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The Crystal Structure and ESR Studies of Diamminecopper(II) Tetracyanoniccolate(II) Dibenzene Clathrate: $Cu(NH_3)_2Ni(CN)_4.2C_6H_6$*

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The crystal structure of $Cu(NH_3)_2Ni(CN)_4 . 2C_6H_5$ *was determined by three-dimensional X-ray methods. The crystal is tetragonal with the dimensions of* a = *7.345 A and* c = *16.519 A, and the space group is P4/mcc* (Z = 2). *Reflection data were collected with an automatic four circle diffractometer and monochromatized Mo Kα radiation. The structure was solved by the heavy-atom method and was refined by the block-diagonal least-squares method for 690 independent reflections to a final R-index of 0.068. The copper ions and the nickel ions are linked crosswise with the cyanide anions to form a polymeric two-dimensional metal complex network, and the benzene molecules are trapped among the layers of the networks. This host lattice structure is similar to those of the other Hofmann-type clathrates,* $Ni(NH_3)_2Ni(CN)_4 . 2C_6H_6$ *and* $Cd(NH_3)_2Ni(CN)_4 . 2C_6H_6$*, but the* c*-axis of the cell is doubled due to different orientation of the benzene molecules in alternate guest layers. The copper(II) ion takes a compressed tetragonal coordination with the four nitrogen atoms of the cyanide anions in the (001) plane (the Cu-N distance, 2.20 A) and with the two nitrogen atoms of the ammonia molecules on the [001] axis at the compressed apical positions (the Cu-N distance, 2.05 A). The ESR spectra of the magnetically dilute single crystal of* $(Cd, Cu)(NH_3)_2Ni(CN)_4 . 2C_6H_6$ *can be interpreted in terms of* A_{1g} *symmetry of the electronic ground state of the copper(II) ion in the compressed tetragonal environment which was previously concluded from the spectra of the polycrystalline samples.*

Introduction

One of the Hofmann-type clathrates, $Cu(NH_3)_2Ni(CN)_4 . 2C_6H_6$, has been reported for the copper(II) ion in its host lattice to take a compressed tetragonal configuration from the results of ESR spectroscopy.[1] In the previous paper, the ESR spectra of the polycrystalline samples of $Cu(NH_3)_2Ni(CN)_4 . 2C_6H_6$ and of magnetically dilute $(Cd, Cu)(NH_3)_2Ni(CN)_4 . 2C_6H_6$ supported the A_{1g} symmetry of the electronic ground state of the copper(II) ions. The present paper will report on the crystal structure analysis of $Cu(NH_3)_2Ni(CN)_4 . 2C_6H_6$ and the ESR spectra of the magnetically dilute $(Cd, Cu)(NH_3)_2Ni(CN)_4 . 2C_6H_6$ single crystal.

The stereochemistry of copper(II) complexes has been investigated fully as examples of the Jahn-Teller effect.[2-4] Theoretical calculations by Liehr and Ballhausen have shown the possibility of both elongated and compressed distortions from O_h symmetry in the ligand configuration around the copper(II) ions.[5] Most of the copper(II) complexes so far studied by the X-ray diffraction method have demonstrated the elongated distortion along the tetragonal axis; the only compressed structures have been reported on are those of K_2CuF_4,[6] $Cu(NH_3)_2Cl_2$,[7] $Cu(NH_3)_2Br_2$[7] and $Cu(dien)_2(NO_3)_2$,[8] The electronic ground state of the copper(II) ion in the compressed tetragonal environment is expected to have an A_{1g} symmetry by the ligand field theory, although none have ever proved it experimentally. ESR spectroscopy can be a potential method to prove it. However, these complexes with the compressed structures are not always appropriate for such studies because the dipolar and the exchange interactions between the copper(II) ions in their crystal structures. In fact, nearly isotropic ESR spectra caused by the exchange interaction were observed in $Cu(dien)_2(NO_3)_2$.[9] The dipole-dipole interaction made the ESR spectrum of $Cu(NH_3)_2Br_2$ so broad (ΔH = 2000 Oe) that the spectrum could not be analyzed.[1] It is highly desirable to find a complex with the compressed structure in which both the crystal structure anlaysis and the ESR studies are successful. The present compound, $Cu(NH_3)_2Ni(CN)_4 . 2C_6H_5$, is such a case.

