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The Metal Ammine Cyanide Aromatics Clathrates. I. The Preparation and Stoichiometry of the Diamminemetal(II) Tetracyanoniccolate(II) Dibenzene and Dianiline*[1]

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Benzene and aniline clathrates of metal-complex host lattices with a general formula of $M(II)(NH_3)_2Ni(CN)_4 \cdot 2G$, in which M(II) was nickel, copper, or cadmium, and G, benzene or aniline as the guest molecule, were prepared. The stoichiometry was established through the analytical data and the structural information obtained from the powder X-ray diffractometric data. They are tetragonal with reasonable lattice parameters except for $Cu(NH_3)_2Ni(CN)_4 \cdot 2C_6H_5NH_2$, which may be estimated to be orthorhombic or monoclinic. The host lattices of all the compounds have almost the same space character. The occupation of divalent metal M(II) at the octahedral site of the metal-complex host lattice was proved through the magnetic data.

A number of clathrate compounds consisting of a metal-complex host lattice have been prepared and described by several authors.1) One of the longest-known compounds is diamminenickel(II) tetracyanoniccolate(II) dibenzene, $Ni(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ ($=Ni(NH_3)(CN)_2 \cdot C_6H_6$),2) prepared in 1897 by Hofmann and Küspert.3) The crystal structure was determined through an X-ray diffraction analysis of a single crystal by Powell and Rayner4) fifty-five years after the first preparation of this compound. The benzene is clathrated among the layers of the polymerized diamminenickel(II) tetracyanoniccolate(II) net plane. There are two kinds of nickel(II) sites in the host lattice of the complex net plane, ones are octahedrally hexacoordinated with four nitrogen atoms of cyanide and with two nitrogen atoms of ammonia, and the others are in square-planar tetracoordination with four carbon atoms of cyanide. The elongated cubic cavity for a guest benzene molecule is surrounded by eight nickel(II) ions. Each of the two diagonal corners in the upper and lower networks is occupied by an octahedral site. The octahedral site in the lower network is just beneath that in the upper network. Aniline, pyrrole, or furan that has a molecular volume less than about 90 can also be enclosed in this cavity.5) An attempt

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[1] Partly read at the Annual Meeting of the Chemical Society of Japan, Yokohama, April, 1966, and at the 9th International Conference on Coordination Chemistry, St. Moritz, September, 1966.

1) *Cf.* reviews: F. Cramer, "Einschlussverbindungen," Springer-Verlag, Berlin-Göttingen-Heidelberg (1954); L. Mandelcorn, *Chem. Revs.*, **59**, 827 (1959); V. M. Bhatnagar, *J. Chem. Educ.*, **40**, 646 (1963); M. Hagan, "Clathrate Inclusion Compounds," Reinhold, New York (1962).

2) In the original paper, this "monomeric" formula had been adopted. However, from the structure clarified, the "dimeric" formula seems proper and so has been adopted in this paper.

3) K. A. Hofmann and F. Z. Küspert, *Z. anorg. Chem.*, **15**, 204 (1897).

4) H. M. Powell and J. H. Rayner, *Nature*, **163**, 566 (1949); J. H. Rayner and H. M. Powell *J. Chem. Soc.*, **1952**, 319.

5) K. A. Hofmann and H. Arnoldi, *Ber.*, **39**, 339 (1906).

to replace the octahedral nickel(II) with another divalent metal ion, copper, zinc,*2 or cadmium, was made by Baur and Schwarzenbach.6) The compounds prepared by them were, however, "aromatics deficient" with a general formula of $M(II)(NH_3)_2Ni(CN)_4\cdot nC_6H_6$, in which n was 3/2 for cadmium and 1 for copper as M(II). Moreover, they showed no physical proof of the replacement. Hofmann and Arnoldi5) also reported an aromatics deficient compound of thiophene, $Ni(NH_3)_2$-$Ni(CN)_4\cdot \frac{3}{2}C_4H_4S$. If these deficient numbers of aromatic molecules have correctly denoted the chemical state of these compounds, they should express the difference in interaction between the respective metal-complex host lattice and the respective guest molecule, and should refer to the space character of these host lattices. If these host lattices have an analogous space character, the numbers may substantially be 2 with each cavity containing a guest molecule.

In Part I of this series, the present authors dealt with the preparative study, magnetic susceptibility measurement, and powder X-ray diffractometry of the $M(II)(NH_3)_2Ni(CN)_4\cdot 2G$-type clathrates, in which M(II) was nickel, copper, or cadmium, and G was benzene or aniline. The stoichiometric number 2 was established by a study of all the compounds prepared through the chemical analyses, the replacement of the octahedral site with M(II) was established by the data of magnetic susceptibility, and almost the same space character of the host lattices of these compounds was estimated through the powder X-ray diffractometry.

