The Metal Ammine Cyanide Aromatic Clathrates.
XIII. The Crystal Structure of the Hofmann-type Biphenyl Clathrate,
Diamminenickel(II) Tetracyanonickelate(II) Di-biphenyl: $Ni(NH_3)_2Ni(CN)_4.2C_{12}H_{10}$

By Toschitake Iwamoto,* Tadahiko Miyoshi† and Yukiyoshi Sasaki

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo 113, Japan

The crystal structure of a biphenyl clathrate, $Ni(NH_3)_2Ni(CN)_4.2C_{12}H_{10}$, was determined from three-dimensional data collected by diffractometry. The crystals are tetragonal, space group $I422$, $a = 7\cdot240$ (3) and $c = 25\cdot30$ (1) Å, and $Z = 2$. The structure was refined to an R value of $0\cdot081$ for the 627 observed reflexions. The host lattice has the layer structure of the two-dimensional networks of $[Ni(NH_3)_2Ni(CN)_4]_\infty$, and the guest biphenyl molecules are accommodated between the inorganic layers with their longest axes perpendicular to the layers. The structure is substantially similar to that of the Hofmann-type benzene clathrate, $Ni(NH_3)_2Ni(CN)_4.2C_6H_6$. However, the stacking mode of the inorganic layers is different: each layer is alternately shifted by $(a+b)/2$, thus the c axis is doubled. The two phenyl rings of the biphenyl molecule are twisted with a dihedral angle of $33\cdot2°$. The steric repulsion between the hydrogen atoms at the *ortho* positions in the biphenyl molecule may make the coplanar structure unstable in the present clathrate.

Introduction

In the Hofmann-type clathrate, $M(NH_3)_2M'(CN)_4.2G$, the polymeric, two-dimensional networks of $[M(NH_3)_2M'(CN)_4]_\infty$ are stacked along the c axis of the tetragonal system, and the guest molecules, G, are accommodated in the cavities formed between the layers of the networks (Rayner & Powell, 1952; Iwamoto, Nakano, Moriata, Miyoshi, Miyamoto & Sasaki, 1968; Sasaki, 1969; Miyoshi, Iwamoto & Sasaki, 1973). These cavities are surrounded by the inorganic polymers, and the steric repulsions from the surroundings restrict the shape and the volume of the guest molecule. It was believed that only aromatic molecules with molecular volumes (cm³ mole⁻¹) less than 90 could be enclathrated (Hofmann & Arnoldi, 1906). In fact toluene or xylene, with molecular volumes of 106 or 123 respectively, cannot be the guest species of the Hofmann-type clathrate. However, the clathrate of biphenyl, whose molecular volume is 130, has been reported as an exception (Leicester & Bradley, 1955).

The present paper deals with the crystal structure analysis of the biphenyl clathrate. As the volume of the guest biphenyl is considerably larger than those of the guest molecules in the other Hofmann-type clathrates, an entirely different structure may be expected. Moreover, the molecular structure of biphenyl in the clathrate is of much interest, since the molecular shape of biphenyl varies with the change in its phase: it is planar in the crystalline state (Trotter, 1961; Har-

greaves & Rizvi, 1962), while a dihedral angle of $41\cdot6°$ between two phenyl rings has been observed in the gaseous state (Bastiansen & Trætteberg, 1962).

Experimental

(a) Sample

The single crystals of $Ni(NH_3)_2Ni(CN)_4.2C_{12}H_{10}$ were prepared by contacting a xylene solution of biphenyl with an ammoniacal solution of $NiCl_2$ and $K_2Ni(CN)_4$ in an equimolar ratio for six months. Xylene was chosen as the solvent because it is not trapped in the Hofmann-type host lattice. The pale-violet crystals with tabular shape were grown on the boundary surface of the two solutions. Analysis, found: C, 59·64; H, 4·71; N, 15·05; Ni, 20·9%; calculated for $Ni(NH_3)_2Ni(CN)_4.2C_{12}H_{10}$: C, 59·63; H, 4·65; N, 14·90; Ni, 20·82%. Leicester & Bradley (1955) gave the composition $Ni(NH_3)_2Ni(CN)_4.C_{12}H_{10}$ to their powder product with the following description: 'there appeared to be a tendency, which was specially marked in the diphenyl complex, for the precipitate to hold a small excess of the organic molecules very tenaciously and it was only with difficulty removed by washing'. Their guest-poor composition would have been caused by the imperfect enclathration of the guest biphenyl, or by the inclusion of inorganic impurities. The preparation of the powder samples was repeated in this laboratory by vigorous mixing of the two solutions. The products gave non-stoichiometric composition $Ni(NH_3)_2Ni(CN)_4.nC_{12}H_{10}$ in which n varied between 1 and 2 from sample to sample. The powder diffraction patterns and the infrared spectra of these powder samples showed the same features as those of the single crystals. No evidence was observed for the existence of a $Ni(NH_3)_2Ni(CN)_4.C_{12}H_{10}$ phase.