Experimental Section

a) *X-ray Structure Analysis.* The single crystal of

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* The Metal Ammine Cyanide Aromatics Clathrates. XIV.

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(1) T. Miyoshi, T. Iwamoto, and Y. Sasaki, *Inorg. Chim. Acta, 2,* 329 (1968).

(2) H.A. Jahn and E. Teller, *Proc. Roy Soc., A 161,* 220 (1937); H.A. Jahn, *ibid., A 164,* 117 (1938).

(3) J.H. Van Vleck, *J. Chem. Phys., 7,* 72 (1939).

(4) U. Opik and M.H.L. Pryce, *Proc. Roy Soc., A 238,* 425 (1956).

(5) A.D. Liehr and C.J. Ballhausen, *Ann. Physics, 3,* 304 (1956).

(6) K. Knox, *J. Chem. Phys., 30,* 991 (1959).

(7) F. Hanic and I.A. Cakajdova, *Acta Cryst., 11,* 610 (1958).

(8) F.S. Stephens, *J. Chem. Soc., (A),* 883 (1969).

(9) J. Hathaway, M.J. Bew and D.E. Billing, *ibid., (A),* 1090, (1970).

Table I. Observed and calculated structure factors (×10).

H	K	L	10FO	10FC
0	1	0	131	101
0	2	0	1177	1051
0	3	0	62	-39
0	4	0	913	863
0	5	0	237	208
0	6	0	593	580
0	7	0	127	131
0	8	0	180	212
0	9	0	123	115
0	10	0	165	149
1	1	0	649	539
1	2	0	518	437
1	3	0	724	722
1	4	0	292	302
1	5	0	610	601
1	7	0	201	246
1	9	0	169	161
2	2	0	1617	1543
2	3	0	83	106
2	4	0	702	685
2	6	0	487	487
2	7	0	114	149
2	8	0	295	316
3	3	0	979	879
3	4	0	108	101
3	5	0	211	226
3	6	0	193	193
3	7	0	211	230
4	4	0	715	651
4	5	0	109	126
4	6	0	360	382
4	8	0	201	222
5	5	0	394	366
5	7	0	122	159
5	8	0	101	79
6	6	0	242	241
7	7	0	135	161
1	2	1	365	298
1	3	1	179	-122
1	4	1	91	81
1	5	1	109	-100
2	3	1	214	-216
2	4	1	173	160
3	5	1	87	-91
0	0	2	957	-1094
0	1	2	83	-75
0	2	2	154	-110
0	3	2	292	-297
0	4	2	833	-792
0	6	2	460	-425
0	8	2	135	-146
0	10	2	168	-136
1	1	2	1548	-1627
1	2	2	172	109
1	3	2	609	-616
1	5	2	582	-571
1	7	2	301	-302
1	9	2	120	-145
2	2	2	1101	-1107
2	3	2	160	-144
2	4	2	497	-501
2	6	2	251	-254
2	7	2	97	-76
2	8	2	210	-202
3	3	2	835	-845
3	5	2	336	-344
3	6	2	62	-82
3	7	2	326	-332
3	9	2	149	-152
4	4	2	405	-402
4	5	2	145	-124
4	6	2	206	-212
4	8	2	121	-130
5	5	2	376	-409
6	6	2	236	-221
1	2	3	218	157
1	3	3	96	-78
1	5	3	72	-66
2	3	3	134	-140
2	4	3	103	106
2	6	3	82	41
0	0	4	1535	1695
0	1	4	344	-277
0	2	4	69	97
0	3	4	217	-176
0	4	4	429	436
0	6	4	351	325
1	1	4	754	799
1	2	4	96	-68
1	3	4	636	613
1	5	4	544	524
1	7	4	234	231
1	9	4	121	134
2	2	4	707	768
2	3	4	92	-98
2	4	4	286	299
2	6	4	241	233
3	3	4	772	767
3	5	4	200	225
3	7	4	222	226
3	9	4	117	115
4	4	4	358	341
4	6	4	194	193
4	8	4	114	118
5	5	4	317	337
5	7	4	117	127
0	0	6	1745	-1764
0	2	6	556	-574
0	4	6	722	-704
0	6	6	442	-441
0	8	6	174	-161
1	1	6	599	-591
1	3	6	364	-379
1	4	6	67	-59
1	5	6	396	-388
1	7	6	193	-182
1	8	6	94	-43
1	9	6	97	-105
2	2	6	1010	-1069
2	4	6	508	-523
2	6	6	306	-327
