



# Vibrational Spectroscopic Studies on the $T_d$ -type Adenine metal(II) tetracyanometallate(II) Benzene Clathrates: $M(\text{ad})_2M'(\text{CN})_4 \cdot \text{C}_6\text{H}_6$ ( $M = \text{Mn}$ or $\text{Cd}$ , $M' = \text{Cd}$ or $\text{Hg}$ )

SEVGI BAYARI<sup>a</sup>, CELAL BAYRAK<sup>a</sup> and ZIYA KANTARCI<sup>b</sup>

<sup>a</sup>Hacettepe Üniversitesi, Eğitim Fakültesi, Fizik A.B.D. Beytepe, 06532 Ankara, Turkey;

<sup>b</sup>Gazi Üniversitesi, Fen-Edebiyat Fakültesi, Teknikokullar, 06500 Ankara, Turkey

(Received: 20 November 1998; in final form: 12 August 1999)

**Abstract.** IR spectra of  $\text{Mn}(\text{adenine})_2\text{M}(\text{CN})_4 \cdot \text{C}_6\text{H}_6$  ( $M = \text{Cd}$  or  $\text{Hg}$ ), and IR and Raman spectra of  $\text{Cd}(\text{adenine})_2\text{M}(\text{CN})_4 \cdot \text{C}_6\text{H}_6$  ( $M = \text{Cd}$  or  $\text{Hg}$ ) are reported. The spectral data suggest that the host frameworks of these compounds are similar to those of the Hofmann- $T_d$ -type and the adenine coordination is via N(10).

**Key words:** clathrates, inclusion compounds, adenine, tetracyanometallate, benzene, IR spectra, Raman spectra.

## 1. Introduction

In a recent paper [1], we reported that the IR and Raman spectral results suggest that the structure of  $\text{Mn}(\text{NH}_3)_2\text{M}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$  ( $M = \text{Cd}$  or  $\text{Hg}$ ) compounds are similar to those found in  $T_d$ -type clathrates given with the formula  $\text{Cd}(\text{II})(\text{NH}_3)_2\text{Cd}(\text{II})(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$  [2] and  $\text{Cd}(\text{II})(\text{NH}_3)_2\text{Hg}(\text{II})(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$  [3]. In the host frameworks of these, which are substantially isostructural, the M atom (Cd or Hg) in the  $\text{M}(\text{CN})_4$  unit is tetrahedrally coordinated to the carbon atoms of four cyanide groups, while the cadmium atom is octahedrally surrounded by six nitrogen atoms, two from the  $\text{NH}_3$  ligands attached to the Cd atom in positions trans to each other and four are from cyanide groups. The  $\text{M}(\text{CN})_4$  groups are linked by the  $\text{Cd}(\text{NH}_3)_2$  moieties to form a three-dimensional network. This structure provides two kinds of cavities,  $\alpha$  and  $\beta$ , for the guest molecules. The  $\alpha$  cavity is a rectangular box similar to those in Hofmann-type hosts, while the  $\beta$  cavity is a twisted biprism [2, 3]. The number of guest molecules may vary stepwise from 2, 3/2, 1 to 1/2 according to the number of cavities (0, 1, 2, 3) occupied by substituents [4]. For the present purposes, it is appropriate to mention Hofmann-type clathrates containing ethanolamine as ligand: In the host structure of this clathrate, one of the cavities is occupied by the free end of the ligand [5].

In this paper we present the IR spectra of  $M(\text{adenine})_2M'(\text{CN})_4 \cdot \text{C}_6\text{H}_6$  ( $M=\text{Mn}$ ,  $M'=\text{Cd}$  or  $\text{Hg}$ ) (abbreviated to  $M\text{-ad-}M'\text{-Bz}$ ) and IR and Raman spectra of the  $\text{Cd}(\text{adenine})_2M'(\text{CN})_4 \cdot \text{C}_6\text{H}_6$  ( $M'=\text{Cd}$  or  $\text{Hg}$ ) compounds and adenine.

## 2. Experimental

All starting chemicals used were reagent grade (Merck) and used without further purification.

The clathrates  $M\text{-ad-}M'\text{-Bz}$  ( $M'=\text{Cd}$  or  $\text{Hg}$ ) in fine powder form were synthesized by adding 2 mmol of adenine solution in alcohol and 1 mmol of  $\text{K}_2\text{M}(\text{CN})_4$  ( $M=\text{Cd}$  or  $\text{Hg}$ ) solution in water to 1 mmol of  $\text{MCl}_2$  ( $\text{Mn}$  or  $\text{Cd}$ ) solution in water. The precipitate formed was filtered, washed with water, ethanol and ether successively and kept in a desiccator.

