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# The Infrared Spectra of the Diamminemetal (II) Tetracyanoniccolate (II) Benzene and Aniline Clathrates*

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*The infrared spectra of the clathrate compounds of the type $M(NH_3)_2Ni(CN)_4 . 2G$ (where M is Ni, Cu, Zn, or Cd and G is benzene or aniline) in the region 4000-200 $cm^{-1}$ are reported with a complete set of assignments. The force constants for the fundamental out-of-plane vibration of the clathrated benzene molecule were computed from the data. The values are found to be larger than those for gaseous benzene and are explained by assuming an electron cloud repulsion between the host lattice and the guest molecules in the clathrate.*

## Introduction

The well-known clathrate compound, diamminenickel(II) tetracyanoniccolate(II) benzene clathrate $Ni(NH_3)_2Ni(CN)_4 . 2C_6H_6$, and similar compounds containing aromatics instead of benzene were prepared by Hofmann and his colleagues[1,2,3] more than sixty years ago. These clathrates were later found to contain both paramagnetic and diamagnetic nickel atoms in octahedral and square planar coordination sites respectively and in a 1:1 ratio. An X-ray diffraction study[4] has shown that the nickel atoms form an infinite polymer plane network with cyanide anions as bridges between adjacent metal atoms. The diamagnetic nickel atoms are surrounded by four carbon atoms of cyanide anions in plane, while the paramagnetic nickel atoms are bonded to four cyanide anions through nitrogen atoms. The octahedral configuration of the paramagnetic atoms is completed by the addition of two ammonia molecules stretched out of the plane to the two sides.

These planes in layers compose the host lattice of the clathrate, with aromatic guest molecules between the layers.

The ammonia molecules sticking out of one plane fall on the same molecules of the contiguous plane, and these N-N axes are surrounded by four guest molecules which are accommodated parallel to the axes.

In our previous papers[5,6] it was reported that the paramagnetic nickel in these complexes can be replaced by Mn(II), Fe(II), Co(II), Cu(II), Zn(II) or Cd(II), while the diamagnetic nickel can also be replaced by Pd(II) or Pt(II).[7]

The present infrared study was undertaken not only to get a complete set of vibrational assignments for these clathrates, but also to obtain quantitative information about the interaction of guest molecules in the compounds with their host lattices.

The samples used in the study described here are clathrates obtained with stoichiometric compositions corresponding to the general formulae: $M(NH_3)_2Ni(CN)_4.2C_6H_6$ and $M(NH_3)_2Ni(CN)_4.2C_6H_5NH_2$, where M is Ni(II), Cu(II), Zn(II), or Cd(II).

In addition, two deuterated compounds, $Cd(ND_3)_2Ni(CN)_4 . 2C_6H_6$ and $Cd(NH_3)_2Ni(CN)_4 . 2C_6D_6$, were used. The cadmium compounds were chosen because of their stability and ease of preparation.

A residual host lattice. $Cu(NH_3)_2Ni(CN)_4$, left after the escape of the guest benzene from its corresponding clathrate, was also subjected to study.

## Experimental Section

*Samples.* Benzene and aniline clathrates of the following formulae: $Ni(NH_3)_2Ni(CN)_4 . 2C_6H_6$, $—2C_6H_5NH_2$, $Cu(NH_3)_2Ni(CN)_4 . 2C_6H_6$, $—2C_6H_5NH_2$, $Cd(NH_3)_2Ni(CN)_4 . 2C_6H_6$, $—2C_6H_5NH_2$ and $Zn(NH_3)_2Ni(CN)_4 . 2C_6H_6$, were prepared as has been described in previous works.[5,6] The residual host lattice, $Cu(NH_3)_2Ni(CN)_4$, was obtained by leaving the clathrate in an open atmosphere for a few days, this resulted the almost complete escape of benzene, without any significant loss of ammonia. *Anal.* Found: C, 18.6; H, 2.0; N, 31.6; Ni, 23.1; Cu, 25.0%. Calcd. for $Cu(NH_3)_2Ni(CN)_4$: C, 18.5; H, 2.3; N, 32.3; Ni, 22.5; Cu, 24.4%. The powder X-ray diffraction data seem to indicate the distortion and the disorder of the host lattice caused by the loss of the guest benzene. The X-ray spectrum was found to change their pattern entirely from that of the clathrate and could not be assigned to any single crystal phase; moreover, it shows an intense background.

The deuterobenzene clathrate was prepared in the same manner except that an equivalent amount of hexadeuterobenzene (99.0%, Showa-Denko Co.) was

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(*) This is Part IV of the series «The Metal Ammine Cyanide Aromatics Clathrates». For Part I, II and III, see the references 5, 6 and 7.

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

(2) K. A. Hofmann and F. Höchtlen, *Chem. Ber.*, 36, 1149 (1903).

(3) K. A. Hofmann and H. Arnoldi, *ibid.*, 39, 339 (1906).

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

(5) T. Iwamoto, T. Miyoshi, T. Miyamoto, Y. Sasaki and S. Fujiwara, Part I of this series, *Bull. Chem. Soc. Japan*, *40*, 1174 (1967).

(6) T. Iwamoto, T. Miyoshi, T. Nakano and Y. Sasaki, Part II of this series, *Bull. Chem. Soc. Japan*, *40*, 1297 (1967).

(7) T. Iwamoto, T. Miyamoto, M. Morita and Y. Sasaki, Part III of this series, *Bull. Chem. Soc. Japan*, *40* (1967).