2	7	6	98	-72
2	8	6	201	-230
3	3	6	554	-571
3	5	6	166	-163
3	6	6	98	-90
3	7	6	194	-195
3	9	6	121	-100
4	4	6	410	-458
4	6	6	231	-263
5	5	6	279	-277
5	7	6	103	-97
6	6	6	171	-205
0	0	8	944	984
0	1	8	137	133
0	2	8	356	349
0	3	8	183	207
0	4	8	586	596
0	6	8	371	359
0	8	8	133	134
1	1	8	970	1013
1	2	8	80	64
1	3	8	547	551
1	4	8	96	76
1	5	8	466	472
1	7	8	249	253
1	9	8	132	132
2	2	8	767	815
2	3	8	120	132
2	4	8	407	423
2	6	8	252	268
2	8	8	170	184
3	3	8	620	662
3	5	8	253	267
3	7	8	259	267
4	4	8	342	348
4	5	8	122	115
4	6	8	176	197
5	5	8	303	334
6	6	8	153	187
1	2	9	96	-97
2	3	9	79	86
0	0	10	1045	-1050
0	1	10	77	59
0	2	10	294	-274
0	4	10	316	-305
0	6	10	267	-249
1	1	10	505	-524
1	3	10	458	-487
1	5	10	407	-398
1	7	10	172	-181
1	9	10	136	-114
2	2	10	515	-522
2	4	10	259	-241
2	6	10	205	-196
2	8	10	145	-150
3	3	10	523	-549
3	5	10	171	-181
3	7	10	154	-169
4	4	10	252	-268
4	6	10	169	-163
5	5	10	214	-254
6	6	10	124	-111
2	3	11	93	84
0	0	12	537	514
0	1	12	76	-83
0	2	12	246	232
0	3	12	81	32
0	4	12	421	398
0	6	12	260	238
0	7	12	114	-83
1	1	12	384	378
1	2	12	91	-121
1	3	12	155	129
1	5	12	182	167
2	2	12	498	507
2	4	12	301	284
2	6	12	170	145
3	3	12	257	253
3	5	12	95	82
3	7	12	122	123
4	4	12	217	222
5	5	12	171	150
0	0	14	557	-569
0	2	14	189	-179
0	4	14	187	-201
0	6	14	177	-166
1	1	14	340	-307
1	3	14	290	-271
1	5	14	237	-235
1	7	14	103	-113
2	2	14	328	-322
2	4	14	152	-162
3	3	14	317	-322
4	4	14	163	-171
4	6	14	108	-106
5	5	14	147	-161
0	0	16	355	351
0	2	16	144	148
0	4	16	221	209
0	6	16	131	150
1	1	16	329	337
1	3	16	221	224
1	5	16	202	203
2	2	16	281	280
2	4	16	159	161
2	6	16	128	101
3	3	16	267	270
3	5	16	124	122
4	4	16	132	144
5	5	16	130	151
0	0	18	341	-294
0	2	18	169	-139
0	4	18	203	-175
1	1	18	143	-160
2	2	18	246	-232
2	4	18	158	-139
3	3	18	149	-145
4	4	18	157	-122
0	0	20	204	192
0	2	20	96	52
1	1	20	142	101
3	3	20	153	115
0	0	22	151	-95

$Cu(NH_3)_2Ni(CN)_4 . 2C_6H_5$ was prepared by leaving an ammoniacal solution of an equimolar mixture of $CuSO_4$ and $K_2Ni(CN)_4$ in contact with a layer of benzene for six months. The pale green crystals thus obtained had a tabular shape and cleaved easily along the (001) plane. As these crystals had a tendency to grow with partial deformations, most of them were not single crystals and their Bragg spots split into two or more parts. Precession photographs were taken about the [110] and the [001] axes with Mo Kα radiation, and the Laue group was determined to be P4/mcc. The unit cell dimensions were determined from the least-squares refinement of the θ values which were obtained from Weissenberg photographs. The density was determined by the flotation method in an aqueous potassium tetraiodomercurate solution.

