A packing diagram for (II), which illustrates the $BF_4^-\cdots$ cation approaches, is shown in Fig. 4. The only intermolecular contacts less than the van der Waals limit are F···H (2·55 Å; Pauling, 1960) interactions, ranging from 2·20–2·50 Å. Many of the F···H contacts occur in pairs, involving F atoms from both tetrahedra in the disordered BF_8 moieties. The similarities between the two sets of contacts probably favor the BF_4 disorder.

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The Crystal Structure of a Hofmann-type Clathrate, $Mn(NH_3)_2Ni(CN)_4.2C_6H_6$

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The crystal structure of a clathrate compound, $Mn(NH_3)_2Ni(CN)_4.2C_6H_6$, has been determined from three-dimensional X-ray data collected by diffractometry. The crystals are tetragonal, space group $P4/m$, $Z=1$, with the cell constants: $a=7·432$ (6) and $c=8·335$ (5) Å. The structure was refined by the block-diagonal least-squares method to give an R value of 0·060 for 824 observed reflexions. The host lattice is isostructural with other Hofmann-type clathrates; however, the benzene molecules are disordered, taking two alternative orientations. The population of the two orientations depends on the conditions of crystal growing, taking different values from crystal to crystal.

Introduction

Among a series of Hofmann-type clathrates $M(NH_3)_2Ni(CN)_4.2C_6H_6$, hereafter abbreviated to M–Ni–Bz, crystal structures of Ni–Ni–Bz, Cd–Ni–Bz and Cu–Ni–Bz have been determined by single-crystal X-ray diffraction (Rayner & Powell, 1952; Miyoshi, Iwamoto & Sasaki, 1973; Sasaki, 1969). The three compounds have isostructural host lattices. The last compound possesses a superstructure and the c axis is doubled owing to the different arrangement of the guest molecules. The present compound, Mn–Ni–Bz, has been subjected to X-ray crystal analysis in order to study the effect of the replacement of the atom M by Mn on the mode of clathration.

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Experimental

Crystals of Mn–Ni–Bz were obtained on standing an ammoniacal aqueous solution containing an equimolar mixture of manganese(II) chloride and potassium tetracyanonickelate(II) in contact with a layer of benzene for a month under a nitrogen atmosphere (Iwamoto, Nakano, Morita, Miyoshi, Miyamoto & Sasaki, 1968). The bright-yellow crystals grown at the interface between the aqueous and organic phases are tabular. The density of the crystals was measured by the flotation method employing potassium tetraiodomercurate(II) solution. Accurate measurement was not possible owing to the easy escape of benzene vapour from the specimen. In order to prevent the crystal deteriorating, it was sealed in a glass capillary with benzene vapour. Both precession and Weissenberg photographs taken about the [110] axis with Mo $K\alpha$ and Cu $K\alpha$ radiations respectively showed the Laue symmetry $4/m$. The unit-cell dimensions were determined from higher-order reflexions recorded on the zero-layer Weissenberg photographs by the least-squares method ($\lambda = 1{\cdot}5418$ Å).

Crystal data are: $Mn(NH_3)_2Ni(CN)_4.2C_6H_6$; F.W. 408·01; tetragonal, $a = 7{\cdot}432$ (6), $c = 8{\cdot}335$ (5) Å, $U = 460{\cdot}4$ Å^3; $D_m = 1{\cdot}48$, $D_x = 1{\cdot}50$ g cm^{-3}, $Z = 1$. Space group $P4/m$, $P\bar{4}$ or $P4$. Linear absorption coefficient $\mu = 17{\cdot}6$ cm^{-1} (Mo $K\alpha$).

Intensities of 824 independent reflexions up to $2\theta = 60°$ were measured on a Rigaku automated four-circle diffractometer. Mo $K\alpha$ radiation monochromated by a LiF crystal was used ($\lambda = 0{\cdot}7107$ Å). A crystal of dimensions $0{\cdot}2 \times 0{\cdot}2 \times 0{\cdot}1$ mm was mounted with the c axis approximately parallel to the φ axis of the diffractometer. The ω–2θ scan technique was employed. A set of standard reflexions was measured every 50 reflexions during the data collection to check the electronic stability of the instrument and to check for any deterioration of the crystal. The intensities were converted to $|F_o|$'s by applying the Lorentz and polarization corrections. No absorption correction was made.