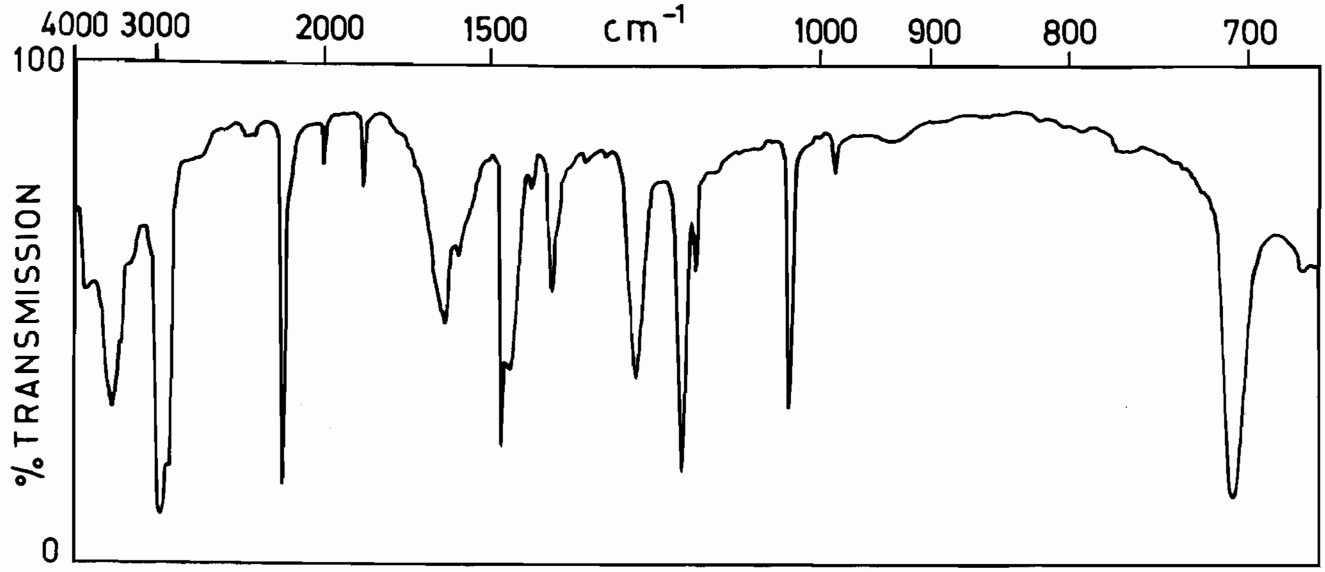

Figure 1. Infrared Spectrum of $Ni(NH_3)_2Ni(CN)_4 . 2C_6H_6$.

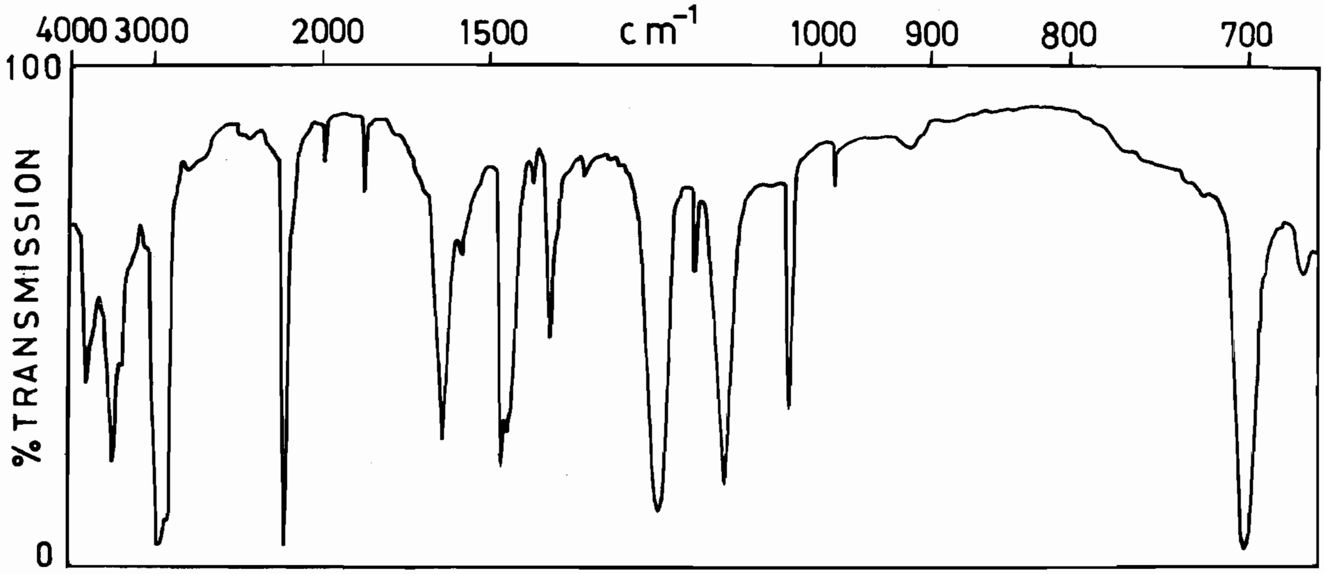

Figure 2. Infrared Spectrum of $Cd(NH_3)_2Ni(CN)_4 . 2C_6H_6$.