The host complexes  $\text{Cd-ad-Cd}$  and  $\text{Cd-ad-Hg}$  were prepared by a similar method to that given above in the absence of benzene. The freshly prepared compounds were analyzed for C, H and N [the  $\text{Cd}(\text{en})\text{Cd}(\text{CN})_4$  complex [6] has been used as a reference] with the following results (found %/calculated %):

$\text{Cd}(\text{C}_5\text{H}_5\text{N}_5)\text{Cd}(\text{CN})_4 \cdot \text{C}_6\text{H}_6$ :	C = 35.27/35.46	H = 2.29/2.38	N = 28.63/28.95
$\text{Cd}(\text{C}_5\text{H}_5\text{N}_5)\text{Hg}(\text{CN})_4 \cdot \text{C}_6\text{H}_6$ :	C = 31.14/31.38	H = 2.21/2.10	N = 25.27/25.61
$\text{Mn}(\text{C}_5\text{H}_5\text{N}_5)\text{Cd}(\text{CN})_4 \cdot \text{C}_6\text{H}_6$ :	C = 38.17/38.75	H = 2.69/2.60	N = 31.08/31.64
$\text{Mn}(\text{C}_5\text{H}_5\text{N}_5)\text{Hg}(\text{CN})_4 \cdot \text{C}_6\text{H}_6$ :	C = 33.69/33.93	H = 2.86/2.28	N = 28.01/27.70
$\text{Cd}(\text{C}_5\text{H}_5\text{N}_5)\text{Cd}(\text{CN})_4$	C = 35.16/35.07	H = 1.91/1.80	N = 27.21/22.54
$\text{Cd}(\text{C}_5\text{H}_5\text{N}_5)\text{Hg}(\text{CN})_4$	C = 24.31/24.46	H = 1.41/1.46	N = 28.71/28.53

The IR spectra of the compounds were recorded between 4000 and  $200\text{ cm}^{-1}$  on Perkin Elmer 621 and Mattson 1000 FTIR spectrometers, which were calibrated using polystyrene. The samples were prepared as mulls (without grinding) in nujol and hexachlorobutadiene between CsI plates. Raman spectra of the  $\text{Cd-ad-Cd-Bz}$  and  $\text{Cd-ad-Hg-Bz}$  clathrate compounds (in powder form) in a home-made spinning cell were excited using the 514.5 nm line of a Spectra-Physics Model 2016-4S argon-ion laser and recorded on a Jobin-Yvon U1000 spectrometer which was calibrated against the laser plasma emission lines.

## 3. Results and Discussion

Before embarking upon the vibrational features of the compounds, a word may be in order regarding the number of benzene molecules accommodated. In spite of our efforts to trap more benzene molecules in the host structure of the present clathrates, we have only obtained the composition  $M(\text{ad})_2M'(\text{CN})_4 \cdot \text{C}_6\text{H}_6$ . The decrease of the number of benzene molecules from 2 in  $\text{en-T}_d$ -type [6] and Hofmann- $T_d$ -type [1] clathrates to 1 in our cases may be due to the bulkiness of the adenine

ligand; therefore, one of the cavities may be occupied by a pair of imidazole rings and so only the other cavity may be effective in accommodating the guest molecule.

The spectral features of the compounds under study are found to be similar to each other, suggesting that they also have similar structural features. The IR spectra of the Cd-ad-Cd-Bz clathrate and the Cd-ad-Cd complex are shown in Figure 1 (a and b) as representative illustration. It will be convenient to divide the vibrations into three groups arising from the adenine ligand, from the  $M(CN)_4$  units and from the benzene moieties. The spectral bands due to the  $M'(CN)_4$  and benzene species are straightforward since these bands are persistent and picked out with ease [1, 7–9]. The vibrational wavenumbers of the bands in the spectra of these species are tabulated in Tables I–III, respectively, along with some relevant spectral data for comparison.

### 3.1. ADENINE VIBRATIONS

For adenine (6-aminopurine) several tautomeric forms can be envisaged in the isolated state. The N(9)H aminic form being the most stable is established by theoretical calculations [10, 11], infrared and Raman [12, 13], NMR [14], microwave [15] and ultraviolet photoelectron studies [16] but in more polar environments the polar N(7)H form may be more stable [17]. These two forms are illustrated in Figure 2.

In dealing with the band assignments of the adenine in the compounds studied, the N<sub>9</sub>H form will be treated. This treatment is reasonable in that in the proposed structure, there is the possibility that two adenine molecules may be tail to tail in such a way that the H atom of one N(9)H tautomer is bound to the N(3) donor atom of the other and vice versa. Such a hydrogen bonding may stabilize the N(9)H form.

In spite of the high complexity of adenine molecule and its lack of symmetry, considerable efforts have been made to characterize its vibrational bands, since it is one of the components of nucleic acids which are constituents of DNA and RNA, the biologically most important molecules. Of the vibrational studies of adenine, two reports are relevant for our purpose. Hirakawa *et al.* examined Raman and infrared spectra of adenine, adenine-1,3- $^{15}N_2$ , adenine-2- $^{13}C$  and adenine-8- $^{13}C$ , and their amino- $d_2$ -9-d derivatives in crystalline powders [12]. Based on these spectral data, together with a single-crystal infrared spectrum of 9-methyladenine [18] and infrared spectra of six different deuterated derivatives of adenine [19], the fundamental bands of adenine in the 1800–200  $cm^{-1}$  region were assigned. These assignments have also been supported by a normal coordinate treatment through an *ab initio* MO calculation of the force constants of adenine [10, 20] (Table I). Nowak *et al.* presented infrared spectra of adenine and its  $^{15}N$  isotopomers with  $^{15}N$  at the N(9) or N(7) positions isolated in a low-temperature matrix of argon and compared those with the spectra predicted at the DFT (density functional theory with the Becke3-LYP functions using the 6-31G (d, p) basis set) level (Table I) [11]. It

