



Guest–Host Interactions in Hofmann- T_d -type Aniline Clathrates: IR Spectral Study

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Abstract. Synthesis and IR spectra of novel Hofmann- T_d -type aniline clathrates, $M(\text{NH}_3)_2\text{Zn}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_5\text{NH}_2$ ($M = \text{Zn}$ or Cd) are reported for the first time. All the vibrational modes of aniline are characterised. The shifts in $\nu_a(\text{NH}_2)$ and $\nu_s(\text{NH}_2)$ reveal hydrogen bonding between the NH_2 group of aniline and the cyanide group of the host lattice to be stronger than in Hofmann-type aniline clathrates. However, the out of plane deformation mode of aniline indicates absence of hydrogen bonding between ammonia and the π -cloud of the aniline ring. The related aniline clathrates with bridging $\text{Cd}(\text{CN})_4$, $M(\text{NH}_3)_2\text{Cd}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_5\text{NH}_2$ ($M = \text{Zn}$ or Cd), exhibit similar behaviour.

Key words: inclusion compounds, Hofmann- T_d -type clathrates, IR study, guest–host interactions, hydrogen bonding

1. Introduction

Inclusion compounds are formed by host lattices with voids or tunnels in which guest molecules are enclathrated. Although organic compounds are well known to show inclusion behaviour, only a very few inorganic complexes exhibit such a property, notable examples being the Hofmann-type and related clathrates which originate from the ammine- or amine-metal(II)-tetracyanometallate(II) host structures [1]. Studies on guest–host interactions in inclusion compounds are of current interest due to the importance of these compounds in molecular recognition, separation of isomers and synthesis of asymmetric and polymeric compounds [1–3]. Guest–host interactions in these clathrates provide an explanation for the effects of enclathration on the structural and spectroscopic properties of both the guest and the host molecules. Despite being weak in nature, these interactions produce

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significant changes in IR, Raman, EPR, NMR and optical spectra of the inclusion compounds [4–14]. The origin of the guest–host interactions varies from charge transfer forces to hydrogen bonding [15, 16] and to weak Van der Waals interactions. Hofmann-type clathrates form typical models for studying such interactions [17–19].

In contrast to the Hofmann-type, Hofmann-en-type or Hofmann- T_d -type benzene clathrates [20–28], studies on the Hofmann- T_d -type aniline clathrates are very limited. The only reference available provides partial IR data for the Hofmann- T_d -type aniline clathrate, $\text{Cd}(\text{NH}_3)_2\text{Hg}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_5\text{NH}_2$ (abbreviated to Cd-Hg-An) [29] wherein the synthesis of $\text{Cd}(\text{NH}_3)_2\text{Cd}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_5\text{NH}_2$ (abbreviated to Cd-Cd-An) is also given. Nevertheless, Hofmann- T_d -type aniline clathrates with $\text{Cd}(\text{CN})_4$ or $\text{Zn}(\text{CN})_4$ units have not been subjected to detailed IR study. Only the synthesis and crystal structures of $\text{Cd}(\text{NH}_3)_2\text{Cd}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_5\text{NH}_2$ are available [29, 30]. This prompted us to synthesise the clathrates of the type, $\text{M}(\text{NH}_3)_2\text{M}'(\text{CN})_4 \cdot 2\text{C}_6\text{H}_5\text{NH}_2$ (M and M' = Zn and Cd) and to study the guest–host interactions in these clathrates by IR spectroscopy. The clathrates studied are,

- (1) $\text{Cd}(\text{NH}_3)_2\text{Zn}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_5\text{NH}_2$ (abbreviated to Cd-Zn-An),
- (2) $\text{Zn}(\text{NH}_3)_2\text{Zn}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6\text{NH}_2$ (abbreviated to Zn-Zn-An),
- (3) $\text{Cd}(\text{NH}_3)_2\text{Cd}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_5\text{NH}_2$ (abbreviated to Cd-Cd-An),
- (4) $\text{Zn}(\text{NH}_3)_2\text{Cd}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_5\text{NH}_2$ (abbreviated to Zn-Cd-An).