Experimental

Reagents. *Nickel Chloride.* Commercially-available nickel chloride of G. R. grade was dissolved in 9 N hydrochloric acid, and the solution was passed through an anion-exchange resin column (Diaion SA♯100, Cl-form) in order to eliminate cobalt, iron, or other impurities. The evaporation of the effluent gave crystals of nickel chloride hexahydrate.

Copper Sulfate. G. R. grade copper sulfate pentahydrate was purified through recrystallization.

TABLE 1. THE ANALYTICAL DATA, EFFECTIVE MAGNETIC MOMENTS AND APPEARANCES OF CLATHRATES PREPARED

Compound*	Analytical results Found/(Calcd.), %					χ_g $\times 10^6$	μ_{eff} B. M.	Color
	C	H	N	Ni	M(II)			
Ni-Ni-Bz $C_{16}H_{18}N_6Ni_2$	46.2 (46.7)	4.4 (4.4)	19.8 (20.4)	28.2 (28.5)		10.19	3.20	Pale violet
Ni-Ni-An $C_{16}H_{20}N_8Ni_2$	43.7 (43.5)	4.6 (4.6)	25.5 (25.4)	26.3 (26.6)		10.71	3.40	Pale violet
Cd-Ni-Bz $C_{16}H_{18}N_6NiCd$	39.7 (41.3)	4.1 (3.9)	17.9 (18.1)	12.7 (12.6)	24.6 (24.2)	−0.5	Diamag.	Light yellow
Cd-Ni-An $C_{16}H_{20}N_8NiCd$	38.8 (38.8)	3.9 (4.2)	22.6 (22.6)	12.0 (11.9)	23.4 (22.7)	−0.5	Diamag.	Light yellow
Cu-Ni-Bz $C_{16}H_{18}N_6NiCu$	44.6 (46.1)	4.1 (4.4)	19.7 (20.2)	14.1 (14.1)	15.3 (15.3)	3.43	1.97	Grayish pale green
Cu-Ni-An $C_{16}H_{20}N_8NiCu$	41.8 (43.0)	4.6 (4.5)	24.5 (25.1)	13.9 (13.2)	15.1 (14.2)	3.19	1.98	Dark green

* The abbreviation is illustrated in the text.

TABLE 2. THE OPTIMUM pH RANGE FOR THE FORMATION OF CLATHRATES AND pH VALUES BEFORE AND AFTER THE PRECIPITATION

Host	Guest		$p[NH_3]$ of $M(NH_3)_2{}^{2+}$ *	Example of pH change in the precipitation of benzene clathrate	
	Benzene	Aniline		Before	After
Cu-Ni	6.6— 9.2	7.5— 9.9	3.4	7.6	8.6
Ni-Ni	9.0—11.0	9.0—11.0	2.0	9.5	10.3
Cd-Ni	9.8—11.2	10.0—12.3	1.7	9.2	10.0

* The values where the diamminemetal(II) ions exist as being in the greatest existing ratio were taken from a figure on J. Bjerrum, " Metal Ammine Eormation in Aqueous Solution," P. Haase & Son, Copenhagen (1957), p. 287.

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*2 The zinc compound reported was benzene- and ammonia-deficient $ZnNi(CN)_4\cdot \frac{1}{2}C_6H_6$. Recently the present authors, however, could prepare a stoichiometric clathrate, $Zn(NH_3)_2Ni(CN)_4\cdot 2C_6H_6$. The results will be reported in detail (Ref. 7 and T. Nakano, T. Miyoshi and Y. Sasaki, This Bulletin, **40**, 1297 (1967)).

6) R. Baur and G. Schwarzenbach, *Helv. Chim. Acta*, **43**, 842 (1960).

Cadmium Chloride. G. R. grade cadmium chloride hydrate, $CdCl_2 \cdot 5/2H_2O$ (Wako Pure Chemicals), was used without further purification.

Potassium Tetracyanoniccolate. This was prepared with the purified nickel chloride and potassium cyanide of G. R. grade (Wako Pure Chemicals).

Aniline. This was distilled prior to use.

The other chemicals used were of G. R. grade and were employed without further purification.

