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The Hofman-type Clathrate: $M(NH_3)_2M'(CN)_4 . 2G$*

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A series of clathrates with the general formula $M(NH_3)_2M'(CN)_4 . 2G$ were prepared. Their structures have been ascertained by powder X-ray diffractometry to be similar to that of Hofmann's clathrate $Ni(NH_3)_2$-$Ni(CN)_4 . 2C_6H_6$. The variation in the lattice constants of the tetragonal unit cells can be correlated with the change in the bond length between the metal, M, at the octahedral site and the nitrogen of the cyanide and in that between the metal, M', at the square-planar site and the carbon of the cyanide, and with the change of the size of the guest molecules. Their infrared spectra have been interpreted in terms of the weak host-guest interaction depending on the M', and as being almost independent of the change in the M.

Introduction

A series of clathrate compounds formed between a diamminemetal-M^{II} tetracyanometallate-M'^{II} as the host lattice and an aromatic compound, G, as the guest molecules have been prepared with the general formula $M(NH_3)_2M'(CN)_4 . 2G$. Their structures have been ascertained by powder X-ray diffractometry to be similar to that of Hofmann's clathrate $Ni(NH_3)_2$-$Ni(CN)_4 . 2C_6H_6$.[1a-1c] Their infrared spectra showed the general features common in these compounds. Therefore, to these clathrates the present authors wish to give a name «Hofmann-type clathrates». The structure of this Hofmann's clathrate had been determined by Powell and Rayner[2] to be as illustrated in Figure 1. In the present series of compounds, the M, which is one of the first transition metals from manganese to zinc, or cadmium, occupies the octahedral sites, while the M', nickel, palladium or platinum, occupies the square-planar sites, in the host lattice. As the guest molecule, G, benzene, aniline, thiophene, or pyrrole can be clathrated in these host lattices.

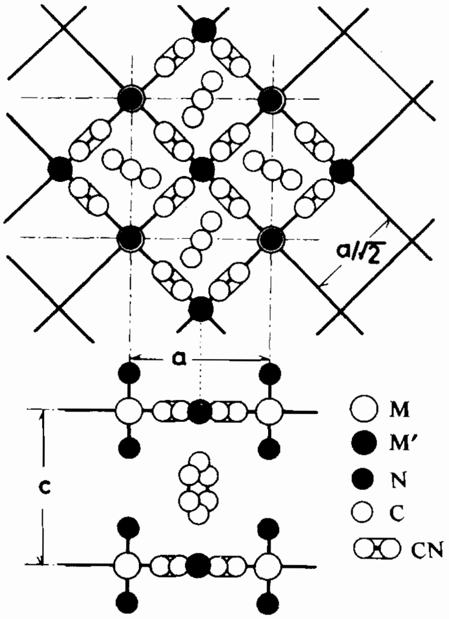

Figure 1. The structure of Hofmann-type clathrate $M(NH_3)_2$-$M'(CN)_4 . 2C_6H_6$. M = M' = Ni in Hofmann's clathrate. Protons of the benzene and ammonia are not shown.

Experimental Section

The principles of the method of preparation have been described in the previous paper.[3] When the M was manganese, iron, or cobalt, all the procedures were carried out by using an apparatus under a nitrogen stream in order to avoid the air oxidation of the divalent ions of these metals. As is illustrated in Figure 2, solutions of the metal (M) salt and potassium tetracyanometallate (M') were added to an ammonia—ammonium chloride solution buffered at an appropriate pH value in a flask cooled with an iced-water bath. After the pH value had been checked, an aromatics of the guest was added and the resulting mixture was vigorously stirred by a magnetic stirrer, thus precipitating the clathrate. The clathrate was then transferred onto a glass filter without any exposure to air, and was washed with ammoniacal water, ethanol, and ether successively. The clathrate thus obtained was dried on a glass filter by being passed through with dry nitrogen.

(*) The Metal Ammine Cyanide Aromatics Clathrates. V. Read at the Xth International Conference on Coordination Chemistry, Nikko, September (1967). Part IV: T. Miyoshi, T. Iwamoto, and Y. Sasaki, *Inorg. Chim. Acta*, *1*, 120 (1967).

(1) (a) K. A. Hofmann and F. Z. Küspert, *Z. anorg. Chem.*, *15*, 204 (1897); (b) K. A. Hofmann and F. Höchtlen, *Chem. Ber.*, 36, 1149 (1903); (c) K. A. Hofmann and H. Arnoldi, *ibid.*, 39, 339 (1906).