2. Experimental

2.1. PREPARATION OF THE CLATHRATES

All the chemicals were of Analar grade and used without further purification. The clathrates were prepared by a slight modification of the reported procedure for Cd-Cd-An [29, 30]. A typical synthesis is outlined briefly below for Cd-Zn-An.

$\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ (4.3868 g; 20 mmol) and 60 mL of concentrated ammoniacal water (25%) were added with stirring to a 50 mL aqueous solution of 20 mmol $\text{K}_2\text{Zn}(\text{CN})_4$ (4.9516 g). The resultant solution was concentrated to 50 mL on a water bath. A mixture of aniline and *m*-xylene (1 : 1) was added to form an upper layer. Colourless crystals of Cd-Zn-An appeared at the interface of the two layers within a month. Cd-Cd-An was prepared by a similar procedure, using $\text{K}_2\text{Cd}(\text{CN})_4$ in place of $\text{K}_2\text{Zn}(\text{CN})_4$. Zinc clathrates, Zn-Cd-An and Zn-Zn-An were also prepared by a similar method, substituting $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ by $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$.

Crystals collected from the interface between the organic and aqueous layers were found to be clathrates. However, crystals collected from the bottom of the aqueous layer were found, in most cases, to be the host lattices. Pure host complexes were obtained by using a similar procedure without adding the guest, aniline.

Table I. Analytical results for the Hofmann- T_d -type clathrates

Compound	Found (%)				Calculated (%)			
	Cd	Zn	N	C ₆ H ₅ NH ₂	Cd	Zn	N	C ₆ H ₅ NH ₂
Cd-Cd-An	41.1	–	20.1	34.3	40.4	–	20.4	33.9
Zn-Cd-An	22.4	13.1	21.8	37.6	21.9	12.8	22.3	37.1
Cd-Zn-An	22.4	13.0	21.9	36.9	22.0	13.1	22.3	37.1
Zn-Zn-An		28.8	24.2	36.0	–	28.4	24.6	35.5

2.2. ANALYTICAL MEASUREMENTS

The metal analysis was carried out by atomic absorption spectroscopy. Nitrogen was estimated by Kjeldahl's method. Benzene and aniline were estimated by weight-loss measurements which were carried out by keeping the clathrate samples at 100 °C in an air oven for about an hour. The samples were cooled and weighed to constant weight. The analytical results are presented in Table I.

2.3. SPECTRAL MEASUREMENTS

IR spectra of the clathrates and their hosts were recorded on a Perkin Elmer 783 spectrometer in the 4000–200 cm⁻¹ region. The instrument was calibrated with a polystyrene film. Clathrates, removed from their mother liquor, were dried using tissue paper and the IR spectra were recorded immediately to avoid any de-clathration/decomposition. Spectra were recorded both in KBr pellets and in nujol mulls.

3. Results and Discussion

3.1. ANILINE VIBRATIONS

Typical IR spectra of the clathrates, Cd-Cd-An, Zn-Cd-An, Cd-Zn-An and Zn-Zn-An are shown in Figures 1–3. The band assignments for these clathrates **1–4** are given in Table II. Comparison with the various vibrational modes of liquid aniline reveals the presence of all characteristic bands of aniline in these clathrates. Aniline vibrations of the Hofmann-type clathrates, Cd(NH₃)₂Ni(CN)₄·2C₆H₅NH₂ (abbreviated to Cd-Ni-An) and Cd-Hg-An, are also provided for comparison.

In Hofmann-type aniline clathrates, the out-of-plane deformation mode, γ (CH), of aniline shows an upward shift of about 14 cm⁻¹, in comparison to neat aniline (751 cm⁻¹) [31]. It is attributed to the formation of weak hydrogen bonding between the π -cloud of the phenyl ring and the NH₃ of the host [31, 32]. The corresponding shift in benzene clathrates is 30 cm⁻¹ [31]. The absence of such an upward shift in the Hofmann- T_d -type clathrates, studied here, reveals the ab-