$Cu(NH_3)_2Ni(CN)_4 . 2C_6H_6$ $M = 416.6$

tetragonal $a = 7.345 \pm 0.003$,
$c = 16.519 \pm 0.004$ A

systematic absences: $h0l$ and $0kl$; $l = 2n + 1$
hhl; $l = 2n + 1$

space group: P4/mcc or P4cc
$Z = 2$. $D_m = 1.53$, $D_c = 1.55$

A crystal of dimensions, 0.1×0.2×0.3 mm, sealed in a thin-walled soft glass capillary to prevent the escape of benzene was used for intensity measurements. Intensity data were collected on an automatic four-circle diffractometer, Rigaku Electric Co. R 71774, with monochromatized Mo Kα radiation. The details of the measurements have been described elsewhere.[10] Of the 690 independent, non-systematically-absent reflections with 2θ less than 60°, 391 had non-zero values and only 244 of them were more than three times their estimated standard devitaions. Lorentz and polarization factors were applied, but no correction for absorption was made (linear absorption coefficient for Mo Kα, $\mu = 23.0$ cm^{-1}).

b) *ESR Measurements.* The single crystal of $(Cd, Cu)(NH_3)_2Ni(CN)_4 . 2C_5H_5$ was prepared with the procedure similar to the above-mentioned by the use of the carefully-purified inorganic reagents.[1] The aqueous phase used was a solution of $Cd(NO_3)_2$, $CuSO_4$ and $K_2Ni(CN)_4$ mixed in an 8:1:9 molar ratio. The appearance of the crystal was the same as that of $Cd(NH_3)_2Ni(CN)_4 . 2C_6H_5$ in both shape and color.[11]

(10) Miyoshi, Y. Sasaki, and T. Iwamoto, *Acta Cryst.*, to be submitted.

Table II. Final fractional atomic coordinates and their standard deviations (in parentheses).

	Wyckoff's notation	point group	x/a	y/b	
Ni	a	42	0.0000(0)	0.0000(0)	0.2500(0)
C(1)	c	42	0.5000(0)	0.5000(0)	0.2500(0)
N(1)	j	2	0.3191(20)	0.3191(20)	0.2500(0)
N(2)	j	2	0.2115(16)	0.2115(16)	0.2500(0)
C(2)	g	4	0.0000(0)	0.0000(0)	0.3740(14)
C(2)	i	2	0.5000(0)	0.0000(0)	0.4151(11)
Cu	n	1	0.4304(23)	0.1447(25)	0.4563(9)

Table III. Thermal parameters.*

	β_{11} or B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.0103(8)	0.0103(8)	0.0037(2)	0.0(0)	0.0(0)	0.0(0)
Ni	0.0160(11)	0.0160(11)	0.0025(2)	0.0(0)	0.0(0)	0.0(0)
C(1)	3.46(36) A^2					
N(1)	4.19(37)					
N(2)	2.78(39)					
C(2)	4.23(35)					
C(3)	4.71(42)					

* The temperature factor expressions used are $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})]$ or $\exp[-B(\sin\theta/\lambda)^2]$.

The ESR spectra were recorded with a JEOL-JES 3BS-X spectrometer with an X-band frequency and a field modulation of 100 kHz. The crystal was rotated about the [001] and the [110] axes, and the temperature of the sample was varied from –30°C to the liquid nitrogen temperature. The magnetic paramemeters were obtained with the second order perturbation method of Bleany.[12] The ESR experiments were also examined for the single crystals of $Cu(NH_3)_2Ni(CN)_4 . 2C_6H_6$, but available crystals were too small to give any significant results.

Structure Deterfmination

Between two possible space groups P4/mcc and P4cc, P4/mcc was assumed at first. As the unit cell containes only two units of $Cu(NH_3)_2Ni(CN)_4 . 2C_6H_6$, most atoms must be at the special positions. The atomic positions were determined by the use of the three-dimensional Patterson and Fourier syntheses. The atomic parameters were refined by the block-diagonal least-squares method with the 244 reflections, which were more than three times their standard deviations. The final R-index was 6.8%. The calculated and the observed structure factors are listed in Table I. The three-dimensional ΔF-syntheses with all the observed reflections did not show any significant peaks and hollows. The least-squares refinement with the sapce group of P4cc gave almost the same R-index as that of P4/mcc, but the standard deviations of the atomic parameters became significantly larger. Therefore, the space group of P4/mcc is preferable to that of P4cc.