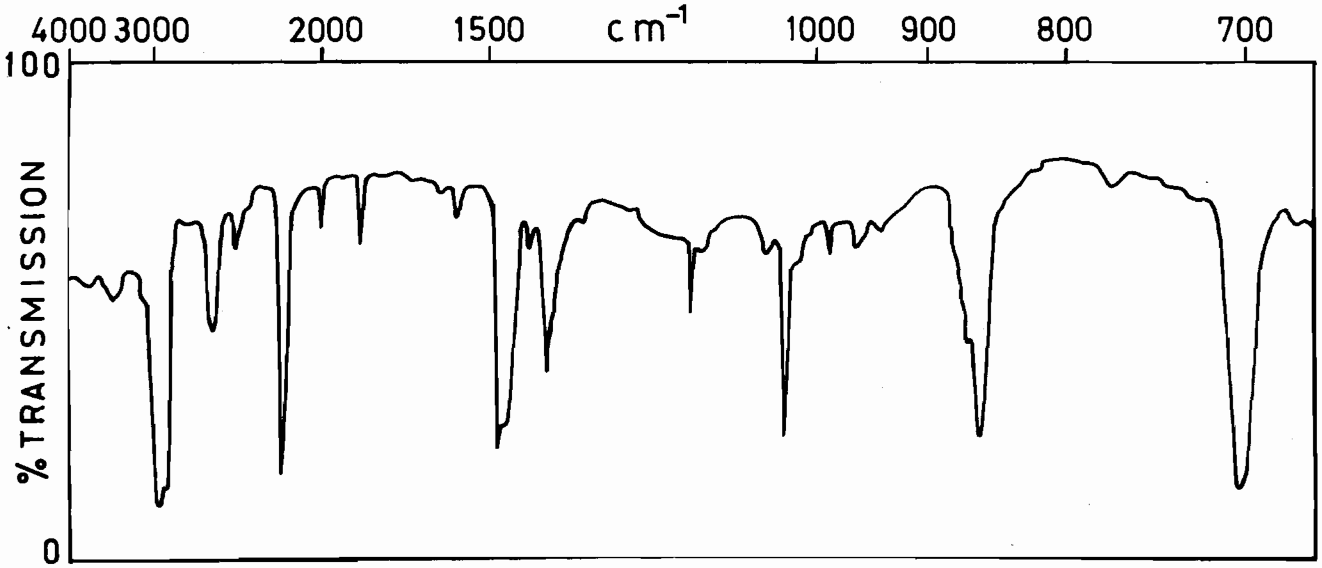

Figure 3. Infrared Spectrum of $Cd(ND_3)_2Ni(CN)_4 . 2C_6H_6$.

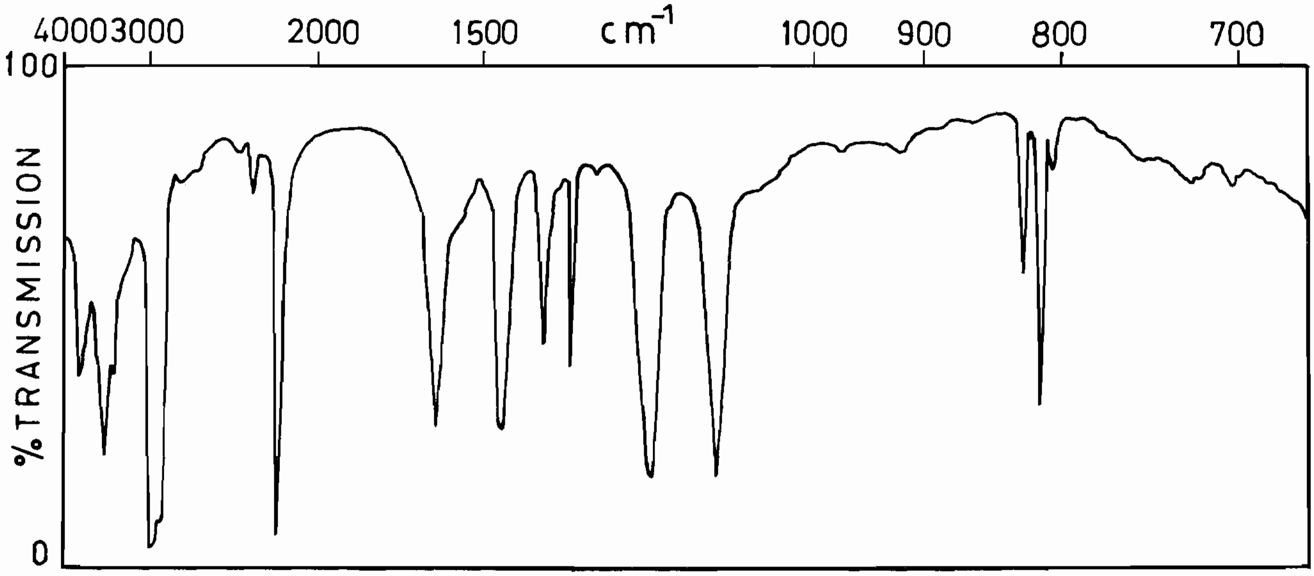

Figure 4. Infrared Spectrum of $Cd(NH_3)_2Ni(CN)_4 . 2C_6D_6$. (The bands at 3000, 1462 and 1376 cm$^-$ in all the figures are due to Nujol.)