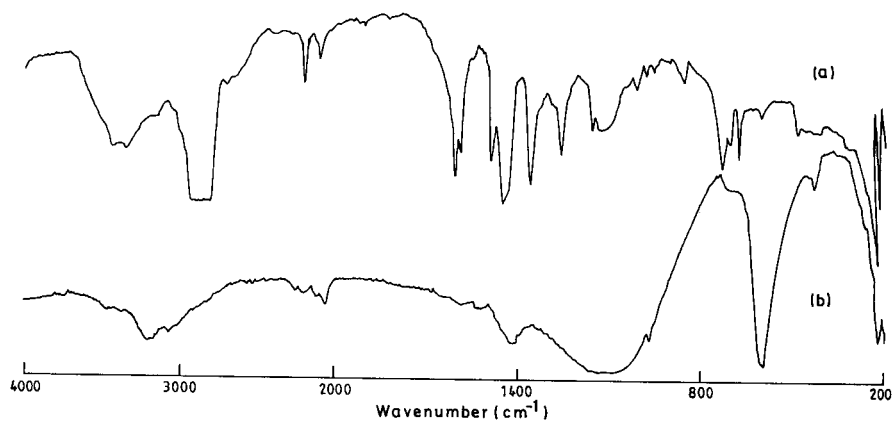


Figure 1. IR spectra of the Hofmann- T_d -type aniline clathrate Zn-Zn-An (mull) (a) and its host, $Zn(NH_3)_2Zn(CN)_4$ (KBr disc) (b).

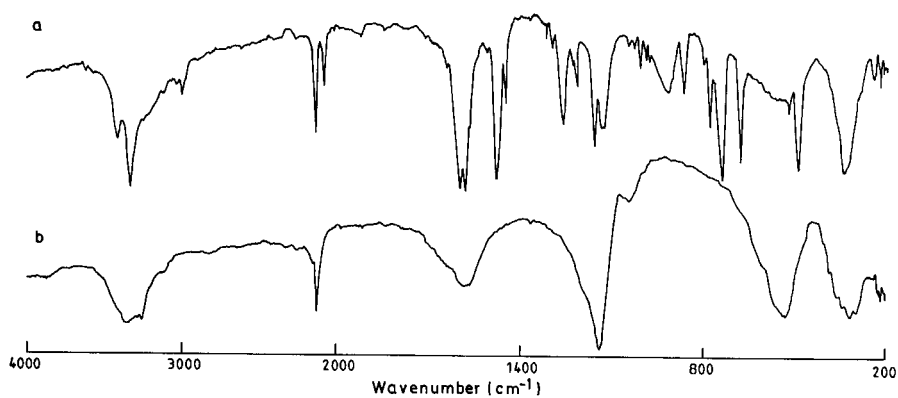


Figure 2. IR spectra of KBr discs of the Hofmann- T_d -type aniline clathrate, Cd-Cd-An (a) and its host, $Cd(NH_3)_2Cd(CN)_4$ (b).

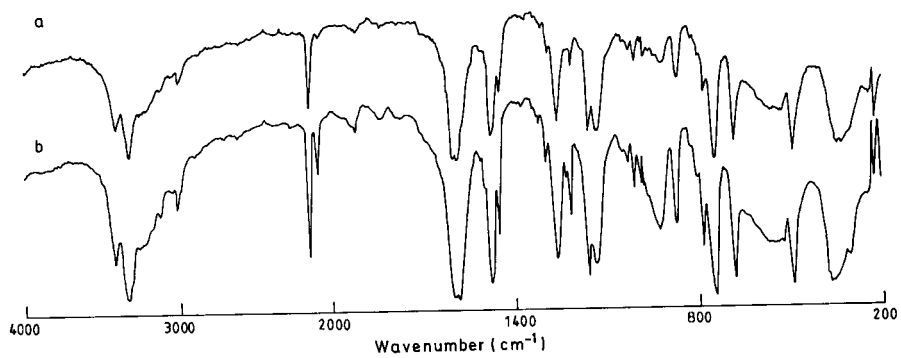


Figure 3. IR spectra of KBr discs of the Hofmann- T_d -type aniline clathrates, Cd-Zn-An (a) and Zn-Cd-An (b).