* Present address: Department of Chemistry, College of General Education, The University of Tokyo, Komaba, Meguro, Tokyo 153, Japan.
† Present address: Hitachi Research Laboratory, Kuji, Hitachi, Ibaraki, Japan.

(b) X-ray structure analysis

The crystal of dimensions, $0.2 \times 0.3 \times 0.4$ mm, was sealed in a thin-walled glass capillary to prevent the escape of biphenyl. Weissenberg photographs were
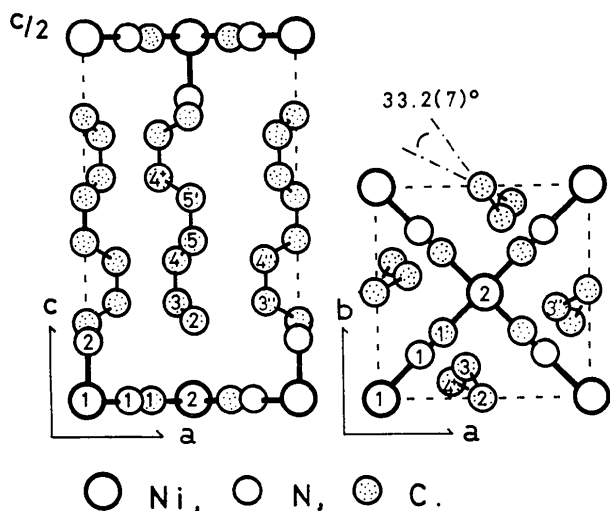

Fig. 1. Projections of the structure along the b and c axes. A half of the unit cell is shown in the b projection.
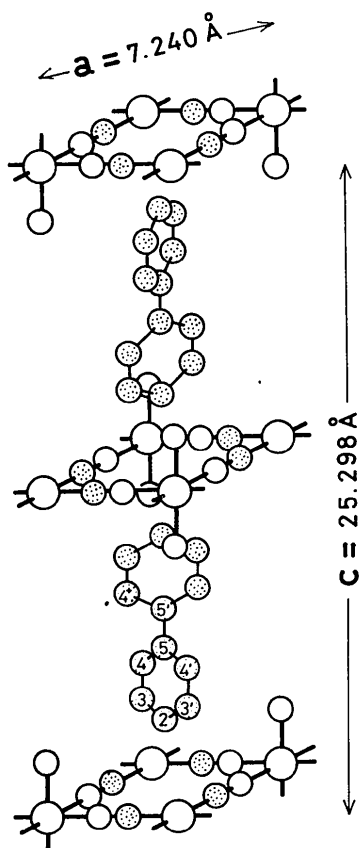

Fig. 2. A perspective drawing of the enclathrated biphenyl molecules. The notation of atoms and the numbering scheme are the same as those in Fig. 1.

taken with Ni-filtered Cu $K\alpha$ radiation about the [001] and the [110] axes. The Laue symmetry was determined to be $4/mmm$. The unit-cell dimensions were obtained by the least-squares method from higher order reflexions recorded on Weissenberg photographs. The density of the crystal was measured by the flotation method in a K_2HgI_4 solution.

Crystal data are:

$Ni(NH_3)_2Ni(CN)_4.2C_{12}H_{10}$, M.W. 564.0.
Tetragonal, $I422$, $a = 7.240$ (3), $c = 25.30$ (1) Å, $Z = 2$.
Systematic absences: hkl; $h + k + l = 2n + 1$.
$D_m = 1.39$, $D_x = 1.41$ g cm^{-3}.
μ(Mo $K\alpha$) $= 14.4$ cm^{-1}.

Intensity data were collected on a Rigaku automated four-circle diffractometer with Mo $K\alpha$ radiation monochromated by LiF crystal ($\lambda_{K\alpha} = 0.7107$ Å). The $2\theta-\omega$ scanning technique was employed. Two standard reflexions were remeasured every 50 reflexions: no significant variation in the intensities was observed. 627 independent reflexions with 2θ less than 60° were observed. The Lp corrections were applied, but no correction for absorption was made.