Determination of the structure

Since no systematic absence was observed, the space group was tentatively assumed to be $P4/m$. This was verified at a later stage by calculation of structure amplitudes.

The coordinates of the manganese and nickel atoms were deduced from the Patterson maps. A three-dimensional Fourier map calculated with phases based on these atoms revealed the positions of all the non-hydrogen atoms in the unit cell. Several cycles of block-diagonal least-squares refinement were carried out with anisotropic temperature factors for the non-hydrogen atoms. The R index became 0·10. The atomic scatter-

Table 1. *Atomic parameters*

Positional and thermal parameters foı the non-hydrogen atoms (× 10^4), with e.s.d.'s in parentheses. The β_{ij}'s are defined by: $\exp\,[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mn	0	0	0	41 (2)	41 (2)	125 (3)	0	0	0
Ni	5000	5000	0	36 (2)	36 (2)	105 (2)	0	0	0
N(1)	2135 (8)	2133 (8)	0	75 (8)	95 (9)	167 (10)	−38 (15)	0	0
N(2)	0	0	2725 (14)	129 (16)	129 (16)	155 (16)	0	0	0
C(1)	3223 (7)	3215 (7)	0	61 (8)	61 (8)	134 (10)	−16 (14)	0	0
C(2)	5000	0	3331 (14)	189 (17)	278 (24)	152 (15)	128 (33)	0	0
C(3)*A*	5670 (14)	1474 (14)	4158 (16)	143 (16)	150 (17)	207 (20)	−25 (30)	52 (32)	36 (32)
C(3)*B*	4353 (28)	1523 (26)	4120 (30)	315 (43)	259 (37)	176 (33)	−293 (70)	−18 (65)	7 (61)

Table 2. *Interatomic distances and bond angles with their estimated standard deviations in parentheses*

Mn····N(2)		2·27 (1) Å	Mn····N(1)		2·243 (6) Å
Ni·····C(1)		1·871 (5)	C(1)···N(1)		1·141 (8)
C(2)···C(3)	*A*	1·39 (1)	C(3)···C(3^{i})	*A*	1·39 (2)
	B	1·39 (2)		*B*	1·40 (2)
N(1)···C(2)		3·841 (9)	N(2)···C(2)		3·750 (2)
N(2)···C(3)	*A*	3·60 (1)	N(1)···C(3)	*A*	3·86 (1)
	B	3·62 (2)		*B*	3·84 (2)
C(1)···C(3)	*A*	3·78 (1)			
	B	3·75 (2)			
Mn····N(1)–C(1)		179·9 (4)°	Ni·····C(1)–N(1)		179·7 (6)°
C(3)—–C(2)–C(3^{ii})	*A*	120·3 (9)	C(2)—–C(3)–C(3^{i})	*A*	119·8 (6)
	B	123·8 (6)		*B*	122·6 (6)

The labelling scheme for symmetry-related atoms is as follows:

Coordinates	Superscript
x, y, z	None
$x, y, 1-z$	i
$1-x, y, z$	ii

ing factors were taken from *International Tables for X-ray Crystallography* (1962). The weighting scheme employed was: $\omega = 0$ for $|F_o| \leq 3\sigma$ (σ = standard deviation), $\omega = 1{\cdot}0$ for $7{\cdot}82 \leq |F_o| \leq 39{\cdot}24$, $\omega = (39{\cdot}24/|F_o|)^2$ for $|F_o| \geq 39{\cdot}24$. The overall structure was confirmed to be similar to that of other Hofmann-type clathrates. At this stage, however, serious disagreement was observed between $|F_o|$ and $|F_c|$ for some lower-order reflexions with indices $h+k$ = odd, in particular the following six reflexions: 120, 210, 121, 211, 122 and 212. The contributions of the heavy atoms almost cancel out when $h+k$ = odd, and the arrangement of benzene molecules plays an important role for the six reflexions. In addition, the temperature factors of C(3) of the benzene molecule (see Fig. 1) are unusually large. These facts suggest that there is some question about the orientation of the benzene molecules. A difference synthesis indicated an alternative orientation of the benzene molecules. The two orientations, denoted *A* and *B* (Fig. 1), are mirror images of each other with respect to (100). The population parameter for these two orientations was also refined, and the *R* value reduced to 0·060 when the population parameters for arrangements *A* and *B* were 0·4 and 0·6 respectively.* At the same time the unusually large thermal parameters of C(3) became normal.