Table II. Aniline vibrations (cm^{-1}) and band assignment of Hofmann- T_d -type aniline clathrates, $\text{M}(\text{NH}_3)_2\text{M}'(\text{CN})_4 \cdot 2\text{C}_6\text{H}_5\text{NH}_2$ ($\text{M} = \text{Zn}$ or Cd ; $\text{M}' = \text{Zn}$, Cd)

Liquid aniline**	Cd-Cd-An	Zn-Cd-An	Cd-Zn-An	Zn-Zn-An	Cd-Hg-An	Cd-Ni-An*	Assignment*
3440 s	3420 s	3419 s	3405 s	3440 s	3450 w	3462 s	ν_s (NH_2)
3360 vs	3340 vs	3340 vs	3322 vs	3350 s		3371 s	ν_s (NH_2)
3072 w	3070 vw		3100 w				ν (CH)
3037 vw	3040 vw	3040 vw	3040 vw	3040 vw		3041 vw	ν (CH)
3010 vw	3000 wm	3000 wm	2990 w			3008 vs	ν (CH)
1621 vs					1620 s	1617 vs	δ (NH_2)
1600 vs	1600 vs	1601 vs	1600 vs	1603 s	1603 s	1598 s	Ring str.
	1582 m, sh						a'
1586 vw	1565 m, sh	1585 vs	1580 vs	1580 vs	1501 s	1584 vw	Ring str.
		1560 m, sh	1565 m, br	1570 m, sh			a''
1500 s						1492 vs	Ring str. a'
1486 vs	1480 vs	1480 vs	1472 s	1484 s		1467 vs	Ring str. a''
	1445 m	1450 s	1445 m	1450 s			
1330 vs	1325 vw	1330 vw	1290 w	1360 s		1341 vw	Ring str. a'
1312 w	1310 vs	1300 w	1290 w	1350 s, sh		1316 w	δ (CH) _{ip}
				1325 w, sh			
1278 s	1260 s	1265 s	1260 s	1260 s	1278 s	1289 s	X-sens
1175 s	1160 s	1160 s	1158 s	1159 m	1176 m	1175 s	δ (CH) _{ip}
1154 s						1152 s	δ (CH) _{ip}
	1130 s	1135 s	1130 s				
1118 vw				1120 w		1103 vw	δ (CH) _{ip}
1050 vw	1045 vw	1050 vw		1041 vw		1041 vw	NH_2 twist
1028 w	1025 w	1030 w	1025 w	1012 w	1027 w	1022 w	δ (CH) _{ip} ring
996 w	990 w	990 w			997 w	993 w	Breath
970 vw	980 w	980 w	978 w	980 w		970 vw	γ (CH) _{op}
			970 w, br	953 w			
880 m	869 m	870 ms	867 m	853 wm	883 m	891 m	γ (CH) _{op}
826 vw	820 vw	822 vw				825 vw	γ (CH) _{op}
810 vw	800 w	805 w				812 vw	X-sens
751 vs	748 vs	749 vs	740 vs	731 s	761 s	765 vs	γ (CH)
691 s	680 vs	688 vs	678 s	708 s		703 s	Ring def.
670 w				675 s		688 w	NH_2 wag
							X-sens
501 s	490 s	499 s	488 s	489 w		512 s	Op.

* From Refs. [31, 32].

** From Ref. [32].

sence of hydrogen bonding between the π -cloud of the phenyl ring and the NH_3 . Nevertheless, the Hofmann- T_d -type clathrates are thermally more stable than the Hofmann-type clathrates [33]. This stability may arise from the presence of another type of hydrogen bonding discussed below.