Structure refinement

The possible space groups are $I4/mmm$, $I4mm$, $I\bar{4}m2$, $I\bar{4}2m$ and $I422$. Since the unit cell contains only two formula units of $Ni(NH_3)_2Ni(CN)_4.2C_{12}H_{10}$, most of the atoms must lie on the special positions. On the tentative assumption of the space group $I4/mmm$, the atomic parameters were deduced by three-dimensional Patterson and Fourier syntheses, and were refined by block-diagonal least-squares calculations. The conventional R index became 0.096 but a poor agreement between the calculated and observed structure factors was recognized in the weak reflexions. Therefore, all the possible space groups were examined. In all cases the structure of the host lattice remained the same from the requirement of the space group and only the conformation and the orientation of the guest molecules were changed according to the space-group symmetry. The R_1 and R_2 values were as follows:

Space group	$I4/mmm$	$I4mm$	$I\bar{4}m2$	$I\bar{4}2m$	$I422$
R_1 for all the reflexions	0.096	0.100	0.097	0.102	0.081
R_1 for the non-zero reflexions	0.080	0.077	0.078	0.079	0.064
R_2	0.102	0.100	0.099	0.097	0.068

Thus the space group $I422$ was adopted as the best of the five.*

All the calculations were carried out with the electronic computer, HITAC 5020E, at the Computation

---

Centre of this University. The programs used were those in UNICS (Crystallographic Society of Japan, 1967). The atomic scattering factors were those listed in *International Tables for X-ray Crystallography* (1962). A weighting scheme, $w = 1$ for $|F_o| > 7.7$ and 0.5 otherwise, was employed.

Description and discussion of the structure

The structure is illustrated in Figs. 1 and 2. The atomic parameters are given in Tables 1 and 2. The bond lengths and the bond angles are listed in Table 3.

Table 1. *Final fractional atomic coordinates and their standard deviations in parentheses* $(\times 10^4)$

	Wyckoff's notation	x/a	y/b	z/c
Ni(1)	a	0	0	0
Ni(2)	b	5000	5000	0
C(1)	g	3154 (8)	3154 (8)	0
N(1)	g	2046 (7)	2046 (7)	0
N(2)	e	0	0	831 (4)
C(2)	f	5000	0	1087 (4)
C(3)	k	4221 (14)	1456 (15)	1361 (3)
C(4)	k	4206 (13)	1470 (14)	1928 (3)
C(5)	f	5000	0	2207 (3)

Table 2. *Final thermal parameters, with their standard deviations in parentheses*

The values of B_{ij} have been multiplied by 10^4 and refer to the expression:

$$\exp \left\{ -(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl) \right\}.$$

	B_{11}	B_{22}	B_{33}	$B_{ij} (i \neq j)$
Ni(1)	39 (3)	39 (3)	14 (0)	0
Ni(2)	32 (3)	32 (3)	12 (0)	0

	$B(\times 10^2)$ (isotropic)
C(1)	211 (12) Å^2
N(1)	247 (12)
N(2)	274 (19)
C(2)	404 (18)
C(3)	434 (19)
C(4)	399 (18)
C(5)	304 (14)

As may be seen in Figs. 1 and 2, the host lattice is built up of inorganic networks, between which the guest biphenyl molecules are trapped. There are two kinds of nickel atoms in the networks; one is coordinated nearly octahedrally with the six nitrogen atoms of two ammonia molecules and four cyanide anions, and the other has a square-planar coordination with four carbon atoms of the cyanide anions. Both kinds of nickel atoms are linked by the cyanide anions alternately in the network, and the two ammonia molecules, coordinating to the octahedral nickel atom in *trans* positions, stick out on both sides of the plane. This network is quite similar to that observed in Hofmann's benzene clathrate (Rayner & Powell, 1952): its a dimension, 7.242 (7) Å, is almost the same as that of the present clathrate, 7.240 (3) Å. However, there are some differences in the atomic distances between the benzene