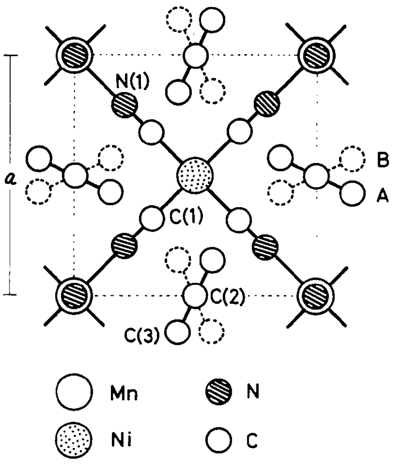

Fig. 1. A projection of the structure along the *c* axis and the numbering of the atoms.

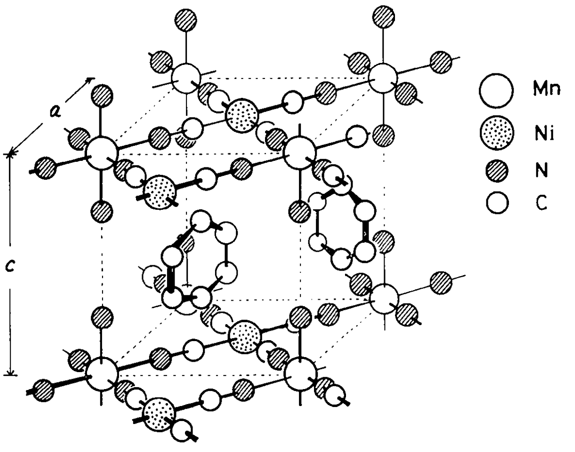

Fig. 2. A perspective drawing of $Mn(NH_3)_2Ni(CN)_4\ 2C_6H_6$

Description of the structure and discussion

The final atomic coordinates and thermal parameters with their estimated standard deviations are listed in Table 1. The crystal structure is illustrated in Fig. 2. Interatomic distances and bond angles are given in Table 2.

The host lattice is isostructural with other Hofmann-type clathrates. A manganese atom is coordinated nearly octahedrally to six nitrogen atoms, two from

Table 3. *Lattice constants, interatomic distances and bond angles in a series of Hofmann-type clathrates*

		Mn–Ni–Bz	Ni–Ni–Bz	Cu–Ni–Bz	Cd–Ni–Bz
a		7·432 (6) Å	7·242 (7) Å	7·345 (3) Å	7·575 (6) Å
c		8·335 (5)	8·277 (8)	16·519 (4)	8·317 (5)
M——N(NH_3)		2·27 (1)	2·08 (6)*	2·05 (2)	2·32 (1)
M——N(CN)		2·24 (1)	2·15 (14)*	2·20 (1)	2·34 (1)
Ni——C(CN)		1·87 (1)	1·78 (17)*	1·88 (1)	1·86 (1)
C≡N		1·14 (1)	1·20 (22)*	1·12 (2)	1·15 (1)
$NH_3\cdots NH_3$		3·80 (2)	4·13 (9)*	4·16 (3)	3·67 (1)
C(3)···N(NH_3)	*A*	3·60 (1)	3·59 (9)*	3·60 (2)	3·67 (1)
	B	3·62 (2)			
φ†	*A*	65·5 (2)°	65·9 (1·9)°*	64·3 (8)°	66·7 (3)°
	B	66·9 (4)			
References		This work	Rayner & Powell (1952)	Miyoshi, Iwamoto & Sasaki (1973)	Nakayama, Kuroda & Sasaki, unpublished data

* Interatomic distances and bond angles were recalculated on the basis of Rayner's data.
† φ stands for the dihedral angle between the benzene ring and the plane (100).