The ability of hydrogen bond formation by the NH_2 group of aniline with the π -cloud of the CN of the lattice has been demonstrated in Hofmann-type clathrates [31, 32]. The $\nu_a(\text{NH}_2)$ and $\nu_s(\text{NH}_2)$ modes in Hofmann-type clathrates shift to lower frequencies than in aniline vapour (3500 cm^{-1} and 3418 cm^{-1} respectively), and to slightly higher frequencies than in liquid aniline (3440 cm^{-1} and 3360 cm^{-1}). This has been taken to represent hydrogen bonding interactions between the NH_2 group of aniline and the π -cloud of the CN group and the strength of this hydrogen bonding is less than in neat aniline [31]. In the Hofmann- T_d -type aniline clathrates studied here, the ν_a and ν_s modes occur in the regions of $3405\text{--}3440\text{ cm}^{-1}$ and $3322\text{--}3350\text{ cm}^{-1}$ respectively. This downward shift of these modes compared to aniline vapour is larger than in the Hofmann-type clathrates, indicating stronger H-bonding between the NH_2 and the CN groups.

3.2. AMMONIA VIBRATIONS

The assignment of NH_3 vibrations was done by considering the six normal modes of vibration of a simple 1 : 1 (metal/ligand) complex model [34]. The antisymmetric and symmetric NH_3 stretching, NH_3 degenerate deformation, NH_3 symmetric deformation and NH_3 rocking vibrations occur in the regions, $3000\text{--}3400$, $1550\text{--}1650$, $1370\text{--}1000$ and $950\text{--}990\text{ cm}^{-1}$ respectively. The symmetric stretching, ν_s and bending, δ_s vibrations of NH_3 , are observed in the regions, $3200\text{--}3260\text{ cm}^{-1}$ and $1130\text{--}1175\text{ cm}^{-1}$, respectively for the four clathrates studied here. The antisymmetric stretching, bending and rocking vibrations, ν_a , δ_a and ρ of the NH_3 molecule occur at $3320\text{--}3340$, 1600 and $550\text{--}580\text{ cm}^{-1}$ respectively. The $\nu_a(\text{NH}_3)$ vibrational mode overlaps with the $\nu_a(\text{NH}_2)$ of aniline. In general, the vibrational modes of NH_3 in Hofmann- T_d -type aniline clathrates occur at lower frequencies than in Hofmann-type aniline clathrates as seen in Table III. (The corresponding vibrations in the host lattice, $\text{Cd}(\text{NH}_3)_2\text{Cd}(\text{CN})_4$ is also provided in Table III for comparison). The $\delta_a(\text{NH}_3)$ and $\rho(\text{NH}_3)$ modes show splitting or broadening. Such a splitting or broadening has been observed in Hofmann-type clathrates also and is attributed to inequivalent hydrogens of NH_3 [31]. The hydrogen atoms are rendered inequivalent due to their longer stay in one of the twelve minima for free rotation with respect to the phenyl ring or due to the non-negligible interaction with the π cloud of the phenyl ring during free rotation [31]. The order in which the hydrogen bonding affects the various modes is given by,

degenerate deformation < NH_3 symmetric deformation = antisymmetric stretching < rocking vibrations.

This may be due to the fact that only the perpendicular vibrations are affected by the free rotation. The half-height width of the bands are 100 cm^{-1} and 60 cm^{-1} for

Table III. Ammonia vibrations (cm^{-1}) of Hofmann- T_d -type aniline clathrates

Cd-Cd-An	Zn-Cd-An	Cd-Zn-An	Zn-Zn-An	Cd-Ni-An*	Assignment*
3340 s	3340 s	3322 s	3322 s	3382 s, br	ν_a (NH_3)**
3240 wm	3260 m, br	3200 m	3240 m	3290 w	ν_s (NH_3)
1600 s	1602 s	1600 s	1605 s	1600 s	δ_a (NH_3)
1582 s	1585 s	1580 s	1588 s		
1130 vs	1136 s	1158 s	1175 s	1161 s	δ_s (NH_3)
550 m, br	550 m, br	560 vw	550 vw	528 s, br	ρ (NH_3)

* From Refs. [31, 32].

** Overlaps with ν_a (NH_2) of aniline.

the antisymmetric modes at 3370 cm^{-1} and 1600 cm^{-1} respectively. Although the low temperature spectra were not measured for want of facilities, these band widths are comparable to those noted for Hofmann-type clathrates [31]. Such large band widths in benzene clathrates have been attributed to free rotation by NH_3 molecules [31] which has been further confirmed by a temperature dependent ^{13}C NMR study [35]. This may not be inconsistent with the degeneracy splitting discussed earlier, provided that the internal rotation is not too fast.

