

An Infrared and Raman Spectroscopic Study of Td-type 4,4'-bipyridylcadmium(II) Tetracyanometallate (II) Benzene (1/2) Clathrates: $\text{Cd}(\text{C}_{10}\text{H}_8\text{N}_2)\text{Cd}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ and $\text{Cd}(\text{C}_{10}\text{H}_8\text{N}_2)\text{Hg}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$

SEVGİ BAYARI

Gazi Üniversitesi, Fen Bilimleri Enstitüsü, Teknikokullar, Ankara, Turkey.

ZİYA KANTARCI*

Gazi Üniversitesi, Fen-Edebiyat Fakültesi, Fizik Bölümü, Teknikokullar Ankara, Turkey.

and

SEVİM AKYÜZ

Istanbul Üniversitesi, Fen Fakültesi, Fizik Bölümü, Vezneciler, İstanbul, Turkey.

(Received: 3 December 1993; in final form: 29 March 1994)

Abstract. Two new benzene clathrates of the form $\text{Cd}(4,4'\text{-bipyridyl})\text{M}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$, ($\text{M}=\text{Cd}$ or Hg) have been prepared in powder form. Their spectral data were compared with those of the corresponding host complexes and found to be consistent with the host structure found in Td-type clathrates.

Key words: Hofmann-Td-type clathrate, Cd-bipyridyl tetracyanometallate complexes, 4,4'-bipyridyl benzene inclusion compounds, IR and Raman spectra.

1. Introduction

In a recent paper [1], we reported that the IR and Raman spectral results suggest that the structure of $\text{Cd}(\text{pyrazine})\text{M}(\text{CN})_4 \cdot \text{Benzene}$ ($\text{M}=\text{Cd}$ or Hg) compounds are similar to those found in Td-type clathrates given with a general formula $\text{Cd}(\text{II})\text{L}_2\text{M}(\text{II})(\text{CN})_4 \cdot n\text{G}$, where L_2 is a bidentate ligand or a pair of unidentate ligand molecules, M is Cd or Hg and n is the number of G (guest) molecules depending on the bulkiness of the ligands. The host framework is formed from infinite $-\text{Cd}-\text{L}_2-\text{Cd}-$ chains extending along the a and b axes alternately and tetrahedral $\text{M}(\text{CN})_4$ ions arranged between the consecutive crossing $-\text{Cd}-\text{L}_2-\text{Cd}-$ chains with the N-ends bound to the Cd atoms [2–5]. This structure provides two kinds of cavities, α and β , for the guest molecules. The α cavity is a rectangular box

* Author for correspondence.

similar to those in Hofmann-type hosts, while the β cavity is a twisted biprism, as has been demonstrated in previous papers [2–4].

We have prepared two similar new compounds of the form $\text{Cd}(4,4'\text{-bipyridyl})\text{M}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ ($\text{M}=\text{Cd}$ or Hg , abbreviated to Cd-M-bipy-2G). In this paper, an IR and Raman spectroscopic study on these clathrates is reported. For the purposes of comparison and discussion, the corresponding host complexes Cd-Cd-bipy and Cd-Hg-bipy have been prepared and their infrared spectral data are also reported.

2. Experimental

2.1. PREPARATIONS

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

Cd-Cd-bipy-2G

$\text{Cd}(\text{CN})_2$ (0.3288g, 2 mmol), 0.1718g (1.1 mmol) bipyridyl and 10 mL of benzene were added to 50 mL of water. After vigorous stirring for a week the white precipitate was filtered, washed with water, ethanol and ether successively, and kept in a desiccator under benzene saturated vapor pressure.

Cd-Hg-bipy-2G

The preparation of this clathrate was similar to the previous one using $\text{Cd}(\text{CN})_2$ (1 mmol) and $\text{Hg}(\text{CN})_2$ (1 mmol) in place of $\text{Cd}(\text{CN})_2$ (2 mmol).

Cd-Cd-bipy and Cd-Hg-bipy

In the absence of benzene the preparations given above result in the corresponding host complexes. See Table I.