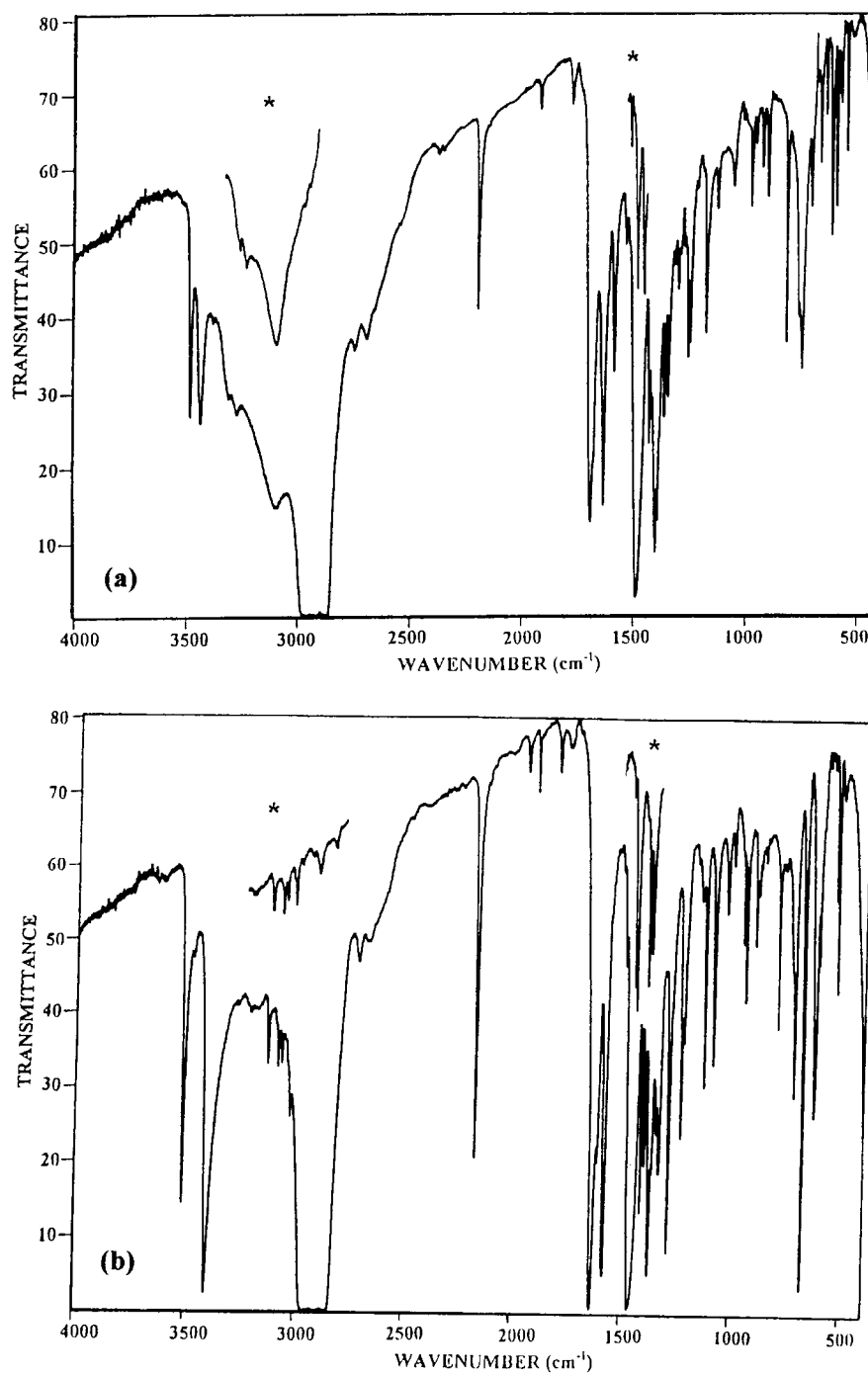


Figure 1. The infrared spectra of the Cd-ad-Cd complex (a) and the Cd-ad-Cd-B clathrate (b) in nujol (\* in hexachlorobutadiene).

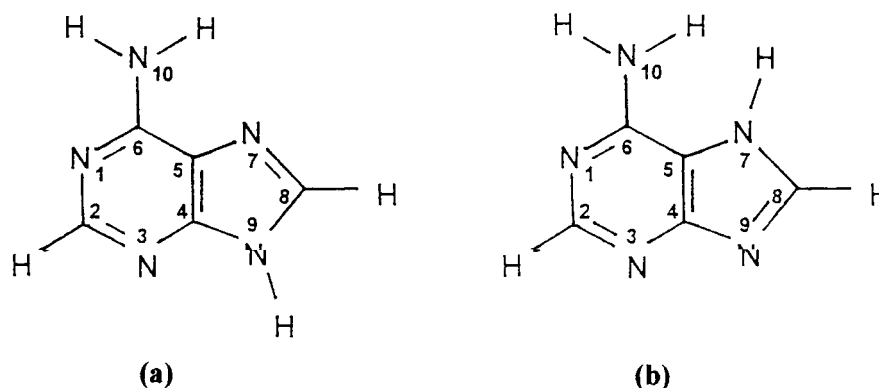


Figure 2. The N(9)H (a) and N(7)H; (b) tautomers of adenine.

should be noted that the infrared spectra of gas-phase adenine have been recorded from 100 to 3700  $\text{cm}^{-1}$  [21]. The wavenumbers of the fundamental vibrations of adenine in powder form, and in an argon matrix, and their assignment given by Hirakawa *et al.* [12] and Nowak *et al.* [11], respectively, are presented in Table I. Table I also tabulates the wavenumbers predicted from the DFT (density functional theory) [11] and the gas-phase infrared spectra of adenine for comparison [21]. A glance at Table I shows that there are several discrepancies between the two assignments given by Hirakawa *et al.* [21] and Nowak *et al.* [11]. These cannot be assessed here.