Table 3. *Interatomic distances less than 4 Å and bond angles*

Ni(1)–N(1)	2·095 (5) Å	C(2)–C(1)	3·815 (8) Å
Ni(1)–N(2)	2·103 (11)	C(2)–N(1)	3·785 (8)
Ni(2)–C(1)	1·890 (6)	C(2)–N(2)	3·677 (3)
C(1)–N(1)	1·135 (8)	C(3)–C(1)	3·736 (9)
C(2)–C(3)	1·382 (11)	C(3)–N(1)	3·810 (9)
C(3)–C(4)	1·436 (11)	C(3)–N(2)	3·499 (11)
C(4)–C(5)	1·401 (10)	C(3)–C(3″)	3·716 (15)
C(5)–C(5′)	1·480 (16)	C(4)–C(3″)	3·987 (14)
		C(4)–C(4″)	3·705 (14)

C(3)–C(2)–C(3′)	119·7 (9)°
C(2)–C(3)–C(4)	120·7 (9)
C(3)–C(4)–C(5)	119·7 (8)
C(4)–C(5)–C(5′)	120·3 (5)
C(4)–C(5)–C(4′)	119·5 (8)

Key to symmetry operations: C(3) at (x,y,z), C(3′) at $(\bar{x},\bar{y},z)$ and C(3″) at $(\bar{y},x,z)$; C(4) at (x,y,z), C(4′) at $(\bar{x},\bar{y},z)$ and C(4″) at $(\bar{y},x,z)$; C(5) at $(\frac{1}{2},0,z)$ and C(5′) at $(\frac{1}{2},0,\frac{1}{2}-z)$.

and the biphenyl clathrates. The octahedral Ni coordination is almost regular in the biphenyl clathrate with the Ni–N(1) distances of 2.095 (5) Å and with Ni–N(2) of 2.10 (1) Å, while that in the benzene clathrate appears to be compressed along the N(2)–Ni–N(2′) axis with Ni–N(1) and Ni–N(2) distances of 2.15 (3) and 2.06 (?) Å respectively.

The biphenyl molecule is trapped with its longest axis vertical to the network. The interatomic distances between the networks and the guest biphenyl, and those between the guest molecules are 3.5 Å or more. These values support the supposition that the biphenyl molecules have no direct bonding either to the host lattice or to each other. The environment of each phenyl ring of the biphenyl molecule resembles that of the benzene molecule in the benzene clathrate.

The c dimension of the biphenyl clathrate, 25.30 (1) Å, is much longer than that of the benzene clathrate, 8.277 (8) Å, even if the size of the biphenyl molecule is taken into account. Another contribution to the increase in the c dimension is the alternate stacking of the metal complex layers accompanied with the shift of $(a+b)/2$. The shift alleviates the steric repulsion between the ammonia molecules of the host lattice and the guest molecule, in which two phenyl rings are twisted about the C(5)–C(5′) bond. If the shift does not occur, the shortest distance between the nitrogen atom of the ammonia and the carbon atom of the biphenyl becomes as short as 2.9 Å. The alternate shift of the metal complex layers makes the hexa-coordinated and the tetra-coordinated nickel atoms line up alternately along the c axis, while in the benzene clathrate the nickel atoms in one kind of coordination line up along the axis. This represents a remarkable difference between the structures of the biphenyl and the benzene clathrates. The c dimension of about 13 Å reported previously for the powder sample (Leicester, Bradley & Burr, 1962) appears to have been caused by the systematic absences of the 00l reflexions with odd l.

The variation of the distance between the adjacent metal-complex layers upon replacing the guest species

Table 4. *The structure of the biphenyl molecule in various phases*

	Biphenyl molecule			
	in a clathrate	in its crystalline state		gas phase
	(Present study)	(Trotter, 1961)	(Hargreaves & Rizvi, 1962)	(Almenningen & Bastiansen, 1958)
C(2)–C(3)	1·382 (11) Å	1·376 (16) Å	1·361 (12) Å	
C(3)–C(4)	1·436 (11)	1·416 (16)	1·421 (9)	
C(4)–C(5)	1·401 (10)	1·372 (16)	1·383 (12)	
C(5)–C(5')	1·480 (16)	1·507 (32)	1·506 (17)	1·4890 (75) Å
C(3)–C(2)–C(3')	119·7 (9)°	118·9°	121·4°	
C(2)–C(3)–C(4)	120·7 (9)	120·4	119·4	
C(3)–C(4)–C(5)	119·7 (8)	120·7	120·5	
C(4)–C(5)–C(4')	119·5 (8)	118·9	118·8	
C(4)–C(5)–C(5')	120·3 (5)	120·6	120·6	
Dihedral angle	33·2 (7)	0·0	0·0	41·6°

