimensional host lattice with its sixfold axis parallel to the (001) plane as in the case of the Hofmann-type clathrates.[14,20] A projection of the structure on the (001) plane is presented in Figure 3, where Ψ is the angle between the ring plane of benzene and the a-axis. The orientation of the guest benzene in the (001) plane appears to depend considerably upon the surroundings. The benzene molecule in this clathrate is arranged with the Ψ angle of 85°, which is much larger than that of 59° observed for the corresponding Hofmann-typ clathrate $Cd(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$.[14] The increment in the Ψ angle is deduced from the replacement of the ammonia molecules by more bulky en molecule, because the Ψ angle must become larger in order for the electron cloud of the guest benzene to be in contact with that of the en molecule.

Owing to the rotation of en molecule in the crystal at room temperature, the conformaion abou the C–C′ bond of the en could not be determined from the present data. Although the infrared data suggested the trans form,[1] Raman studies are necessary to establish the conformation.

b) *NMR Studies.* The ^1H–NMR spectra and the temperature dependence of the line width for the powder sample of $Cd(en)Ni(CN)_4 \cdot 2C_6D_6$ are shown in Figure 5. The second moments of the spectra could not be calculated owing to the weak intensities of the signals. As the temperature increases from −100° to −40°C, the line width of the spectrum decreases drastically with the change in the line shape. This fact supports that the motion of the en molecule begins in this temperature range. The line shape and the line width of the proton signal depend mainly on the magnetic dipole-dipole interactions among the resonant nuclei. The spin system of the present compound is too complicated for the line shape to be analyzed. The line width of 14.4 Oe at −120°C, however, indicates a rigid en molecule, while that of 6.5 Oe at room temperature may support the rotation of en molecule about the Cd–Cd axis. This feature resembles that of 1,2-dichloroethane where the rotation about an axis perpendicular to the H–H line on the CH_2 group narrows the line width to a half of the rigid one.[21]

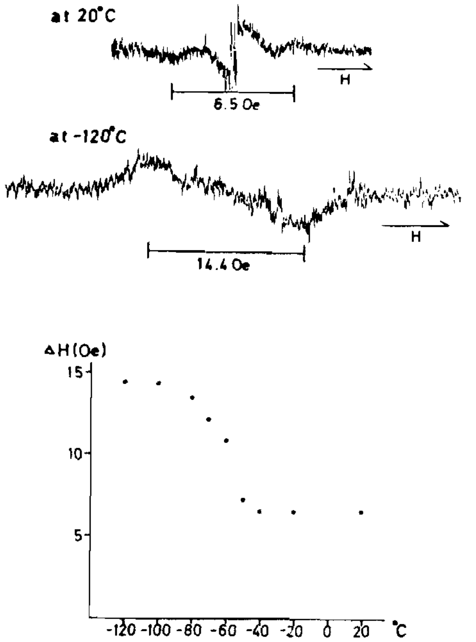

Figure 5. The ^1H-NMR Spectra of $Cd(en)Ni(CN)_4 \cdot 2C_6D_6$ and the Temperature Dependence of the Line Width of the Spectra.

The en molecule appears to be rotating at room temperature with little hindrance so that the electron density for the nitrogen atom is almost uniformly spread along the torus. The symmetry of the crystal shows a fourfold potential barrier against the rotation of the en molecule. The height of the barrier may be determined by the repulsion from four sets of two nearest-neighboring atoms, *i.e.*, the nitrogen atom of the cyanide anion, N(1), and the carbon atom of the benzene molecule, C(3). When the nitrogen atom of the en is on the (010) plane upon rotation, it is 2.95 A from the former and 3.23 A from the latter. These distances become 2.80 A and 3.45 A respectively when it is on the (110) plane. Although the repulsive forces from each atom vary considerably with the roation of the en molecule, their variations may mostly offset each other. Therefore, a nearly-free rotation of en appears to be allowed in the present compound at room temperature. This may be the first observation of the rotating ethylenediamine molecule in the coordination compounds.

Although diffuse scatterings due to the rotation of the en molecule may be expected,[15,22] the X-ray photographs did not show any features except the thermal diffuse scatterings due to the vibration. It is not known, therefore, whether the en molecules rotate with any correlation with each other or not.

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(20) Rayner J.H. and Powell H.M., *J. Chem. Soc.*, 319 (1952).

(21) Gutowsky H.S. and Pake G.E., *J. Chem. Phys.*, *18*, 162 (1950).

(22) Oda T. and Matsubara T., *X-rays*, *6*, 27 (1950).