From Table I it is clear that the assignments of the fundamental bands in the 4000–1800  $\text{cm}^{-1}$  region due to the stretching vibrations of N-H and C-H bands are straightforward while the proper assignment of the bands in the 1800–200  $\text{cm}^{-1}$  region, on the basis of experimental data only, is practically not possible. The notable spectral features are the following:

The  $\text{NH}_2$  stretching frequencies of the adenine molecules in the clathrate compounds are found to be ca. 50  $\text{cm}^{-1}$  lower than those of adenine in an Ar matrix (Table I). In addition, the C(6)- $\text{NH}_2$  stretching frequencies in the clathrates are ca. 15  $\text{cm}^{-1}$  lower than that of adenine in the solid form. These downward frequency shifts may be explained as weakening of the N(10)-H and C(6)-N(10) bands resulting from the electrons draining from the N(10) atom on account of its coordination to the metal atom M. The infrared band observed at ca. 1088  $\text{cm}^{-1}$  in the clathrate compounds are assigned to the  $\omega(\text{NH}_2)$  wagging vibration, which appears at 660  $\text{cm}^{-1}$  in solid adenine. Such a large upward frequency shift of the  $\omega(\text{NH}_2)$  mode in Hofmann-type aniline complexes,  $\text{M}(\text{aniline})_2\text{M}'(\text{CN})_4$  (M=Mn, Fe, Co or Cu and M'=Ni, M=Ni or Cd and M'=Pt), is suggested to be due to the effect of the changes in hybridization about the nitrogen atom, caused by the binding of the metal (M) to the N(10) site [22]. Similar shifts have been observed in other metal complexes of aniline [23]. It should be noted that the six-membered ring and five-membered ring in-plane stretching bands remain essentially unaltered suggesting that the expected

second coordination site (possibly N(3) or N(9)) is not possible to be assigned [13, 24].

### 3.2. $M'(CN)_4$ GROUP VIBRATIONS

The fact that in the host framework of the  $T_d$ -type clathrates [1, 7, 8] and the  $T_d$ -type host complexes [9] the metal atom  $M'$  in  $M'(CN)_4$  is tetrahedrally surrounded by the carbon ends of four CN ions suggests that the host framework of the clathrates studied here also have tetrahedral  $M'(CN)_4$  units. In order to assign the bands attributable to the  $M'(CN)_4$  ( $M' = \text{Cd}$  or  $\text{Hg}$ ) ion in the spectra of our clathrate compounds, we refer to the work of Jones who presented vibrational data for the salts  $K_2M'(CN)_4$  ( $M' = \text{Cd}$  or  $\text{Hg}$ ) in the solid state [25]. The structural studies on these salts have shown that the K-NC distance is ca. 2.9 Å in  $K_2\text{Cd}(\text{CN})_4$  [26], and  $K_2\text{Hg}(\text{CN})_4$  [27], while the Cd-NC distances are ca. 2.3 Å in  $T_d$ -type host frameworks [4]. Therefore, they can be used as references to account for the vibrational changes when the stiffer Cd-NC bonding takes place. The vibrational data for  $M'(CN)_4$  groups in the clathrate compounds under study are given in Table II, together with the vibrational wavenumbers of  $K_2\text{Cd}(\text{CN})_4$  and  $K_2\text{Hg}(\text{CN})_4$  [25]. Table II also lists the wavenumbers of the infrared and Raman spectra of the  $\text{Cd}(\text{CN})_4$  unit in the  $\text{Cd}(\text{NH}_3)_2\text{Cd}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$  clathrate [1] for comparison. The assigned wavenumbers for the  $M'(CN)_4$  group in the compounds studied appear to be much higher than those for  $M'(CN)_4$  groups in  $K_2M'(CN)_4$  ( $M' = \text{Cd}$  or  $\text{Hg}$ ) (Table II). Such frequency shifts have been observed for other Hoffman- $T_d$ -type clathrates [1, 7] and Hoffman- $T_d$ -type host complexes [8, 9], in which both ends of the CN group are coordinated and explained as the mechanical coupling of the internal modes of  $M'(CN)_4$  ( $M = \text{Zn}$ ,  $\text{Cd}$  or  $\text{Hg}$ ) with the metal M-NC vibrations. It follows that the N-ends of the  $M'(CN)_4$  groups are also bound to a M atom in our clathrate compounds. Another notable feature is that  $\nu_5$  is at a higher frequency for Cd ( $2179 \text{ cm}^{-1}$ ) than for Mn ( $2177 \text{ cm}^{-1}$ ) suggesting that the strength of the Cd-N bond is higher than that of the Mn-N bond. This is due to the fact that the second ionization potential of Cd is higher than that of Mn.