Analytical results

The freshly prepared samples were analyzed for Cd and Hg by AAS (Perkin Elmer 2280 and Hitachi 180–70).

TABLE I

Compound	Found(%)		Calculated(%)	
	Cd	Hg	Cd	Hg
$\text{Cd}(\text{C}_{10}\text{H}_8\text{N}_2)\text{Cd}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$:	35.13	–	35.05	–
$\text{Cd}(\text{C}_{10}\text{H}_8\text{N}_2)\text{Hg}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$:	15.46	26.92	15.41	27.50
$\text{Cd}(\text{C}_{10}\text{H}_8\text{N}_2)\text{Cd}(\text{CN})_4$:	46.67	–	46.34	–
$\text{Cd}(\text{C}_{10}\text{H}_8\text{N}_2)\text{Hg}(\text{CN})_4$:	19.97	33.86	19.61	34.99

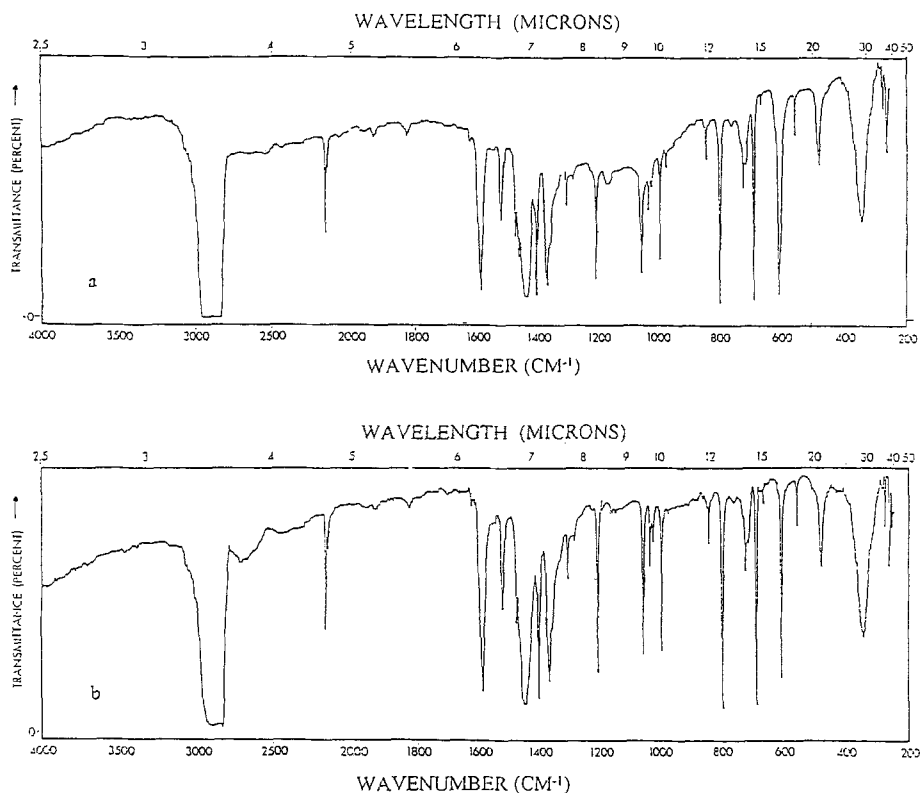


Fig. 1. The IR spectra of the Cd-Cd-bipy-2C₆H₆ (a) and Cd-Hg-bipy-2C₆H₆ (b) clathrates.

2.2. APPARATUS

The IR spectra of the compounds were recorded between 4000 and 300 cm^{-1} on Perkin Elmer 1330 and 621 spectrometers, which were calibrated using a standard indene/camphor/cyclohexanone solution. The samples were prepared as mulls in Nujol and hexachlorobutadiene in a CsI cell.