Preparations. By Baur-Schwarzenbach method9) modified as will be described below, the six clathrate compounds shown in Table 1 were prepared. To an ammoniacal metal(II) salt solution the equivalent amount of an aqueous potassium tetracyanoniccolate solution was added. The mixture was then cooled in an iced water bath and titrated with 6 N hydrochloric acid to the appropriate pH value. The value for each metal-aromatics system is shown in Table 2. Then an excess of benzene or an equivalent amount of aniline was added, and the resultant mixture was stirred vigorously with a magnetic stirrer fo 1/2—1 hr. The precipitates thus formed were filtered out with a glass filter and washed with ethanol and ether successively. This filtering and washing procedure was done as quickly as possible. The product was dried in a desiccator over calcium chloride, in which the atmosphere had been saturated with benzene or aniline vapor. The carbon, hydrogen, and nitrogen contents were determined through elementary analyses, while the metal contents were established through EDTA chelatometry. The presence of ammonia, cyanide, and benzene or aniline was checked on the infrared spectra.7) The analytical results and the appearances of the products are tabulated in Table 1 together with the data of magnetic susceptibility.

Magnetic Susceptibility. The volume susceptibilites of the powdered samples were measured with a Gouy balance at room temperature. From the values of the volume susceptibility, the effective magnetic moment of the divalent metal ion at the octachedral site was calculated. Cobalt(II) mercury(II) tetrathiocyanate was used as a standard paramagnetic substance ($\chi_g = 16.44 \times 10^{-6}$).8)

Powder X-Ray Diffractometry. The powder X-ray diffraction pattern was recorded with a Rigaku Denki X-ray diffractometer; CuK_α radiation with a nickel filter was employed.

Results and Discussion

Preparation and Stoichiometry. The formation of these clathrates can be described as follows:

$$M(NH_3)_2{}^{2+} + Ni(CN)_4{}^{2-} + 2G = M(NH_3)_2Ni(CN)_4 \cdot 2G \qquad (1)$$

$$M(NH_3)_n{}^{2+} \xrightarrow{+H^+} M(NH_3)_2{}^{2+} + (n-2)NH_3 \qquad (2)$$

In an ammoniacal solution of the M(II) salt, the dominant species of M(II) is $M(NH_3)_n{}^{2+}$, where n is larger than 2, perhaps 4 to 6. The addition of acid in Reaction (2) causes the equilibrium concentration of $M(NH_3)_2{}^{2+}$ to increase; thus Reaction (1) goes forward to precipitate the clathrate. The precipitation causes an increase in pH as a result of the release of ammonia in Reaction (2). In Table 2, the pH values before and after the precipitation for each clathrate are shown. The increase in pH value after the precipitation was clearly observed. The order of the optimum regions of pH where the precipitation occurred

TABLE 3. POWDER X-RAY DATA

Ni-Ni-Bz
$a=7.24$, $c=8.28$

theta	$d_{obs.}$	(hkl)	$d_{calcd.}$
5°20′	8.29	001 vs	8.28
8°42′	5.10	110 w	5.12
10°12′	4.35	111 vs	4.35
10°43′	4.15	002 vs	4.14
12°20′	3.61	200 s	3.62
13°48′	3.23	210 s	3.24
14°47′	3.02	211 vw	3.02
16°09′	2.77	003 s	2.76
17°33′	2.56	220 m	2.56
18°23′	2.44	221 m	2.45
20°30′	2.20	311 w	2.21
21°48′	2.08	004 vw	2.07
22°39′	2.00	312 vw	2.00
23°36′	1.93	114 m	1.92
24°15′	1.88	223 w	1.88

Ni-Ni-An
$a=7.29$, $c=9.33$

theta	$d_{obs.}$	(hkl)	$d_{calcd.}$
4°42′	9.41	001 s	9.33
9°30′	4.67	002 s	4.67
9°50′	4.51	111 vs	4.51
12°14′	3.64	200 s	3.65
12°54′	3.45	201 m	3.40
13°42′	3.26	210 m	3.26
14°24′	3.10	003 s	3.11
16°51′	2.66	212 w	2.67
17°30′	2.56	220 s	2.58
18°09′	2.47	221 m	2.49
19°24′	2.32	004 vw	2.33
19°37′	2.30	310 w	2.31
20°12′	2.23	311 w	2.24
21°21′	2.12	114 vw	2.13
22°00′	2.06	312 vw	2.07
23°00′	1.97	321 vw	1.98

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7) T. Miyoshi, T. Iwamoto and Y. Sasaki *Inorg. Chim. Acta*, **1**, (1967).

8) J. Lewis and R. G. Wilkins, eds., "Modern Coordination Chemistry," Chap. 6, Intersience Pub., New York (1960).