### 3.3. BENZENE VIBRATIONS

The assignments and the frequencies of the vibrational bands arising from the enclathrated benzene observed in the spectra of the  $M(\text{adenine})_2M'(CN)_4 \cdot \text{Bz}$  ( $M = \text{Mn}$ ,  $M' = \text{Cd}$  or  $\text{Hg}$ ;  $M = \text{Cd}$ ,  $M = \text{Cd}$  or  $\text{Hg}$ ) compounds are given in Table III, along with the wavenumbers of benzene in the liquid phase [28] and in the  $\text{Cd}(\text{NH}_3)_2\text{Cd}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$  clathrate [1] for comparison. The most structurally informative spectral features are the following.

The CH out-of-plane mode ( $A_{2u}$ ) in the spectra of the clathrates are found to be shifted to higher frequency ( $681 \text{ cm}^{-1}$ ) (Table III) from that of liquid benzene ( $670 \text{ cm}^{-1}$ ). Similar positive frequency shifts were observed for Hofmann- $T_d$ -type [1,

Table I. The infrared wavenumbers ( $\text{cm}^{-1}$ ) of adenine in the M-ad-M'-Bz clathrates\*

Gas-phase Adenine <sup>a</sup> IR	Adenine in a Ar matrix <sup>b</sup>		Theory (DFT) potential energy distribution <sup>b</sup>	Adenine as crystalline powder <sup>c</sup>		Assignment <sup>c</sup>	Cd-ad- Cd-Bz	Cd-ad- Hg-Bz	Mn-ad- Cd-Bz	Mn-ad- Hg-Bz	Cd-ad-Cd	Cd-ad-Hg
	IR	I(rel)		IR	R							
3552m	3565 3557 3555 3552 3552	84	$\nu(\text{NH}_2)$ antisym (100)	–	–	–	3512m	3512m	3512vs	3514vs	no	no
3501s	3506 3503 3502 3498 3494 3489	135	$\nu(\text{N9H})$ (100)	–	–	–	3473m	3479sh	no	no	3474m 3455vw	3474m
3434s	3448 3441 3438	110	$\nu(\text{NH}_2)$ sym (100)	–	–	–	3406s 3265m 3132w	3402s no 3134w	3404s no 3140w	3404s no 3138w	3424m 3263m no	3423m no
3061m	3057	6	$\nu \text{C8H}(99)$	–	–	–	3070vw	no	no	no	no	3070vw
–	3041	3	$\nu \text{C2H}(100)$	–	–	–	no	3052vw	3043vw	3043vw	3051vw	no
1625vs	1639		$\beta \text{NH}_2$ scis(28)	1673vs,b	1677vw	$\text{NH}_2$ scis	1641vs	1641vs	1641vs	1633	1669vs	1669s
1625vs	1633	447	$\nu \text{C6N10}(21), \nu \text{C5C6}(19)$									
–	–	–	–	1638w	–	$\nu_1$	1612m	1618sh	1624sh	1623sh	1611vs	1611s
–	1612	219	$\nu \text{N3C4}(27), \nu \text{C5C6}(12)$	1604vs,b	1612w 1597w	$\nu_2$	1585vs	1585vs	1583vs	1583s	1564m	1564m
–	–	–	–	1508m	1514vw 1508m	$\nu_3$	1514w	1525w	1529vw	no 1516vw	1518w 1512w	1517w
–	1482	11	$\nu \text{N7C8}(48), \beta \text{C8H}(12)$	–	1485	$\nu_4$	1497w	1497w	1498sh	1497sh	no	no
–	–	–	–	–	1482m	–	1470s	1470s	1470s	1468s	1475w	1475w
1468s	1474	71	$\nu \text{C6N1}(24), \beta \text{C2H}(22),$ $\nu \text{C6N1O}(13),$ $\beta \text{NH}_2$ scis (12), $\nu \text{C2N3}(12)$	1451m	1462w 1442vw	$\text{N}(9)\text{-H}$ bend	1462w	no	1465w	no	1468m	1468m

Table I. Continued.