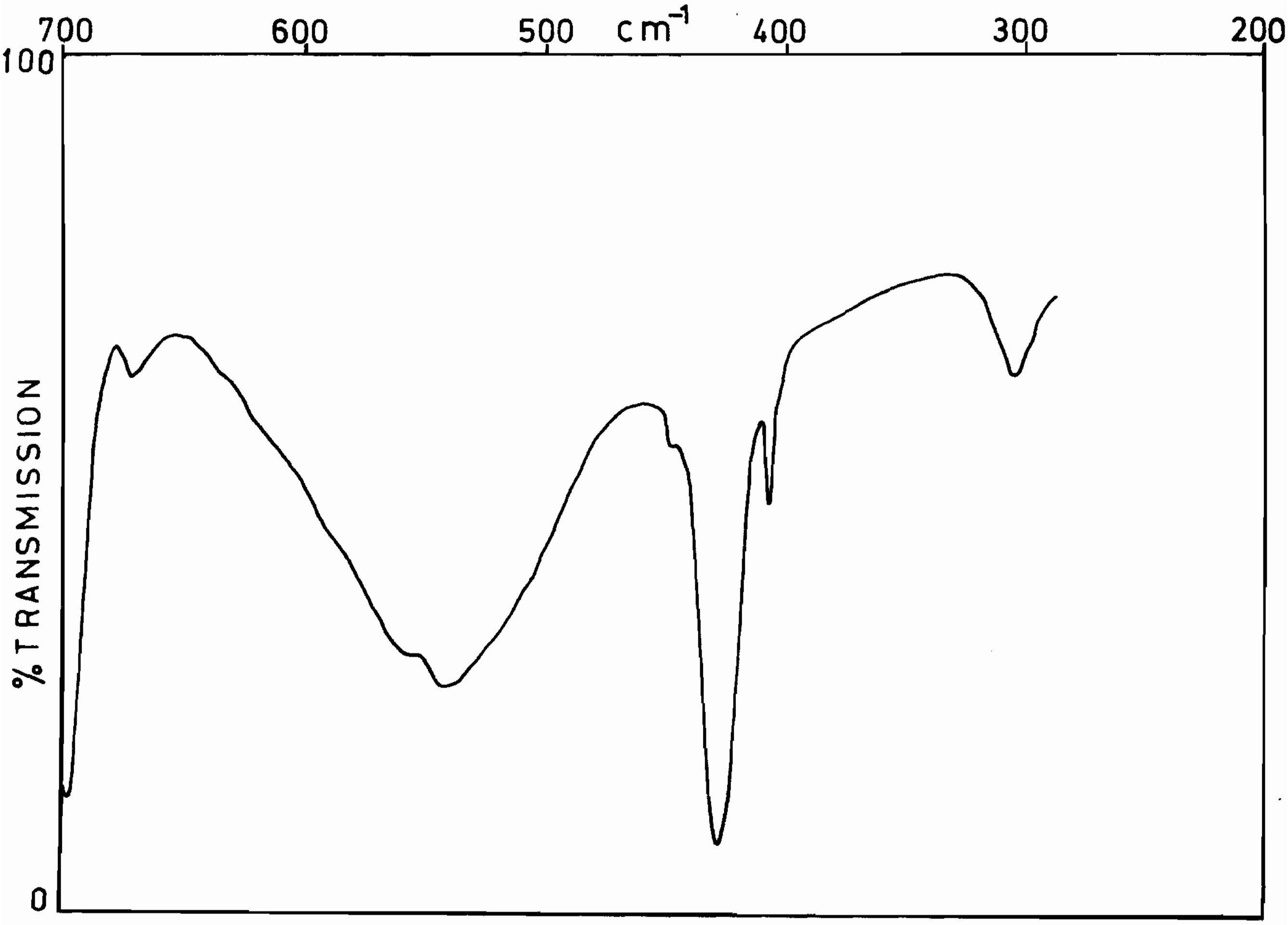

Figure 5. Far Infrared Spectrum of $Cd(NH_3)_2Ni(CN)_4 . 2C_6H_6$.

used in place of ordinary benzene. The deuteroammine compound was prepared through the following process: In a stream of nitrogen free from water and oxygen, magnesium was heated at 800°C for four hours. The magnesium nitride thus obtained was pulverized and reacted with deuterium oxide (99.8%, Showa-Denko Co.) vapour after being heated in a vacuum line. The deuteroammonia was absorbed into deuterium oxide in a trap connected to the vacuum system. This solution was distilled into a Schlenk tube containing an equimolar mixture of cadmium nitrate and potassium tetracyanoniccolate which had been dehydrated by gentle heating in a vacuum. To the resulting solution, an equivalent amount of benzene was added and the mixture was stirred well mechanically, the temperature being kept down by cooling by an ice-bath. The clathrate thus obtained was filtered out in a dry box and dried in a desiccator over sodium hydroxide in an atmosphere saturated with benzene vapour.

*Infrared Measurement.* The accurate wave number of each absorption band was read from the spectra recorded using Hitachi EPI-2 and EPI-LO2 spectrometers in the regions of 650-4000 and 200-700 $cm^{-1}$ respectively.

A Perkin-Elmer Infracord 137 spectrometer was also used in the preliminary scanning of the spectra. The spectra shown in Figs. 1-5 were recorded with the Infracord and the EPI-LO2. The samples were measured as the Nujol and the HCB mulls. The KBr disk techniques were avoided because an almost complete escape of guest molecules, especially of benzene, often occurs during the preparation of the disk in a vacuum. The mull of $Cd(ND_3)_2Ni(CN)_4 . 2C_6H_6$ was prepared in a dry box filled with dry nitrogen. When it was treated in an open atmosphere, a rapid exchange between the deuterium of deuteroammonia and the hydrogen in the humidity water occurred.