TABLE 3 (Continued)

Cd-Ni-Bz
$a=7.64$, $c=8.37$

theta	$d_{\text{obs.}}$	(hkl)	$d_{\text{calcd.}}$
5°16′	8.40	001 vs	8.37
5°43′	7.74	100 w	7.64
7°50′	5.66	101 w	5.64
8°11′	5.42	110 w	5.40
9°47′	4.54	111 s	4.54
10°37′	4.18	002 s	4.20
11°40′	3.81	200 w	3.82
13°07′	3.40	120 w	3.41
13°31′	3.30	112 m	3.31
16°05′	2.78	003 s	2.79
16°41′	2.69	220 w	2.70
17°34′	2.55	221 m	2.57
18°11′	2.47	113 m	2.48
19°32′	2.31	131 w	2.32
19°59′	2.26	222 w	2.27
20°03′	2.25	132 w	2.24
21°41′	2.09	004 m	2.09
23°32′	1.94	114 m	1.95

Cd-Ni-An
$a=7.56$, $c=8.66$

theta	$d_{\text{obs.}}$	(hkl)	$d_{\text{calcd.}}$
5°06′	8.67	001 s	8.66
5°51′	7.56	100 w	7.56
7°47′	5.70	101 w	5.70
8°15′	5.37	110 w	5.35
9°30′	4.67	111? s	4.55
9°59′	4.46	111? s	
10°15′	4.33	002 s	4.33
11°42′	3.80	200 m	3.78
12°54′	3.45	201 w	3.46
13°09′	3.39	120 w	3.38
13°33′	3.29	112 w	3.37
15°30′	2.88	003 s	2.89
16°39′	2.69	220 m	2.68
17°12′	2.61	221 w	2.56
17°45′	2.53	300 w	2.52
19°03′	2.36	310 vw	2.39
20°51′	2.17	004 w	2.17
22°09′	2.04	321 w	2.04
22°24′	2.02	114 w	2.01
23°02′	1.97	223 w	1.96
26°27′	1.73	402 w	1.73

Cu-Ni-Bz
$a=7.39$, $c=8.24$

theta	$d_{\text{obs.}}$	(hkl)	$d_{\text{calcd.}}$
5°22′	8.24	001 vs	8.24
8°30′	5.22	110 m	5.22
10°02′	4.43	111 vs	4.41
10°47′	4.12	002 vs	4.12
12°03′	3.69	200 s	3.69
12°23′	3.60	102 m	3.60
13°30′	3.30	210 w	3.30
13°46′	3.24	112 s	3.24
16°18′	2.75	003 s	2.75
17°09′	2.61	220 m	2.61
18°02′	2.49	221 m	2.49
20°00′	2.25	311 vw	2.43
20°28′	2.21	222 w	2.20
22°00′	2.06	004 vw	2.06
22°17′	2.03	312 vw	2.03
23°44′	1.92	114 m	1.92

Cu-Ni-An
$a=7.27$, $b=6.84$, $c=8.81$; orthorhomic or $a=7.32$
$c=8.81$, $\gamma=94°30'$; monoclinic*

theta	$d_{\text{obs.}}$	(hkl)	$d_{\text{calcd.}}$	(hkl)*	$d_{\text{calcd.}}$*
5°02′	8.79 vs	001	8.81	001	8.81
8°55′	4.97 m	110	4.98	110	4.97
10°03′	4.42 vs	002	4.41	002	4.41
10°18′	4.31 s	111	4.34	111	4.33
10°48′	4.11 w	?	?	?	?
11°50′	3.76 w	102	3.77	102	3.77
11°59′	3.71 w	012	3.70	?	?
12°08′	3.67 w	200	3.63	200	3.65
13°09′	3.39 w	020	3.42	201	3.37
13°44′	3.25 w	210	3.21	112	3.30
14°42′	3.04 vw	120	3.09	211	2.98
15°12′	2.94 s	003	2.94	003	2.94
16°18′	2.75 w	103	2.70	202	2.81
17°48′	2.52 w	113	2.53	113	2.53
20°29′	2.20 m	004	2.20	004	2.20
21°04′	2.15 vw	222	2.17	213	2.15

almost quantitatively and in a pure state was in good agreement with that of the pH where the corresponding diamminemetal(II) complex ions are present in the greatest ratio.9) The benzene clathrates obtained were stable in a closed vessel, but unstable in an open atmosphere. The benzene clathrates have benzene vapor pressures in the order of 10^{0--2} mmHg.6,10) A zeroth-order kinetics had been suggested for the escape reaction of the benzene from the clathrate.11) The aniline clathrates were considerably stable in an open atmosphere. The careful treatment of the benzene clathrates during the filtering and washing procedure and storage under proper conditions brought good analytical results, which ascertained the number of the guest molecules to be 2. The formerly-reported values 3/2 and 1 by Baur and Schwarzenbach6) might arise from the partial escape of benzene from the clathrates that have substantially the

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9) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Hasae & Son, Copenhagen (1957).