Gas-phase Adenine <sup>a</sup> IR	Adenine in a Ar matrix <sup>b</sup>		Theory (DFT) potential energy distribution <sup>b</sup>	Adenine as crystalline powder <sup>c</sup>		Assignment <sup>c</sup>	Cd-ad- Cd-Bz	Cd-ad- Hg-Bz	Mn-ad- Cd-Bz	Mn-ad- Hg-Bz	Cd-ad-Cd	Cd-ad-Hg
	IR	I(rel)		IR	R							
1415s	1419	49	$\nu$ C4C5(27), $\nu$ C4N9(21)	1421s	1419w	$\nu_5$	1429w	1433cq	1439w	1440cw	1431m	1431m
–	1389	45	$\beta$ N9H (27), $\beta$ C2H (27), $\nu$ C8N9 (14), $\beta$ R1 (12)	1368m	1371m	C(2)-H bend	1417m	1417m	1416m	1416m	1404s	1403s
1346(sh)m	1345	21	$\nu$ N9C8 (20), $\beta$ C8H (13), $\beta$ N9H(10), $\nu$ C6N1 (10)	–	–	–	1348sh	(1338)m				no
–	1334	7	–	1335s	1332s	$\nu_6$	(1337)w	1336m	1336m	1334m	1335m	1335m
1326s	1328	40	$\nu$ N1C2(31), $\nu$ C5N7(19), $\beta$ C2H(11)	1309s	1307m	$\nu_7$	1290s	1290vs	1288vs	1288vs	1291w	1273w
1280s	1290	68	$\nu$ C2N3(43), $\nu$ C5N7(13), $\nu$ N1C2 (10)	–	–	–	no	no	no	no	no	no
–	–	–	–	1253s	1249m	C(6)-NH <sub>2</sub> str.	1234s	1236s	1236ms	1234s	1230m	1230m
–	1240	28	$\beta$ C8H (36), $\nu$ N7C8 (16), $\beta$ N9H(10)	–	–	–	no	no	no	no	no	no
1234s	1229	13	$\beta$ NH <sub>2</sub> rock (26), $\nu$ C5N7 (22)	1234w,sh	1235w	$\nu_8$	1221m	1223m	1223sh	1225sh	1220m	1220m
–	–	–	–	1157m	1163w	C(8)-H bend	1159w	1146vw	1155w	1150w	1152m	1152m
1126w	1127	6	$\nu$ C4N9(20), $\beta$ r4(10), $\nu$ C6N10 (10)	1126s	1126m	$\nu_9$	1130m	1130s	1128s	1128s	no	no
–	1032	27	$\nu$ C8N9 (55), $\beta$ N9H (32)	1025s	1025w	NH <sub>2</sub> rock	103 Sm	1036m	1036m	1034m	1033w	1033vw
957w	958	3	$\gamma$ C2H(108)	951w,sh	952w,sh	$\nu_{14}$	no	no	no	no	no	no
–	–	–	–	940s	941m	C(8)-H bend	(944)m	(945)m				
–	–	–	–	–	–	–	947mw		945m	943m	949vw	954vw
926vw	927	13	$\beta$ r4 (42), $\beta$ r5 (32), $\nu$ C4C5 (11)	913s	899w	$\nu_{11}$	903m	903m	903m	903m	905w	905w
–	887	8	$\beta$ R1 (49), $\beta$ R3 (15)	872m,br	–	N(9)-H bend	883m	889m	889m	891mw	881mw	880w
847w	848	6	$\gamma$ C8H (90)	849m	846vw	C(2)-H bend	no	no	no	no	no	no
–	–	–	–	844m	840vw	–						



Table I. Continued.

Gas-phase Adenine <sup>a</sup> IR	Adenine in a Ar matrix <sup>b</sup>		Theory (DFT) potential energy distribution <sup>b</sup>	Adenine as crystalline powder <sup>c</sup>		Assignment <sup>c</sup>	Cd-ad- Cd-Bz	Cd-ad- Hg-Bz	Mn-ad- Cd-Bz	Mn-ad- Hg-Bz	Cd-ad-Cd	Cd-ad-Hg
	IR	I(rel)		IR	R							
801w	802	9	$\tau$ R1 (46), $\tau$ r4 (20), $g$ C6N1O (19), $\gamma$ C8H(15)	797m	797vw	$\nu_{16}$	795m	796m	796m	796m	796s	795s
–	717	5	$\nu$ N3C4 (20), $\beta$ r4 (14), $\nu$ C5N7 (11), $\nu$ C4N9 (10)	723s	724vs	$\nu_{10}$ ring breat.	(720)m	(724)m				
–	698	2	–	684w,sh	–	$\nu_{19}$	no	no	no	no	686m	686m
–	–	–	–	660s,vb	–	NH <sub>2</sub> wag	1088m	1089s	1088s	1086s	1079w	no
650 vw	655	6	$\tau$ r4 (52), $t$ r5 (36)	641m	–	$\nu_{20}$	638s	630m	633w	629w	620w	620w
600vw	610	5	$\beta$ r5 (29), $\nu$ C5C6 (21), $\beta$ R2 (17)	622m	623m	$\nu_{12}$	(618)s	(614)ms				
563w	566	46	$\tau$ R2 (27), $\gamma$ N9H (24), $\tau$ R1 (23) $\tau$ r5 (12)	–	560w	–	no	no	no	no	573m	573m
–	–	–	–	543s	535m	$\nu_{13}$	(533)w	no				
–	–	–	twist NH <sub>2</sub> (62)	–	530w,sh	$\nu_{15}$	no	no	no	no	no	no
–	–	–	–	530w	–	$\nu_{18}$	530sh	no	no	no	no	no
–	–	–	–	380w	–	NH <sub>2</sub> tor	389s	389s	389s	389s	394m	393m
–	–	–	–	337m	331s	C(6)-NH <sub>2</sub>	(311)m	(313)m				
–	–	–	–	–	327s	bend	310w	310w	310w	310,v	320w	315w

\* Raman bands are in parentheses.

a,b,c Taken from refs [21, 11, 12 ], respectively.

v = very, s = strong, w = weak, sh = shoulder, br = broad, no; not observed.

Table II. The vibrational wavenumbers ( $\text{cm}^{-1}$ ) of the  $M'(CN)_4$  group for the M-ad- $M'$ -Bz clathrates\*

Assignment	$K_2Cd(CN)_4^a$	$K_2Hg(CN)_4^a$	$Cd-(NH_3)_2-Cd-2Bz^b$	Cd-ad-Cd-Bz	Cd-ad-Hg-Bz	Mn-ad-Cd-Bz	Mn-ad-Hg-Bz	Cd-ad-Cd	Cd-ad-Hg
$\nu_5(CN)A_1$	(2149)	(2149)	(2178)vs	(2185)s	(2185)s	no	no	no	no
$\nu_2(MC)A_1$	(324)	(335)	–	no	no	no	no	no	no
$\nu_3[\delta(MCN)]E$	–	–	–	no	no	no	no	no	no
$\nu_4[\delta(CMC)]E$	–	–	–	no	no	no	no	no	no
$\nu_5(CN)F_2$	2145	2146	2165vs	2179vs	2179vs	2177vs	2177vs	2167s	2167s
Hot band?	–	–	2154vw	2167vw	2167vw	2164vw	2169vw	2147vw	2147vw
$\nu_5[^{13}CN]$	–	–	2135vw	2142vw	2142vw	2140vw	2141vw	2129vw	2129vw
$\nu_6[\nu(MC) + \delta(NCM)]F_2$	316	330	368s	370s	370s	384s	384s	370s	370s
$\nu_7[\nu(MC) + \delta(NCM)]F_2$	250	235	–	283w	277w	277w	277w	285w	286w

\* Raman bands are in parentheses.