## Results and Discussion

In Table I-III, the absorption bands are tabulated, and their assignments are shown.

*The $Ni(CN)_4^{2-}$ Vibrations.* The absorption bands due to $Ni(CN)_4^{2-}$ were assigned by comparing them with the spectra of $Na_2Ni(CN)_4 . 3H_2O$ crystals.[8] The $\nu_8$(CN stretching, $E_u$) and $\nu_{10}$(Ni-CN bending in plane, $E_u$) modes are both degenerate and observed as single

**Table I.** The wave numbers of the host lattice of the benzene clathrates

| Ni-Ni-Bz [a] | Cu-Ni-Bz | Cu-Ni | Zn-Ni-Bz | Cd-Ni-Bz | Cd-Ni-Bz(D) | Cd(D)-Ni-Bz | Assignment |
|---|---|---|---|---|---|---|---|
| | | | | | | 3665 vw | $H_2O$ ? |
| | | | | 3635 w br | ca. 3630 vw sh | ca. 3620 vw br | |
| 3380 m | 3370 m | 3370 m | 3360 m | 3388 m | 3378 m | ca. 3380 vw br | $NH_3$ sym. & asym. str. |
| ca. 3300 w sh | 3285 w | 3290 w | | ca. 3298 w sh | ca. 3298 w sh | | |
| | | ca. 3190 vw sh | | | | | |
| | | | | | | ca. 2530 w br | $ND_3$ sym. & asym. str. |
| 2166 s | 2174 s | 2178 s | 2192 s | 2155 s | 2155 s | 2154 s | $\nu_{CN}$ ($\nu_8$) [b] |
| | 2150 s | 2146 m | 2157 s | | | | |
| | | 2122 m | ca. 2132 m sh | | | | |
| ca. 1618 m br | 1616 m br | 1607 m | ca. 1618 m br | 1611 s | 1609 w | | $NH_3$ deg. def. |
| 1229 m | 1259 w | 1279 w sh | ca. 1292 w sh | 1196 s | 1193 m | 1212 w | $NH_3$ sym. def. |
| | | 1260 m | 1255 m | | | | |
| | | 1251 m sh | | | | | |
| | | 1238 s | | | | | |
| | | 1226 s | | | | | |
| 1165 s | 1178 s | | 1156 s | 1109 s | 1107 s | ca. 1110 vw sh | |
| | | | | | | 1130 w br | $ND_3$ deg. def. |
| | | | | | | ca. 1045 vw br | $ND_2H$ & $NDH_2$ sym. def.? |
| | | | | | | 953 vw | |
| | | | | | | 937 vw sh | |
| | | | | | | 867 m | $ND_3$ sym. def. |
| | | | | | | 856 m | |
| ca. 610 s br | ca. 640 m br | ca. 670 s br | ca. 595 m br | 555 m br | ca. 555 m br | ca. 550 w sh | $NH_3$ rock. |
| 547 w sh | 547 w | 563 m | 542 m | 543 w | 545 w | ca. 545 w | $\nu_{NiC}$ ($\nu_9$) |
| | | 496 vw | 478 vw | | | | ? |
| 459 m | ca. 454 vw | - - - [c] | - - - | 448 vw | 448 vw | 448 vw | $\pi_{NiCN}$ ($\nu_{12}$) |
| 436 s br | ca. 440 w sh | 454 s | 455 m | 427 s | 427 s | 427 s | $\delta_{NiCN}$ ($\nu_{10}$) |
| | 422 s | 423 s | 426 s | | | | |
| | | | | | | ca. 400 m br | $ND_3$ rock. |
| | | 377 vw | | | | | ? |
| 372 m | ca. 460 m | - - - [c] | 350 w | 304 m | 303 m | 289 m | M-N($NH_3$ or $ND_3$) str. |
| 267 s | 328 w | 340 vw | 225 m | | | | M-N(CN) str. |
| | | 332 vw | | | | | |
| | | 327 vw sh | | | | | |
| | 236 m | 247 m | | | | | N($NH_3$)-M-N($NH_3$) bend. |
| | | 232 m | | | | | |
| | | 216 m | | | | | |

[a] M-Ni-Bz = $M(NH_3)_2Ni(CN)_4 . 2C_6H_6$; Cu-Ni = $Cu(NH_3)_2Ni(CN)_4$ ; Cd-Ni-Bz(D) = $Cd(NH_3)_2Ni(CN)_4 . 2C_6D_6$ ; Cd(D)-Ni-Bz = $Cd(ND_3)_2Ni(CN)_4 . 2C_6H_6$. [b] The notation is in accordance with Ref. 8. [c] The band could not be detected by the overlap with other stronger bands. s = strong, m = medium, w = weak, vw = very weak, br = broad, sh = shoulder, sym. = symmetric, asym. = asymmetric, deg. def. = degenerate deformation, rock. = rocking, bend. = bending.