The calculations were carried out with the electronic computer, Hitac 5020E, in the computation center of the University of Tokyo. The program used were RLC-3, ANSFR-2, HBLS-4 and RDA-4 in UNICS.[13] The atomic scattering factors used were those listed in International Tables for X-ray Crystallography.[14] The $\Sigma w(|F_o|-|F_c|)^2$ function was minimized in the least-squares calculations, and the weight was 1 for the reflections with $|F_o|>13$, and 0.5 for $|F_o|<13$, since the standard deviations of the observed structure factors were much larger in the weak reflections.

Table IV. Interatomic distances and bond angles (those distances longer than 4 A are not presented).

Cu-N(1)	2.20(1) A	C(2)-N(1)	3.79(2) A
Cu-N(2)	2.05(2)	C(2)-C(1)	3.83(2)
Ni-C(1)	1.88(1)	C(2)-N(2)	3.73(1)
C(1)-N(1)	1.12(2)	C(3)-C(1)	3.73(2)
C(2)-C(3)	1.36(2)	C(3)-N(1)	3.80(2)
C(3)-C(4)	1.44(3)	C(3)-N(2)	3.60(2)
		C(3)-C(3')	3.76(3)
C(2)-C(3)-C(4)	120.0(1.5)°		

Results and Discussion

a) *Description of the Structure.* The structure of the unit cell is shown in Figures 1 and 2, while the atomic parameters of the asymmetric unit are given in Tables II and III. The bond lengths and the bond angles are presented in Table IV. As Figures 1 and 2 show, the structure of this compound is similar to those of the Hofmann-type clathrates reported previously.[15,16] However, two kinds of arrangement with regard to the orientation of the benzene molecules appear alternately along the [001] axis, as will be described later.

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(11) T. Miyamoto, *Inorg. Chim. Acta·* *3*, 511 (1969).

(12) B. Bleany, *Phyl. Mag.*, *42*, 441 (1951).

(13) Crystallographic Society of Japan (1967) 5020 UNICS, the Universal Crstallographic Computation Program System.

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

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

(16) Y. Sasaki, *Bull. Chem. Soc. Japan*, *42*, 2412 (1969).

Table V. The Cu-ligand distances in the copper(II) complexes with the compressed tetragonal configuration.

	equatorial		axial	
K_2CuF_4 [6]	Cu-F:	2.08 A	Cu-F;	1.95
β-$Cu(NH_3)_2Cl_2$ [7]	Cu-Cl:	2.76	Cu-N:	2.03
β-$Cu(NH_3)_2Br_2$ [7]	Cu-Br:	2.88	Cu-N:	2.01
$Cu(dien)_2(NO_3)_2$ [8]	Cu-N:	2.22	Cu-N:	2.05
$Cu(NH_3)_2Ni(CN)_4 . 2C_6H_6$	Cu-N:	2.20	Cu-N:	1.95 A

The copper(II) ion in the host lattice is coordinated with six nitrogen atoms tetragonally. Of the six nitrogen atoms, two are of the ammonia molecules and four are of the cyanide anions. The Cu-N distances are 2.05 A for the ammonia and 2.20 A for the cyanide so that the copper(II) ion takes a compressed tetragonal configuration of the ligand atoms. For the sake of comparison, the bond lengths or the distances between Cu^{II} and ligand atoms are listed in Table V for the few other copper(II) complexes with the compressed tetragonal configurations.

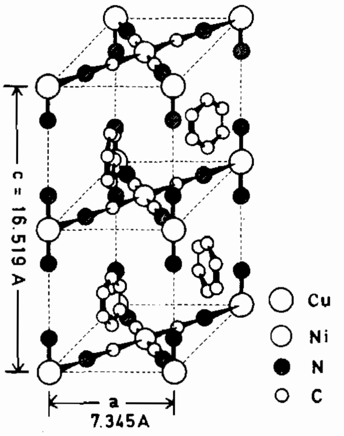

Figure 1.