is also observed in the other Hofmann-type clathrate (Iwamoto *et al.*, 1968). The smaller the size of the guest molecule, the shorter becomes the interlayer separation, which was denoted as c in the cited reference. The values of c decrease in the order of the guest molecule from aniline, benzene, thiophene to pyrrole. This behaviour resembles that observed for the series of quinol clathrates, the lattice constants of which show a certain dependency upon the shape and size of the guest molecules. The range of variation is so wide for the Hofmann-type clathrates that the longest distance between the layers is 12·65 Å in the biphenyl clathrate and the shortest is 7·98 Å in the pyrrole clathrate $Ni(NH_3)_2Ni(CN)_4 . 2C_4H_4NH$. The fact that the toluene and xylene molecules cannot be accommodated in the Hofmann-type host lattice may be due to their shapes with the bulky methyl groups, although their molecular sizes along the aromatic plane are in between those of biphenyl and aniline molecules.

The bond lengths and the bond angles of the enclosed biphenyl molecule are compared with those in its crystalline and gaseous state in Table 4. The crystalline biphenyl has a planar structure (Trotter, 1961; Hargreaves & Rizvi, 1962), while in its vapour phase the molecule is twisted with a dihedral angle of 41·6° and the two phenyl rings oscillate with a rather large amplitude (Bastiansen & Trætteberg, 1962; Almenningen & Bastiansen, 1958). Calculation of the energy of the biphenyl molecule shows that the twisted structure is more stable than the planar structure in the crystal (Casalone, Mariani, Mugnoli & Simonetta, 1968). In the present clathrate, the structure of the biphenyl is twisted with a dihedral angle of 33·2°. As far as the intermolecular forces are concerned, the planar structure would be as preferable as the twisted structure in the clathrate, if the inorganic layers of the host lattice stack without the $(a+b)/2$ shift. The steric repulsion between the hydrogen atoms at the *ortho* positions of the biphenyl molecule, therefore, may make the planar structure unstable, as in the case of gaseous biphenyl (Casalone *et al.*, 1968). As for the biphenyl molecule, this may be the first observation of the non-planar structure in the solid phase.

Finally, a few words on the observed diffuse scattering: Diffuse streaks, elongated along the c^* axis with weak intensities, appeared besides the Bragg reflexions on the Weissenberg photographs with their peaks at the reciprocal-lattice points. This diffuse scattering is considered to be caused by some kind of stacking disorder in the host lattice and/or some kind of disorder in the orientation of the guest biphenyl molecules. In this paper, however, we have determined the crystal structure on the basis of the Bragg reflexions, ignoring the randomness in the structure.

References

ALMENNINGEN, A. & BASTIANSEN, O. (1958). *Kgl. Norske Videnskab. Selskabs.* No. 4, 1–16.
BASTIANSEN, O. & TRÆTTEBERG, M. (1962). *Tetrahedron,* 17, 147–154.
CASALONE, G., MARIANI, D., MUGNOLI, A. & SIMONETTA, M. (1968). *Mol. Phys.* 15, 339–348.
CRYSTALLOGRAPHIC SOCIETY OF JAPAN (1967). 5020 UNICS: The Universal Crystallographic Computation Program System.
HARGREAVES, A. & RIZVI, S. H. (1962). *Acta Cryst.* 15, 365–373.
HOFMANN, K. A. & ARNOLDI, H. (1906). *Ber. dtsch. Chem. Ges.* 39, 339–344.
International Tables for X-ray Crystallography (1962). Vol. III, pp. 202–209. Birmingham: Kynoch Press.
IWAMOTO, T., NAKANO, T., MORITA, M., MIYOSHI, T., MIYAMOTO, M. & SASAKI, Y. (1968). *Inorg. Chim. Acta,* 2, 313–316.
LEICESTER, J. & BRADLEY, J. K. (1955). *Chem. Ind.* p. 1449.
LEICESTER, J., BRADLEY, J. K. & BURR, R. G. (1962). *Chem. Ind.* p. 208.
MIYOSHI, T., IWAMOTO, T. & SASAKI, Y. (1973). *Inorg. Chim. Acta,* 7, 97–101.
RAYNER, J. H. & POWELL, H. M. (1952). *J. Chem. Soc.* pp. 319–328.
SASAKI, Y. (1969). *Bull. Chem. Soc. Japan,* 42, 2412.
TROTTER, J. (1961). *Acta Cryst.* 14, 1135–1140.