3.3. CYANIDE VIBRATIONS

The CN vibrational mode of the host sheet structure in the Hofmann-type pyridine complexes, $\text{M}(\text{Py})_2\text{Ni}(\text{CN})_4$ occurs in the region, $2155\text{--}2170 \text{ cm}^{-1}$, for various metals [36]. The corresponding CN frequency for the Hofmann-type clathrates is observed around 2150 cm^{-1} . This lowering of the ν (CN) stretching mode corresponds to a weak hydrogen bond between the NH_2 group of aniline and the π -cloud of CN [31, 32]. The $\nu(\text{CN})$ of the Hofmann- T_d -type aniline clathrates occurs in the range of $2135\text{--}2145 \text{ cm}^{-1}$ (Table IV). This is lower than that in the Hofmann-type clathrates ($2148\text{--}2161 \text{ cm}^{-1}$). This downward shift indicates a definite hydrogen bonding between the NH_2 group of aniline with the π -cloud of the CN group. Such a hydrogen bonding interaction appears to be facilitated by the disordered state of the guest molecules in the β -cavity of Hofmann- T_d -clathrates [20], which may increase the interaction of CN with the NH_2 of aniline. The occurrence of a second band around 2100 cm^{-1} for the clathrates **1–4** (Table IV) was initially thought to arise from partial decomposition of the clathrates. But repeated measurements with freshly prepared samples yielded the same kind of splitting of the cyanide stretching frequency into two bands, suggesting splitting of the cyanide band by the guest molecule due to a reduction in symmetry. The CN stretching of free $\text{Ni}(\text{CN})_4^{2-}$ occurs at around 2130 cm^{-1} [37]. This stretching mode is increased by about 25 cm^{-1} in Hofmann-type clathrates. This shift is explained on the basis that the cyanide of tetracyano-nickelate residue has to bend or strain, to some extent, to

Table IV. Vibrations (cm^{-1}) of the $\text{M}(\text{CN})_4^{2-}$ group

Cd-Cd-An	Zn-Cd-An	Cd-Zn-An	Zn-Zn-An	Cd-Ni-An*	Assignment*
2136 s	2142 s	2135 s	2185 s	2148 s	ν (CN)
2090 m	2082 m	2080 vw	2085 m	2108 w	
2112 w, sh	2115 w, sh	2115 w, sh	–	2110 w	ν (^{13}CN)
550 m, br	550 m, br	560 m, br	565 m, br	539 m, br	π (NiCN)
490 s	499 s	488 s	489 s	445 w	δ (NiCN)

* From Refs. [31, 32].

bridge the two metal atoms to form the two-dimensional lattice in Hofmann-type clathrates. This shift is small for the aniline clathrates. This reduced magnitude in shift is attributed to the hydrogen bonding between the NH_2 group of aniline and the CN group of the host lattice [31]. The tetrahedrally disposed free $\text{Cd}(\text{CN})_4^{2-}$, $\text{Hg}(\text{CN})_4^{2-}$ or $\text{Zn}(\text{CN})_4^{2-}$ units (ν (CN) at 2152, 2145 and 2146 cm^{-1} respectively), also exhibit an increase (by 20 cm^{-1}) in the Hofmann- T_d -type benzene clathrates [22]. However, the magnitude of this shift is lower for the Hofmann- T_d -type aniline clathrates studied here. This is probably due to stronger hydrogen bonding between the NH_2 group of aniline and the CN group of the host lattice.

4. Conclusion

Weak hydrogen bonding between the π -cloud of aniline and the ammonia of the host lattice is observed in Hofmann- T_d -type aniline clathrates. Band splitting is observed in the ammonia as well as cyanide modes of the clathrates due to the interaction respectively with the phenyl ring and the amino group of aniline. A second type of hydrogen bonding between the NH_2 group of aniline and the cyanide group of the lattice is found to be prominent.

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