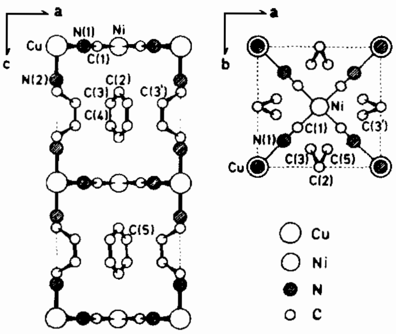

Figure 2.

The cause of axial compression in the copper(II) system has been discussed by Smith in terms of a molecular orbital theory.[17] However, in the present compound, the compression appears to be caused from the steric repulsion between the host lattice and the guest molecule, since the configuration around the copper(II) is axially elongated in the residual host lattice, $Cu(NH_3)_2Ni(CN)_4$, left after the complete escape of the guest benzene from the clathrate.[1]

The benzene molecules are enclathrated in the cavities between the metal complex networks with their ring plane parallel to the [001] axis of the crystal. The interatomic distances between the guest molecules are 3.6 A or more, as listed in Table IV, supporting that there are no direct bonds between them.

Two ammonia molecules, protruding from the both copper(II) ions of the upper and the lower metal complex networks, are inserted between each two benzene molecules along the *a* or *b* axis of the crystal. Since the benzene molecule is on the twofold axis parallel to the [001] axis, its sixfold axis can take any direction in the [001] plane. In the present clathrate, the benzene molecules are arranged with an angle 64.3° against *a* or *b* axis throughout their layer between a pair of the metal complex networks. The arrangement may minimize the steric repulsion between the host lattice and the guest molecules, and that between the guest molecules. As illustrated in Figure 3, the arrangement with the angle (180–64.3)°, the mirror image (M) of that with 64.3° (R) on the (100) or (010) plane, is obtained by turning over the layer of the guest benzene molecules. With regard to the steric repulsive force, the both R and M arrangements are completely equivalent if the intermolecular interaction along the [001] axis is negligible. In the present clathrate, the alternate stacking of the R and M arrangements occurs along the [001] axis, although only one arrangement appears in $Ni(NH_3)_2Ni(CN)_4 . 2C_6H_6$[15] and $Cd(NH_3)_2Ni(CN)_4 . 2C_6H_6$.[16]

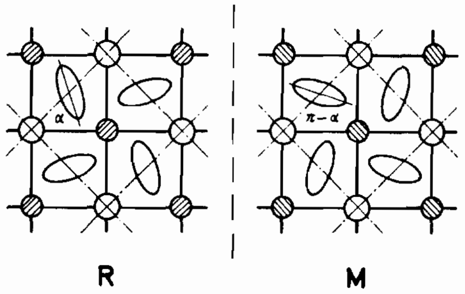

Figure 3.

The unit cell thus contains two layers of the guest molecules and the *c*-dimension is 16.519 A, approximately twice the value 8.24 A previously reported from the powder diffraction data,[18] where the reflections with l = odd were too weak to be observed.

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(17) D.W. Smith, *J. Chem. Soc.*, (A), 1970, 1498.

(18) T. Iwamoto, T. Miyoshi, T. Miyamoto, Y. Sasaki, and S. Fujiwara, *Bull. Chem. Soc. Japan*, *40*, 1174 (1967).

Table VI. The magnetic parameters of (Cd,Cu)$(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ at −130°C.

$g_\parallel = 2.019 \pm 0.001$ $\quad g_\perp = 2.232 \pm 0.001$
$A_\parallel = 90.1 \pm 0.5\ 10^{-4}\ cm^{-1}$ $\quad A_\perp = -58 \pm 1\ 10^{-4}\ cm^{-1}$
$(Q') = 7 \pm 2\ 10^{-4}\ cm^{-1}$