**Table II.** The wave numbers of benzene in the benzene clathrates

| Ni-Ni-Bz | Cu-Ni-Bz | Zn-Ni-Bz | Cd-Ni-Bz | Cd(D)-Ni-Bz | Cd-Ni-Bz(D) | Assignment [b] |
|---|---|---|---|---|---|---|
| ca. 3085 vw | ca. 3080 vw sh | ca. 3080 vw sh | ca. 3076 vw sh | — [a] | 2278 vw | $\nu_{18}(E_{1u})$ |
| ca. 3030 vw | ca. 3030 vw sh | ca. 3030 vw sh | ca. 3026 vw | — | | $\nu_{13}(B_{1u})$ |
| 1994 w | 1995 w | 1992 w | 1987 w | 1992 vw | | combination |
| 1858 m | 1859 m | 1856 m | 1852 w | 1850 w | | |
| 1577 w | 1578 w | 1572 w | 1567 vw | 1565 vw | | |
| 1478 s | 1477 s | 1478 s | 1476 s | 1477 s | 1325 m | $\nu_{19}(E_{1u})$ |
| 1314 vw | 1314 vw | 1313 vw | 1311 vw | 1312 vw | ca. 1280 vw | $\nu_{14}(B_{2u})$ |
| 1148 m | 1148 m | 1148 m sh | 1147 m | 1147 w | 823 m | $\nu_{15}(B_{2u})$ |
| 1035 s | 1035 s | 1036 s | 1034 s | 1034 s | 811 s | $\nu_{20}(E_{1u})$ |
| 986 w | 987 w | 986 m | 985 w | 985 vw | 801 vw | $\nu_{17}(E_{2u})$ |
| 706 s | 706 s | 705 s | 704 s | 702 s | 515 s | $\nu_{11}(A_{2u})$ |
| | | | | | 498 w sh | ? |
| 410 m | 409 w | 408 m | 407 m | ca. 405 w | 356 w | $\nu_{16}(E_{2u})$ |

[a] No accurate data available. [b] The notation for benzene is in accordance with Ref. 11.

**Table III.** The wave numbers of the aniline clathrates

| Ni-Ni-An [a] | Cu-Ni-An | Cd-Ni-An | liq. An[13] | Assignment [b] |
|---|---|---|---|---|
| 3765 vw | 3765 vw | 3760 vw | | ? |
| 3485 w | 3455 w | 3473 w | 3440 | $NH_2$ str. a″ |
| 3385 m | 3375 m | 3378 m | 3360 | $NH_2$ str. a′ + $NH_3$ sym. and asym. str. |
| 3290 vw | ca. 3285 vw sh | | | |
| ca. 3210 vw | 3160 vw | ca. 3220 vw br | 3212 | 2 × 1620 A′ |
| ca. 3035 vw sh | ca. 3035 vw sh | ca. 3010 vw sh | 3037 | CH str. a′ |
| 2165 s | 2174 s | 2148 s | | $\nu_{CN}$ ($\nu_8$) |
| | 2138 m | | | |
| 1618 s | 1616 s | 1619 s | 1618 | $NH_2$ bend. a′ |
| 1603 s | 1600 s | 1602 s | 1600 [c] | ring str. a′ |
| 1494 s | 1492 s | 1493 s | 1500 | ring str. a′ |
| 1466 m | 1466 m | 1466 m | 1468 [c] | ring str. a″ |
| 1313 w | 1315 vw | 1313 w | 1312 [c] | CH bend. i.p. a″ |
| 1289 m | 1281 m | 1287 s | 1278 | X-sensitive a′ |
| 1193 m | 1207 m | 1150 s | | $NH_3$ sym. def. |
| 1175 w | 1175 w | 1175 s | 1175 | CH bend. i.p. a″ |
| 1154 w | 1154 w | --- | 1154 [c] | CH bend. i.p. a″ |
| 1104 vw | 1108 vw br | 1105 vw | 1118 | CH bend. i.p. a″ |
| 1041 w | 1047 vw | 1042 m | 1050 [c] | $NH_2$ twist. a″ |
| 1025 vw sh | 1025 vw | 1022 m | 1028 | CH bend. i.p. a′ |
| 993 w | 994 vw | 992 m | 996 | ring breath. a′ |
| 889 w | 894 w | 891 m | 880 | CH ben. o.p. a′ |
| 768 s | 769 s | 766 s | 751 | CH bend. o.p. a″ |
| 701 m | 703 w sh | 703 s | 691 | ring def. o.p. a′ |
| ca. 665 w br | ca. 665 w br | ca. 665 w br | ca. 670 | $NH_2$ wag. |
| 600 m br | 652 m br | ca. 560 w br | | $NH_3$ rock. |
| ca. 545 vw sh | ca. 552 vw | 540 vw sh | | $\nu_{NiC}$ ($\nu_9$) |
| 515 s | 514 s | 515 s | | X-sensitive o.p. a′ |
| 458 w | ca. 455 vw sh | 450 vw | 501 | $\pi_{NiCN}$ ($\nu_{12}$) |
| 437 s | 437 s | 422 s | | $\delta_{NiCN}$ ($\nu_{10}$) |
| | 422 s | | | |
| 373 m | --- | 325 vw | | M-$N_{(NH_3)}$ str. |
| --- | 380 vw | 380 vw | 390 | X-sensitive i.p. a″ |
| 267 m | 257 m | | | M-$N_{(CN)}$ str. |
| | 234 w br | | | $N_{(NH_3)}$-M-$N_{(NH_3)}$ bend. |

[a] M-Ni-An = $M(NH_3)_2Ni(CN)_4 . 2C_6H_5NH_2$, liq. An = liquid aniline. [b] The notations of the assignment for aniline and cyanide are in accordance with Ref. 13 and Ref. 8. [c] The bands are not detectable in gaseous aniline. --- : The bands could not be detected by the overlap with other stronger bands.

bands in the cases of $Cd(NH_3)_2Ni(CN)_4 . 2C_6H_6$, $Cd(NH_3)_2Ni(CN)_4 . 2C_6H_5NH_2$, $Ni(NH_3)_2Ni(CN)_4 . 2C_6H_6$ and $Ni(NH_3)_2Ni(CN)_4 . 2C_6H_5NH_2$ (abbreviated as Cd-Ni-Bz, Cd-Ni-An, and Ni-Ni-Bz etc.), but are split into doublets in Cu-Ni-Bz and Cu-Ni-An. Similar splittings observed in $Na_2Ni(CN)_4 . 3H_2O$ were explained by assuming the removal of the degeneracy by the presence of sodium cations and water molecules which lower the site symmetry of the $Ni(CN)_4^{2-}$ anion.[3] However, no definitive explanation of the splitting in the present case could be obtained.