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* A list of $|F_o|$ and $|F_c|$ values has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30295 (4 pp.). Copies may be obtained either through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England, or from the authors.

two ammonia molecules in *trans* positions and four from the four cyano groups. The Mn–N distances are 2·24 (1) and 2·27 (1) Å. A nickel atom is surrounded by four carbon atoms of the cyano groups in square-planar coordination. The Ni–C distance is 1·87 (1) Å. Thus manganese and nickel atoms are linked by cyano groups to form an infinite two-dimensional network. These net planes are stacked parallel to each other along the *c* axis. Benzene molecules are enclosed between the layers with their molecular planes parallel to the *c* axis.

In Table 3, relevant interatomic distances in other Hofmann-type clathrates are compared with those of the present study. As seen from Table 3, M–N(CN) and M–N(NH_3) distances increase with increase in the ionic radius of the central metal M. In the present compound, Mn–Ni–Bz, the Mn^{II} (d^5) exhibits regular octahedral coordination, whereas the coordination octahedron around $Cu^{II}(d^9)$ in Cu–Ni–Bz (Miyoshi, Iwamoto & Sasaki, 1973) is distorted to a tetragonal bipyramid due to the Jahn–Teller effect, a rather unusual example of an axial compression. Bond lengths Ni–C(CN) and C≡N are almost the same throughout the series.

Lattice constant *a* increases linearly with ionic radius of M, while *c* does not seem to have such a simple relation. The reason will be discussed later. The azimuthal orientation of benzene molecules in the cavity are nearly the same, the molecular plane being inclined by an angle of about 66° with respect to (100). The closest contact between a guest molecule and the host lattice occurs between C(3) of the benzene molecules and NH_3 of the host lattice. The C(3)···N(NH_3) distances are always 3·60 Å, indicating a van der Waals contact. When a metal atom in the octahedral site M is substituted by another with larger ionic radius, the network of the host lattice expands and this is reflected in the increase in the *a* spacing. At the same time M–N(NH_3) increases. The N(NH_3)···N(NH_3) separation between the two adjacent networks is in the range 3·7∼4·2 Å, which is much longer than the N···N contact distances of 3·380 (4) Å observed in solid ammonia (Olovsson & Templeton, 1959). This means that *c* is determined by the van der Waals contact between C(3) of the guest molecules and NH_3 of the host lattice. An increase in the M–NH_3 distance may expand the *c* spacing. However, this trend is compensated by the increase in N(NH_3)···N(NH_3) separation in the same layer of the host lattice due to substitution of a metal with larger ionic radius. Accordingly *c* does not change linearly with the ionic radius of M.

Orientation of benzene molecules

The two orientations of benzene molecules found in this compound are related by a (100) mirror plane, and the host lattice possesses *P*4/*mmm* symmetry. Accordingly the interaction potential between a guest molecule and the host lattice is equivalent in the *A* and *B* orientations. Occurrence of the two orientations in one layer is, however, forbidden by intermolecular repulsion among them. On the other hand, as for successive layers, interactions between guest molecules are relatively weak, thus in each layer benzene molecules can take the orientation *A* or *B*. In Cu–Ni–Bz, layers in the *A* and *B* arrangements are found alternately along the *c* axis, and the lattice constant *c* is doubled, while in Cd–Ni–Bz only one arrangement is found throughout one crystal. In the present compound Mn–Ni–Bz, both arrangements occur randomly. In order to see whether the population ratio of the two orientations is unchanged from crystal to crystal, intensities of 12*l*, 21*l* ($l=0,1,2$), which are sensitive to the orientation of the benzene molecules, were further measured for seven crystals and *F*(120)/*F*(210) calculated. The ratios ranged from 1·2∼11·0, indicating that the ratio of the *A* orientation to the *B* differs greatly from crystal to crystal even from the same batch.

Computations were performed on the HITAC 5020E at the Computer Centre of the University of Tokyo with the programs *ANSFR*-2 and *HBLS*-4 written by Dr Iwasaki and Dr Ashida, respectively.

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