b) *ESR Results.* The magnetic parameters obtained from the single crystal ESR spectra are listed in Table VI. The $g_\perp$, $g_\parallel$, $A_\perp$, and $A_\parallel$ values coincide well with those of the powder samples reported previously.[1] This fact supports the previous conclusion that the electronic ground state of the copper(II) ions has an A_{1g} symmetry in this compound. Although a small discrepancy, *ca.* 0.02, bteween the experimental and calculated $g_\parallel$ values has been observed, the angular dependency of the magnetic parameters makes no doubt of the A_{1g} ground state being essential as shown in Figure 4. The discrepancy may be ascribed to either (i) a slight distortion of the lignad field from a tetragonal symmetry,[19] (ii) an exchange coupling between crystallographically non-equivalent Cu^{II} ions,[20] or (iii) a dynamical Jahn-Teller effect.[21] The former two can be excluded in the present case because they are inconsistent with the crystal structure. A 0.2% increase of the $g_\parallel$ value and a 0.1% decrease of $g_\perp$ value observed upon raising temperature from −150°C to −30°C could not be significant enough to prove the dynamical Jahn-Teller effect, although the temperature dependency itself is not inconsistent with the theoretical prediction.[21] Such a narrow temperature range may not be adequate for demonstrating the dynamical Jahn-Teller effect and an experiment at higher temperature, which might provide a better test, is impossible owing to the instability of the clathrate at the higher temperature.

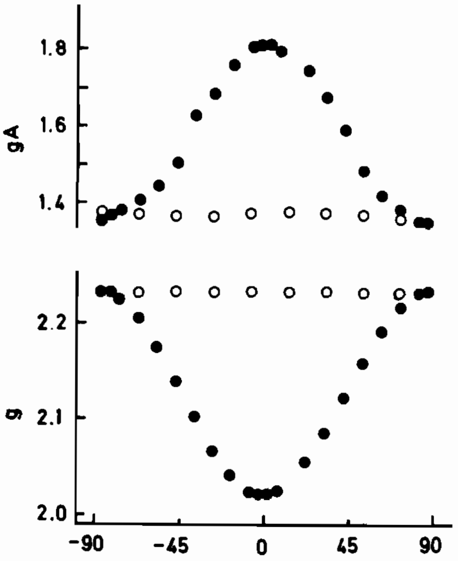

Figure 4.

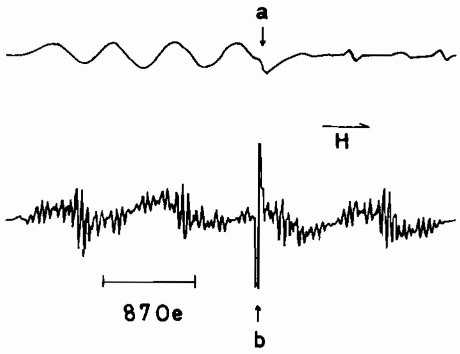

Figure 5.

When the magnetic field is applied parallel to the fourfold axis (the *c*-axis) of the crystal, the ESR spectrum gives a ligand hyperfine (lhf) structure along with a hyperfine structure as shown in Figure 5. The possible nuclei giving the lhf structure are ^{14}N of the cyanide and of the ammonia and ^1H of the ammonia. The observed spectrum can be interpreted in terms of either an overlap of the $N(NH_3)$ and N(CN) lhf structures or the $N\text{-}(NH_3)$ lhf structure secondarily split with the protons of the ammonia. The latter appears to be more likely in the graphically simulated spectra based on the sets of lhf constants $A_{N(NH_3)} = 15 \times 10^{-4}\ cm^{-1}$ and $A_{N(CN)} = 5 \times 10^{-4}\ cm^{-1}$, and $A_{N(NH_3)} = 15 \times 10^{-4}\ cm^{-1}$ and $A_H = 5 \times 10^{-4}\ cm^{-1}$. The studies of the ND_3 species (Cd,Cu)$(ND_3)_2Ni(CN)_4 \cdot 2C_6H_6$ will give a decisive conclusion, although the synthesis of the single crystal has not been successful.

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(19) D.M.S. Bagguley and J.H.E. Griffiths, *Proc. Roy. Soc.*, *A65*, 594 (1952).

(20) R.C. Slade, A.A.G. Tomlinson, B.J. Hathaway, and D.E. Biling, *J. Chem. Soc.*, (A), *61* (1968).

(21) W. Hayes and J. Wilkins., *Proc. Roy. Soc.*, *281*, 340 (1964).