In Zn-Ni-Bz, the splitting of these lines into a doublet and a triplet might be caused not only by the removal

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(8) R. L. McCullough, L. H. Jones and G. A. Grosby, *Spectrochim. Acta, 16,* 929 (1960).

of the degeneracy, but also by the partial distortion of the host lattice through the escape of some benzene during measurements.

The effect of the distortion is more evident in the residual host lattice, $Cu(NH_3)_2Ni(CN)_4$, and the splittings of these bands are more complicated. As the X-ray data showed, the loss of benzene makes the host lattice distorted, and so the retention of the original lattice structure can not be expected.

*$NH_3$ Vibrations* All the wave numbers measured are given in Tables I-III, except those of the ammonia vibrations in the region of 3200-3400 $cm^{-1}$ (Table III), which could not be determined accurately because of their overlapping with aniline bands.

The asymmetric and symmetric stretching, the degenerate deformation, the rocking vibrations of $NH_3$ group, and the metal-nitrogen stretching and bending vibrations were assigned in Table I and require no additional discussion. Strong bands in the 1100-1260 $cm^{-1}$ region (one for aniline and two for benzene clathrates) were identified as symmetric deformations, as will be discussed below. These assignments were confirmed by comparison with the spectra of the corresponding deuterated compounds.

As may be seen in Figs. 2, 3 and 4, the wave numbers of the bands assigned to $NH_3$ modes in Cd-Ni-Bz did not shift in the spectra of the deuterobenzene clathrate, but they did shift to a large extent in that of the clathrate with a deuteroammine host lattice.

The symmetric deformation band of ammonia is split into two bands in the 1100-1260 $cm^{-1}$ region, as Table I shows. One of these bands was erronously assigned in earlier investigations[9,10] to the C-H deformation of benzene in the gerade mode, $E_{2g}$, because its intensity decreases, with a gradual escape of benzene from the clathrate. However, according to the present observations (see Figs. 2, 3 and 4), these bands should both be identified as $NH_3$ symmetric deformation vibrations.

The splitting may be associated with the Fermi resonance interaction of the band with the $NH_3$ rocking band. The absence of Fermi resonance in the aniline clathrates spectra is explained by the lack of high site symmetry of $NH_3$ groups in the aniline compounds necessary for the occurrence. The difference between aniline and benzene in their symmetry and polarity may be the cause.

The disappearance of the splitting on the escape of benzene could also be explained by assuming a change of symmetry in the lattice. In the residual lattice, $Cu(NH_3)_2Ni(CN)_4$, the $NH_3$ symmetric deformation band is split into five peaks, presumably because of the distortion and disorder of the structure.

*The $ND_3$ Vibrations.* As the wave number of the $ND_3$ bands must be almost seven-tenth ($1/\sqrt{2}$) that of the corresponding $NH_3$ bands, the bands in the region of 2500-2550 $cm^{-1}$, at ca. 1130 $cm^{-1}$, in the 850-870 $cm^{-1}$ region, and at ca. 400 $cm^{-1}$ were assigned to the $ND_3$ stretching, the degenerate deformation, the symmetric deformation, and the rocking vibrations respectively.

*The Guest Molecule Vibrations.* The bands due to the guest molecules were assigned by comparison with the spectra of the respective compounds in gaseous, liquid, and solid states.[11,12,13] As has been shown by the X-ray analysis of the single crystal of Ni-Ni-Bz,[4] the site smmetry of the benzene in the clathrate is $C_{2h}$. Therefore, there must be ten «ungerade» fundamental modes of vibration of benzene which are infrared-active. Among these, nine absorption bands were detected in the present measurements, as may be seen in Table II.

*The Interaction between Host Lattice and the Guest Molecule.* As is shown in Table II, the wave number of each fundamental mode of benzene in the clathrates does not shift to any significant degree when the hexacoordinated divalent metal ion in the host lattice changes to cadmium, copper or zinc from nickel. This implies that the interaction is not affected by the change in the hexacoordinated metal ion in the lattice energetically concerned with the infrared spectroscopy. For the aniline clathrates, no similar discussion is possible, because aniline bands are often broad and their wave numbers can not be expected to be as accurate as those of benzene.

In the both series of clathrates, the only indication of interaction between guest and host lattice is the shifts of all the out-of-plane vibrations from those in the gaseous, and liquid states.

Further support for the assumption of the absence of chemical bonds between the host and the guest benzene in the clathrates of this type may be drawn from a comparison of these infrared data with those of $Cr(C_6H_6)_2$[14] and of $(C_6H_6)Cr(CO)_3$,[15] which contain benzene molecules attached to metal atoms through π-bonding.[16,17]

As may be seen in Table IV, no large line shift from the gaseous benzene bands observed in these π-complexes is found in the clathrate spectra. The spectra of the clathrate are rather like those of solid benzene[12] except that the bands in the latter are split into several peaks. Thus, it can be concluded that the interaction between the host lattice and the guest benzene molecule in the clathrates is based solely on the van der Waals force.