<sup>a</sup> Taken from ref. [25].

<sup>b</sup> Taken from ref. [1].

vs = very strong, s = strong, w = weak, m = medium, sh = shoulder; no: not observed.

Table III. The vibrational wavenumbers ( $\text{cm}^{-1}$ ) of benzene in the M-ad-M'-Bz clathrates\*

Assignment <sup>a</sup>	Benzene <sup>b</sup> (Liquid)	Cd-(NH <sub>3</sub> ) <sub>2</sub> -Cd-Bz <sup>c</sup>	Cd-ad-Cd-Bz	Cd-ad-Hg-Bz	Mn-ad-Cd-Bz	Mn-ad-Hg-Bz
$\nu_8$	(3166)	no	no	no	no	no
$\nu_{20}$ E <sub>1u</sub>	3073	3080in	3086m	3086m	3088m	3086m
$\nu_8 + \nu_9$	3075	3064m	3076w	3068w	3070w	3068m
$\nu_{13}$ B <sub>1u</sub>	3048	3028s	3030m	3030mw	3032m	3030w
$\nu_2$ A <sub>1g</sub>	(3062)	(3060)m	(3070)w	no	no	no
$\nu_7$ E <sub>2g</sub>	(3050)	(3040)w	(3041)vw	(3049)vw	no	no
$\nu_5 + \nu_{17}$ E <sub>1u</sub>	1955	no	1957w	1957w	1959vw	1957vw
$\nu_8$ E <sub>2g</sub>	(1586)	(1580)w	(1585)m	(1585)m	no	no
$\nu_{10} + \nu_{17}$	1815	no	1815w	1815vw	1815w	1815w
$\nu_{19}$ E <sub>1u</sub>	1479	1477m	1477s	1477s	1479s	1477ms
$\nu_{14}$ B <sub>2u</sub>	1309	no	no	1307w	no	no
$\nu_9$ E <sub>2g</sub>	(1177)	(1174)m	(1171)vw	(1171)vw	no	no
$\nu_{15}$ B <sub>2u</sub>	1149	1145sh	1154vw	1146vw	1155vw	1150vw
$\nu_{18}$ E <sub>1u</sub>	1036	1032w	1034m	1036m	1036m	1034m
$\nu_1$ A <sub>1g</sub>	(991)	(989)vs	(991)m	(992)m	no	no
$\nu_{10}$ E <sub>1g</sub>	(850)	(854)w	(849)vw	(849)vw	no	no
$\nu_{11}$ A <sub>2u</sub>	670	698s 686vs	681vs	681vs	681vs	681vs

\* Raman bands are in parentheses.

<sup>a</sup> Taken from ref. [33].

<sup>b</sup> IR bands from ref. [28] and Raman bands from ref. [34].

<sup>c</sup> Taken from ref. [1].

v = very, s = strong, w = weak, m = medium, no = not observed.

7] clathrates and Hofmann-type clathrates [29]. Akyüz *et al.* [29], explained this upward shift by the presence of a weak hydrogen bond between the  $\pi$  electrons located above and below the plane of the benzene ring and the ammonia molecules of the host lattice. Therefore, we may reasonably suggest that the frequency shifts in our clathrate compounds are due to the  $\pi$  electron donation from the benzene ring to the hydrogen atoms of adenine which has a more electrophilic character caused by the coordination.

Another essential feature of the out-of-plane CH bending vibration ( $A_{2u}$ ) is that it appears as a very intense single band at  $681\text{ cm}^{-1}$  in the infrared spectra of the clathrate compounds (Table III). A similar single band was observed in the infrared spectra of the  $\text{Cd}(4,4'\text{-bipyridyl})\text{M}'(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$  [30]. This vibrational mode splits into a doublet in  $\text{Cd}(\text{pyrazine})\text{M}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$  ( $\text{M}=\text{Cd}$  or  $\text{Hg}$ ) [31] and  $\text{M}(\text{NH}_3)_2\text{M}'(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$  ( $\text{M}=\text{Mn}$  or  $\text{Cd}$ ,  $\text{M}'=\text{Cd}$  or  $\text{Hg}$ ) [1] and into a triplet in  $\text{M}(\text{ethylenediamine})\text{M}'(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$  ( $\text{M}=\text{Mn}$  or  $\text{Cd}$ ,  $\text{M}'=\text{Cd}$  or  $\text{Hg}$ ) [7]. In the case of clathrates with triplet or doublet features, the splittings have been ascribed to crystal field effects (strong host-guest interactions) [7]. In the case of clathrates with a single band, because of the larger cavities due to the ligands, the host-guest interactions are expected not to be effective for splitting [30].