10) T. Miyamoto, T. Iwamoto, Y. Sasaki and S. Fujiwara, to be published.

11) E. E. Aynsley, W. A. Campbell and R. E. Dodd, *Proc. Chem. Soc.*, **1957**, 210.

number of 2 for the guest molecule. The aniline clathrates had the same number, also. This suggested that these metal-complex host lattices have a similar space character.

Among the compounds dealt with here, diamminecadmium and diamminecopper tetracyanoniccolate dianilines are the new compounds.

Replacement of the Octahedral Site with the Divalent Metals. From the observed volume susceptibilities and chemical formulae determined through the chemical analyses, the gram susceptibilities and molecular susceptibilities, χ_m, were calculated. The diamagnetic correction for the constituent atoms and structural factors was made. Effective magnetic moments, μ_{eff}, were claculated according to the following equation:

$$\mu_{eff} = 2.83\sqrt{\chi_m T}$$

The results in Table 1 show the experimentally-obtained μ_{eff} values agreeing well with those commonly found among these M(II) complexes. The values for two diamminenickel(II) tetracyanoniccolate(II) diaromatics (abbreviated hereafter as Ni-Ni-Arm) coincided moderately with the recalculated values of those reported by Kubo and Kondo[12] and by Cambi *et al.*[13] respectively. They had described the moments of 2.24[*3] for Ni-Ni-Bz and of 2.28 for Ni-Ni-An, regarding these clathrates as containing only one kind of nickel(II), although the former authors concluded that the apparently anomalous value was due to the structural dissimilarity of nickel(II) ions. The diamagnetism of the two Cd-Ni-Arm's showed that the octahedral site was just replaced with cadmium(II) in these compounds. The values for Cu-Ni-Arm's also supported the identical replacement with copper(II).

Structural Similarity. The powder X-ray diffraction data of Ni-Ni-Bz consistently made it clear that it is tetragonal and has the parameter $a=7.24$ and $c=8.28$, as had been determined by Powell and Rayner.[4] As for the Ni-Ni-An, although they had reported only the parameter $c=9.29\pm 0.05$, the present data showed this compound to belong to the tetragonal system and to have the parameters $a=7.29$ and $c=9.33$, values which were in good agreement with their information. The Cd-Ni-Arm data fitted the pattern of the tetragonal system well, and from the graphically-assumed axial ratios, the lattice paramters were calculated. Cu-Ni-Bz was also identified as belonging to the tetragonal system, and the lattice parameters were calculated similarly; these paramters are shown in Table 3.

Cu-Ni-An could not, however, be identified as belonging to the tetragonal system. Its powder pattern might be attributed to either the orthorhombic or the monoclinic system. The assumed lattice parameters were calculated for both the systems. In any case with these values it was reasonable for this compound to have space character analogous to the others. Of course, including Cu-Ni-An, the precise structures of all of them except Ni-Ni-Bz must be discussed on the base of the single crystal diffraction data, but we can estimate to a certain degree the similarity in structure among them from these powder pattern analyses. Their densities measured in xylene pycnometrically, gave values between *ca.* 1.4 and 1.7, values which corresponded with Z being 1 in the unit cell volumes calculated from these lattice paramters for the chemical formula of $M(II)(NH_3)_2Ni(CN)_4 \cdot 2G$.

Considering the cavity for a guest molecule made by these parameters, it was obvious that the cavity for aniline is larger than that for benzene in each M(II)-Ni-Arm system. The a values showed slight differences due to differences among the ionic radii of the respective M(II) ions. In Cd-Ni-Arm's, the difference in c's was rather small compared with those in the others. As cadmium, situated in the fifth row of the periodic table, has a considerable polarizing power, it would contribute to the interaction of the host lattice and the guest molecule.

Thanks are due to Professor Yukichi Yoshino of the College of General Education for his kind permission to use the Gouy balance.

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[12] M. Kondo and M. Kubo, *J. Phys. Chem.*, **61**, 1648 (1957).

[13] L. Cambi, A. Cagnasso and E. Tremolada, *Gazz. Chim. Ital.*, **64**, 758 (1934).

[*3] The value by Cambi *et al.* was reduced into B. M. units.