The most interesting fact is that the spectra of benzene in $CoHg_2(SCN)_6 \cdot C_6H_6$, previously reported to be a «$\sigma+\pi$-complex»[18] and not to be a clathrate,[19,20] resemble those of the present clathrates.

In order to estimate the order of these weak interactions, the force constants for the fundamental out-of-plane vibrations of benzene were calculated from the observed wave numbers by the use of a Hitac 5020 high-speed electronic computer using a program set up

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

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(19) R. Bauer, M. Schllenberg and G. Schwarzenbach, *Helv. Chim. Acta*, *45*, 775 (1962).

(20) R. Grønbaek and J. D. Dunitz, *Helv. Chim. Acta*, *47*, 1889 (1964).

**Table IV.** The wave numbers of benzene in several compounds

| | $C_6H_6$ | | | | | $C_6D_6$ | | | | | Assignment |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | I[11] | II* | III[18] | IV[14] | V[15] | VI[11] | VII* | VIII[18] | IX[14] | X[15] | |
| $\nu_{11}(A_{2u})$ | 675 | 704 | 702 | 796 | 784 | 497 | 515 | 514 | 669 | 702 | CH bend. o.p. |
| $\nu_{12}(B_{1u})$ | 1010 | --- | 1010 | | | 970 | --- | 970 | | | ring def. i.p. |
| $\nu_{13}(B_{1u})$ | 3057 | ca. 3026 | 2907 | | | 2285 | 2278 | | | | CH str. i.p. |
| $\nu_{14}(B_{2u})$ | 1309 | 1311 | | | | 1282 | ca. 1280 | | | | ring str. i.p. |
| $\nu_{15}(B_{2u})$ | 1146 | 1147 | | | | 824 | 823 | | | | CH bend. i.p. |
| $\nu_{16}(E_{2u})$ | 405 | 407 | | | | 352 | 356 | 350 | | | ring def. o.p. |
| $\nu_{17}(E_{2u})$ | 975 | 985 | 978 | | | 793 | 801 | 796 | | | CH bend. o.p. |
| $\nu_{18}(E_{1u})$ | 3068 | ca. 3076 | | 3047 | 2931 | 2288 | 2278 | | 2278 | 2215 | CH str. i.p. |
| $\nu_{19}(E_{1u})$ | 1482 | 1476 | 1482 | 1430 | 1445 | 1333 | 1325 | 1325 | 1273 | 1292 | ring. str. + def. i.p. |
| $\nu_{20}(E_{1u})$ | 1037 | 1034 | 1036 | 1002 | 1016 | 814 | 811 | 813 | 803 | 806 | CH bend. i.p. |

I, VI: in gaseous state, II: Cd-Ni-Bz, III: $CoHg_2(SCN)_6 . C_6H_6$, IV: $Cr(C_6H_6)_2$, V: $(C_6H_6)Cr(CO)_3$, VII: Cd-Ni-Bz(D), VIII: $NiHg_2(SCN)_6 . C_6D_6$, IX: $Cr(C_6D_6)_2$, X: $(C_6D_6)Cr(CO)_3$, * present work. ---: The bands could not be detected. i.p. = in-plane, o.p. = out-of-plane.

by the group of Professor Shimanouchi. The force constants obtained are listed in Table V. The observed and calculated wave numbers are also shown in Table VI.

**Table V.** The force constants of fundamental vibrations of benzene (mdyn. Å)

| | in clathrate | in gaseous state[21] |
|---|---|---|
| $\nu_{11}(A_{2u})$: CH bend. o.p. | 0.318 | 0.294 |
| $\nu_{17}(E_{2u})$: CH bend. o.p. | 0.304 | 0.300 |
| $\nu_{16}(E_{2u})$: ring def. o.p. | —0.059, 0.332 | —0.060, 0.325 |

In general, when aniline coordinates to a metal cation, forming an aniline complex as a ligand, a strong band due to the $NH_2$ wagging vibration appears in the 1100-1200 cm$^{-1}$ region.[22] No such features as the shifting of this band from the original position, 670 cm$^{-1}$ or the drastic increase in intensity were found in the present aniline clathrates. Therefore, it does not seem that aniline is coordinating to the metal atom through a chemical bond of such a strength that could be detected by infrared spectroscopy. Thus, these aniline compounds must be clathrates with structures similar to those of benzene.

**Table VI.** The calculated wave numbers of benzene from the force constants (cm$^{-1}$)

| | in clathrate | | | | in gaseous state[21] | | | |
|---|---|---|---|---|---|---|---|---|
| | $C_6H_6$ | | $C_6D_6$ | | $C_6H_6$ | | $C_6D_6$ | |
| | calcd. | obs. | calcd. | obs. | calcd. | obs. | calcd. | obs. |
| $\nu_{11}(A_{2u})$: CH bend. o.p. | 703 | 704 | 516 | 515 | 676 | 675 | 496 | 497 |
| $\nu_{17}(E_{2u})$: CH bend. o.p. | 985 | 985 | 801 | 801 | 975 | 975 | 793 | 793 |
| $\nu_{16}(E_{2u})$: ring def. o.p. | 408 | 407 | 355 | 356 | 405 | 405 | 352 | 352 |

As may be seen in the table, the force constants in the clathrate are larger than the values in the gaseous state.[21] Such a slight increase in the force constant should be attributed to the electron-cloud repulsion between the host lattice and the guest molecules.

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