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

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

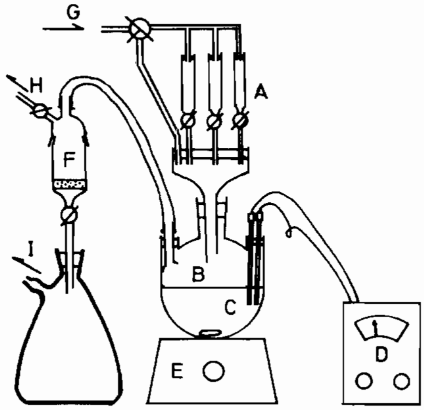

Figure 2. The apparatus for the preparation of M—M′—G (M=Mn, Fe, Co). A: Reservoirs of reagents. B: Reaction flask. C: Glass and Calomel electrodes. D: pH meter. E: Magnetic stirrer. F: Filter unit. G: Nitrogen inlet. H: Nitrogen outlet. I: To a pump.

X-ray Diffractometry, infrared spectroscopy, and magnetic susceptibility measurements were carried out by the methods described in previous papers.[3-6]

Results and Discussion

The clathrates thus prepared are listed in Table I, along with their lattice constants and effective magnetic moments. Their X-ray diffraction patterns can be assigned to those of the tetragonal systems as well as the case of Hofmann's chlathrate, except for some of the Cu—M′—G clathrates (for abbreviations, see Table I).

From the tetragonal crystal structure of the Hofmann's clathrate (see Figure 1), the distance between the octahedral metal, M, and the square-planar metal, M′, through a cyanide bridge is given as $a/\sqrt{2}$. On the assumption that the size of a tetracyanometallate-(M′) is independent of the M in all of the M—*M′*—G clathrates,[*] the bond length between the M and the nitrogen of cyanide, *L*, can be estimated to the first approximation; thereby the size, $R_{M'CN}$, refers to the distance between the M′ and the nitrogen of cyanide coordinating to the M′. In Hofmann's clathrate, R_{NiCN} had been determined to be 2.98 Å by Powell and Rayner.[2] The values of both R_{PdCN} and R_{PtCN} were estimated to be 3.09 Å from the data on $Na_2[Pd(CN)_4].3H_2O$ and $KNa[Pt(CN)_4].3H_2O$.[7] The variation in *a* in each of the M—*M′*—G sub-series can thus be deduced from the difference in the bond length, $L = a/\sqrt{2} - R_{M'CN}$, whose values are listed in Table I. When the M is one of the transition metals from manganese to zinc, it ranges from 2.1 to 2.3 Å. When the M is cadmium, it seems to be approximately 2.4 Å. The almost identical values (within ±0.03 Å) of *L* for an *M* in the *M*—M′—G sub-series suport the validity of the above assumption. Since the lattice constant, *a*, which refers to the size of a host lattice

Table I. The Lattice Constants, Magnetic Properties and Color of the Hofmann-type Clathrates

M—M′—G [a]	*a* Å	$a/\sqrt{2}$ Å	*L* [b] Å	*c* Å	μ_{eff} B.M.	Color
Mn—Ni—Bz	7.46	5.27	2.29	8.38	6.16	pale yellow
Mn—Ni—An	7.53	5.32	2.34	9.06	6.51	pale yellow
Fe—Ni—Bz	7.34	5.19	2.21	8.31	5.34	yellow
Fe—Ni—An	7.30	5.16	2.18	9.18	5.92	yellow
Co—Ni—Bz	7.34	5.19	2.21	8.34	4.88	pink
Co—Ni—An	7.31	5.17	2.19	9.14	5.21	pink
Ni—Ni—Bz	7.24	5.12	2.14	8.28	3.20	pale violet
Ni—Ni—An	7.29	5.15	2.17	9.33	3.40	pale violet
Ni—Ni—Pyr	7.24	5.12	2.14	7.98		pale violet
Ni—Pd—Bz	7.44	5.26	2.17	8.39	3.06	pale violet
Ni—Pt—Bz	7.42	5.25	2.16	8.29	3.10	pale violet
Cu—Ni—Bz	7.39	5.22	2.24	8.29	1.97	greyish pale green
Cu—Ni—An [c]	*a*: 7.27	5.14	2.16	8.81	1.98	dark green
	b: 6.84	4.84	1.86			
Cu—Ni—Thp	7.40	5.23	2.25	8.09		pale green
Cu—Ni—Pyr	7.40	5.23	2.25	7.97	2.5?	dark green
Cu—Pd—Bz	7.58	5.36	2.27	8.29	1.78	sky blue
Cu—Pt—Bz	7.58	5.36	2.27	8.25	1.76	sky blue
Zn—Ni—Bz	7.39	5.22	2.24	8.29	diamag.	light yellow
Zn—Pd—Bz	7.58	5.36	2.27	8.32	diamag.	white
Zn—Pt—Bz	7.64	5.40	2.31	8.24	diamag.	white
Cd—Ni—Bz	7.64	5.40	2.42	8.37	diamag.	light yellow
Cd—Ni—An	7.56	5.34	2.36	8.66	diamag.	light yellow
Cd—Ni—Thp	7.60	5.37	2.39	8.22	diamag.	light yellow
Cd—Ni—Pyr	7.61	5.38	2.40	8.13	diamag.	light yellow
Cd—Pd—Bz	7.77	5.49	2.40	8.38	diamag.	white
Cd—Pd—An	7.81	5.52	2.43	8.65	diamag.	white
Cd—Pt—Bz	7.78	5.50	2.41	8.29	diamag.	white