Based on the present spectral data, it is not possible to determine the conformation of the benzene molecules in the host lattice in our clathrate compounds. As in the Hofmann-type benzene and Hofmann- $T_d$ -type benzene clathrates, the relative orientation of the N-H bands of adenine with respect to the axis of the  $\pi$  cloud of benzene must be the one most favourable for hydrogen bonding [32].

The preceding discussion considered as a whole leads us the conclusion that the host lattice of these clathrates are similar to those of other  $T_d$ -type clathrates.

## References

1. E. Kasap and Z. Kantarcı: *J. Incl. Phenom.* **20**, 33 (1995).
2. H. Yuge and T. Iwamoto: *J. Incl. Phenom.* **14**, 217 (1992).
3. R. Kurada: *Inorg. Nucl. Chem. Lett.* **9**, 13 (1973).
4. T. Iwamoto: 'The Hofmann-type and Related Inclusion Compounds', in J. L. Atwood, J. E. D. Davies and D. D. MacNicol (eds.), *Inclusion Compounds V*, Academic Press, 1984, pp. 29–57.
5. S. Nishikiori and T. Iwamoto: *Chem. Lett.* 1775 (1981).
6. S. Nishikiori and T. Iwamoto: *J. Incl. Phenom.* **3**, 283 (1985).
7. E. Kasap and Z. Kantarcı: *J. Incl. Phenom.* **23**, 1 (1995).
8. Z. Kantarcı, C. Bayrak, and S. Bayari: *J. Mol. Struct.* **407**, 155 (1997).
9. Z. Kantarcı, N. Karacan and B. Davarcıoğlu: *J. Mol. Struct.* **53**, 323 (1994).
10. Y. Nishimura, M. Tsuboi, S. Kato, and K. Morokuma, in J. Lascombe and P. V. Huang (eds.), *Raman Spectroscopy, Linear and Nonlinear*, Wiley, Chichester, UK, 1982, p. 703.
11. M. J. Nowak, L. Lapinski, J. S. Kwiatkowski, and J. Leszczynski: *J. Phys. Chem.* **100**, 3527 (1996).
12. A. Y. Hirakawa, H. Okada, S. Sasagawa, and M. Tsuboi: *Spectrochim. Acta* **41A**, 209 (1985).
13. A. Bertoluzza, C. Fagnano, R. Tosi, M. A. Morelli, and D. A. Long: *J. Raman Spectrosc.* **18**, 83 (1987).

14. N. C. Gonnella, H. Nakanishi, J. B. Holtwick, D. S. Horowitz, K. Kanamori, N. J. Leonard, and J. D. Roberts: *J. Am. Chem. Soc.* **105**, 2050 (1983).
15. R. D. Brown, P. D. Godfrey, D. McNaughton, and A. P. Pierlot: *Chem. Phys. Lett.* **156**, 61 (1989).
16. J. Lin, C. Yu, S. Peng, I. Akiyama, K. Li, L. Kao Lee, and P. R. LeBreton: *J. Am. Chem. Soc.* **102**, 4627 (1980).
17. M. J. Nowak, L. Lapinski and J. S. Kwiatkowski: *Chem. Phys. Lett.* **157**, 14 (1989).
18. Y. Kyogoku, S. Higuchi, and M. Tsuboi: *Spectrochim. Acta* **23A**, 969 (1967).
19. M. Tsuboi and Y. Kyogoku, in W. W. Zorbach and R. S. Typson (eds.), *Synthetic Procedures in Nucleic Acid Chemistry*, Vol. 2, p. 215, Wiley, New York (1973).
20. Y. Nishimura, M. Tsuboi, S. Kato, and K. Morokuma, *Molecular Structure Symposium, Chemical Society of Japan*, Paper 4A 09 (1981).
21. P. Colarusso, K. Q. Zhang, B. Guo and P. F. Bernath: *Chem. Phys. Lett.* **269**, 39 (1997).
22. S. Akyüz and J. E. D. Davies: *J. Mol. Struct.* **95**, 157 (1982).
23. D. A. Thornton: *J. Coord. Chem.* **24**, 261 (1991).
24. S. Shirotake: *Chem. Pharm. Bull.* **28**, 1673 (1980).
25. L. H. Jones: *Spectrochim. Acta* **17**, 188 (1961).
26. B. Ziegler and D. Babel: *Z. Naturforsch.* **46B**, 47 (1991).
27. P. N. Gerlach and B. M. Powell: *J. Chem. Phys.* **85**, 6004 (1989).
28. P. C. Painter and J. L. Koenig: *Spectrochim. Acta* **33A**, 103 (1977).
29. S. Akyüz, A. B. Dempster, and R. L. Morehouse: *Spectrochim. Acta* **30A**, 1989 (1974).
30. S. Bayari, Z. Kantarcı, and S. Akyüz: *J. Incl. Phenom.* **17**, 291 (1994).
31. N. Ekici, Z. Kantarcı, and S. Akyüz: *J. Incl. Phenom.* **10**, 9 (1991).
32. E. Ruiz, J. J. Novoa and S. Alvarez: *J. Phys. Chem.* **99**, 2296 (1995).
33. E. B. Wilson: *Phys. Rev.* **45**, 706 (1934).
34. J. E. D. Davies, A. B. Dempster, and R. L. Suziki: *Spectrochim. Acta* **30A**, 1183 (1974).