The Raman spectra of the samples in a spinning cell were excited using the 514.5 nm line of a Spectra-Physics Model 2016-4s Ar⁺ ion laser and recorded on a Jobin-Yvon U1000 (wavelength drive) spectrometer, which was calibrated against the laser plasma emission lines.

3. Results and Discussion

The IR spectra of the Cd-Cd-bipy-2G and Cd-Hg-bipy-2G clathrates are given in Figures 1a and 1b, respectively. The Raman spectrum of the Cd-Cd-bipy-2G clathrate is given in Figure 2. The vibrational spectral features of the two compounds are found to be very similar, suggesting that they have isomorphous crystal structures. Because of the lack of structural data for the compounds studied,

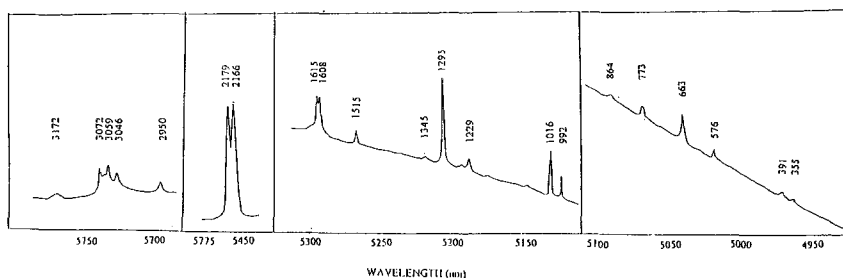


Fig. 2. The Raman spectrum of the Cd-Cd-bipy-2C₆H₆ clathrate. The upper numbers are the wavenumber shifts (cm⁻¹) of the bands.

the vibrational assignment was made by treating the 4,4'-bipyridyl and benzene molecules and the M(CN)₄²⁻ (M=Cd or Hg) ions as isolated units. The IR and Raman spectra and the assignments made are given for 4,4'-bipyridyl, benzene and M(CN)₄²⁻ ions in Tables I, II and III, respectively, along with some relevant spectral data for comparison.

3.1. 4,4'-BIPYRIDYL VIBRATIONS

X-ray structural data of the 4,4'-bipyridyl molecule in the solid state are not available in the literature. However, the assignments based on the IR and Raman spectra of the molecule in the solid phase and the normal coordinate analysis [6–9] have been reported to be in accord with the centrosymmetric and planar structure with the symmetry D_{2h} . The 4,4'-bipyridyl molecule in the Hofmann-type M(4,4'-bipyridyl) Ni(CN)₄ (M=Ni or Cd) complexes and their dioxane, benzene, toluene, aniline and *N,N'*-dimethylaniline clathrates [6], and the monomeric PcML and PcML₂, dimeric PcM-L-MPc and polymeric [PcML]_n (PcM=phthalocyaninato-metal(II), M=Fe or Co and L=4,4'-bipyridyl) complexes [10] has been studied by vibrational spectroscopy. The criterion of the activity of the 4,4'-bipyridyl vibrations as evidence of a centrosymmetric structure with D_{2h} symmetry was used, and, on this basis, found that in metal complexes in which both nitrogen atoms of 4,4'-bipyridyl are coordinated to identical metal atoms, the D_{2h} symmetry is preserved [6, 10] but is removed in unidentate coordination [10].

The assignments and the wavenumbers of the vibrational bands of 4,4'-bipyridyl observed in the IR and Raman spectra of the Cd-Cd-bipy-2G and Cd-Hg-bipy-2G clathrates and the IR spectra of their host complexes are listed in Tables Ia and Ib, respectively, together with the wavenumbers of 4,4'-bipyridyl in the solid and in solution on which the assignments are based. The numbering of frequencies is the same as that used by Sungur *et al.* [6] and Sungur [7]. In Table I, the 4,4'-bipyridyl wavenumbers observed in the IR and Raman spectra of the Cd(4,4'-bipyridyl) Ni(CN)₄ complex, which is assumed to have 4,4'-bipyridyl bridges [6] are also

TABLE Ia
 IR wavenumbers (cm^{-1}) of 4,4'-bipyridyl in Cd-M-bipy-2G (G=C₆H₆) and their host complexes.