[a] M—M′—G = $M(NH_3)_2M'(CN)_4 . 2G$; G: Bz=benzene, An=aniline, Pyr=pyrrole, Thp=thiophene. [b] $L = a/\sqrt{2} - R_{M'CN}$. $R_{M'CN}$ = 2.98 Å (M′=Ni), 3.09 Å (M′=Pd, Pt). [c] Orthorhombic.

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(4) T. Nakano, T. Miyoshi, T. Iwamoto, and Y. Sasaki, *ibid.*, *40*, 1297 (1967).

(5) M. Morita, T. Miyoshi, T. Miyamoto, T. Iwamoto, and Y. Sasaki, *ibid.*, *40*, 1556 (1967).

(6) T. Miyoshi, T. Iwamoto, and Y. Sasaki, *Inorg. Chim. Acta*, *1*, 120 (1967).

(7) H. Brasseur and A. de Rassenfosse, *Mem. Soc. Sci. Liége*, [2] *4*, 397 (1941).

(*) This abbreviation indicates that in this series italic letters refer to definite species.

along its *ab*-plane, was not greatly affected by the change in the guest molecule in a host lattice, the size of the host lattice in these directions may be said to be primarily dominated by the *L* and $R_{M'CN}$.

Another lattice constant, *c*, which refers to the distance between adjacent metal complex networks is almost constant (within ±0.1 Å) among the M–M′–*G* sub-series of an aromatics. As *c* must depend mainly on the size of the guest molecule, the largest values were found in the aniline clathrates; the second largest, in the benzene clathrates, and the smallest, in the pyrrole and thiophene clathrates.

The replacement of the metal, M, at the octahedral sites and the metal, M′, at the square-planar sites in the structure of Hofmann's clathrate was established by the magnetic susceptibility measurements. Each of the M–M′–G where the M was manganese, iron, cobalt, nickel, or copper respectively, gave an effective magnetic moment of the M^{2+} in the high-spin state. When the M was zinc or cadmium, the clathrates were diamagnetic. The temperature dependency of the paramagnetic susceptibility was measured by Faraday method[8] within a temperature range from the temperature of liquid nitrogen to room temperature for two Cu–Ni–G clathrates. The data are shown in Figure 3, along with those of Ni–Ni–Bz, which are cited from an earlier paper.[9] Within the temperature range measured, they obeyed Curie's law and showed no anomaly.

From these facts it can be concluded that these M–M′–G clathrates have structures similar to that of Hofmann's clathrate. To confirm this conclusion, a structural analysis of a single crystal of $Cd(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$ is now being carried out by X-ray diffractometry. Preliminary results of the projections of the Patterson function along the *ab*- and *ac*-planes support an arrangement of the atoms of the host lattice entirely analogous to that of Hofmann's clathrate.[10] Details will be soon reported.

The infrared spectra of these clathrates can be interpreted according to the assignments already published for some M–Ni–Bz and M–Ni–An clathrates.[6] A characteristic feature found among their spectra was that the absorption bands due to a guest molecule do not show any significant shift upon the change of the M in the host lattice. In Table II the absorption bands of benzene in several M–M′–Bz clathrates are tabulated. The wave number of each band coincides with that of gaseous benzene within a few cm^{-1} fluctuations except the bands of some out-of-plane modes. The fact that no significant shift was observed among these M–M′–Bz clathrates proves that the state of the guest benzene is not affected by the change of the M in the host lattice, thereby restricting the energy region that can be detected by infrared spectroscopy.

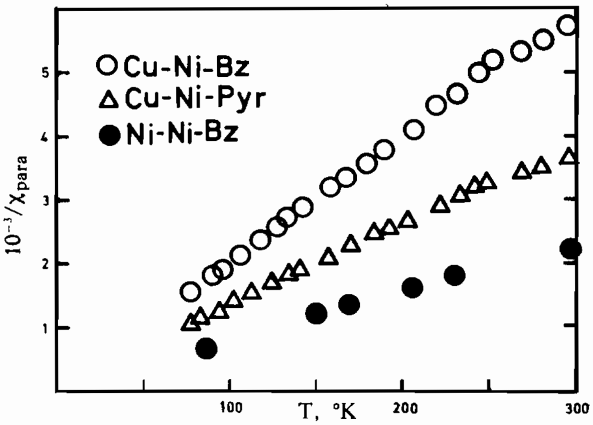

Figure 3. The temperature dependenc of the paramagentic susceptibility.

Another essential feature is the slight shift of an out-of-plane CH bending vibration band in the A_{2u} mode among the M′-replaced host clathrates. As Table II shows, this band has been observed at 675 cm^{-1} in gaseous benzene and around 705 cm^{-1} in M–Ni–Bz. In M–Pd–Bz and M–Pt–Bz, it was detected around 700 cm^{-1} and was shifted by *ca.* 5 cm^{-1} to a lower-frequency side than that of M–Ni–Bz. This shift to a lower side can be correlated with the enlargement of the unit cells of these Pd- and Pt-host clathrates (see Table I). The slight shift of the out-of-plane band may be deduced from the small change in the host-guest interaction caused by the

Table II. IR Absorption Bands of Benzene in M–M′–Bz (cm^{-1})

M M′	Mn Ni	Fe Ni	Co Ni	Ni Ni	Ni Pd	Ni Pt	Cu Ni	Cu Pd	Cu Pt	Zn Ni	Zn Pd	Zn Pt	Cd Ni	Cd Pd	Cd Pt	gaseous benzene
CH str. i.p. (E_{1u})	---	---	---	~3085	---	---	~3080	---	---	~3080	---	---	~3076	---	---	3068
CH str. i.p. (B_{1u})	---	---	---	~3030	---	---	~3030	---	---	~3030	---	---	~3026	---	---	3057
Combination	1986	1990	1986	1994	1985	1983	1995	1987	1985	1992	1985	1985	1987	1984	1985	
Combination	1848	1852	1849	1858	1846	1848	1859	1869	1846	1856	1846	1848	1852	1848	1843	
Combination	1571	1573	1573	1577	1565	1565	1578	---	1567	1572	1562	---	1567	1562	1566	
Ring. str. + def. i.p. (E_{1u})	1477	1477	1478	1478	1476	1479	1477	1476	1476	1478	1477	1476	1476	1476	1476	1482
Ring. str. i.p. (B_{2u})	---	---	---	1314	1313	---	1314	---	1311	1313	1315	---	1311	1314	1312	1309
CH bend. i.p. (B_{2u})	1146	ovlp	ovlp	1148	1148	1150	1148	1147	1147	1148	ovlp	1149	1147	1147	1148	1146
CH bend. i.p. (E_{1u})	1034	1034	1033	1035	1035	1037	1035	1034	1034	1036	1036	1036	1034	1034	1035	1037
CH bend. o.p. (E_{2u})	984	985	985	986	983	984	987	983	983	986	984	982	985	983	983	975
CH bend. o.p. (A_{2u})	702	706	704	706	700	702	706	697	699	705	700	699	704	697	698	675
Ring def. o.p. (E_{2u})	---	---	---	410	---	---	409	---	---	408	---	---	407	---	---	405

---: Not determined. ovlp: Overlapped with other strong band due to the host lattice.

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[8] The apparatus and instrument used were the same to those in: Y. Sato, M. Kinoshita, M. Sano, and H. Akamatu, *Bull. Chem. Soc. Japan*, *40*, 2539 (1967). To the authors the present authors' thanks are due for the kind measurement of the present clathrates.

[9] R. B. Janes, *Phys. Rev.*, *48*, 78 (1935).

[10] Y. Sasaki to be published.

enlargement of the unit cell of the host lattice. According to Hohfmann and Arnoldi,[1c] the host lattice of Hofmann's clathrate $Ni(NH_3)_2Ni(CN)_4$ cannot clathrate an aromatic molecule which has a molecular volume larger than that of aniline (90.5, 15°C). The largest host lattice, $Cd(NH_3)_2Pd(CN)_4$, in the Hofmann-type clathrates listed in Table 1, however, can clathrate fluorobenzene, which has too large a molecular volume (93.8) for Hofmann's host lattice. It is now being subjected to NMR spectroscopy.

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