Symmetry and assignment ^a	4,4-bipyridyl						
	Solid ^b	in CCl ₄ ^b	Cd-Ni-bipy ^a	Cd-Cd-bipy	Cd-Hg-bipy	Cd-Cd-bipy-2G	Cd-Hg-bipy-2G
<i>B</i> _{3u}							
1 ν (CH)	3055	3062	3069	3063w	3063w	3060w	3060w
2 ν (CH)	3047	—	3053	3055w	3055w	3051w	3049w
3 ν ring	1598	1583	1605	1601vs	1601vs	1594vs	1594vs
4 ν ring+ δ (CH)	1481	1481	1488	1488w	1488w	1486m	1487m
5 δ (CH)	1215	1212	1216	1224s	1224s	1216vs	1216vs
6 δ ring	1044	1037	1064	1069m	1068m	1064vs	1064vs
7 ν ring	994	987	1011	1005s	1005s	1002vs	1002vs
8 ν ring	967	971	976	981m	980m	981w	981w
9 δ ring	615	604	632	620vs	620vs	617vs	617vs
<i>B</i> _{2u}							
10 ν (CH)	3078	—	3078	3083m	3083m	3081m	3080m
11 ν (CH)	3029	3021	3036	3038m	3038m	3031m	3030m
12 ν ring	1532	1529	1534	1529m	1528m	1532s	1534s
13 ν ring	1413	1402	1414	1411s	1411s	1410s	1410s
14 δ (CH)	1324	1312	1315	1313w	1313w	1315w	1316w
15 δ (CH)	1223	—	1219	1217sh	1216sh	1220sh	1220sh
16 ν ring	1074	1065	1078	1070w	1069w	1075vw	1075vw
17 δ ring	677	672	668	672w	672w	673w	670w
18 inter ring bend	—	—	—	—	—	—	—
<i>B</i> _{1u}							
19 γ (CH)	862	—	859	860w	860w	851m	850m
20 γ (CH)	810	—	803	830vs	809vs	804vs	804vs
21 γ ring	737	—	729	729s	729s	731s	729s
22 γ ring	507	501	488	478m	479m	490m	489m
23 γ ring	367	—	386	369w	369w	388m	387m

^a Taken from [6], ^b this study.

vs: very strong, s: strong, w: weak, vw: very weak, sh: shoulder.

TABLE Ib

Raman wavenumbers (cm^{-1}) of 4,4'-bipyridyl in Cd-M-bipy-2G ($\text{G}=\text{C}_6\text{H}_6$) clathrates.

Symmetry and assignment ^a	4,4-bipyridyl		Cd-Cd-bipy-2G	Cd-Hg-bipy-2G	
	Solid ^a	in CCl_4^b			
A_g	1 $\nu(\text{CH})$	3059	3057	3072m	3072m
	2 $\nu(\text{CH})$	3048	3037	3046m	3046m
	3 νring	1617	1611	1614vs	1614vs
	4 νring	1514	1503	1515m	1516m
	5 $\nu\text{ring}+\delta(\text{CH})$	1301	1292	1295vs	1296vs
	6 $\delta(\text{CH})$	1230	1219	1229m	1229m
	7 $\nu\text{ring}+\delta(\text{CH})$	1025	1022	–	–
	8 νring	1000	993	1016vs	1014vs
	9 $\delta\text{ring}+\nu\text{ring}$	762	754	–	–
	10 δring	325	–	–	–
B_{1g}	11 $\nu(\text{CH})$	3059	3053	3059w	3059w
	12 $\nu(\text{CH})$	3018	3002	–	–
	13 νring	1605	1602	1608m	1608m
	14 νring	1427	1441	–	–
	15 $\delta(\text{CH})$	1348	–	1343w	–
	16 $\delta(\text{CH})+\nu\text{ring}$	1265	1245	1246w	1246w
	17 $\nu\text{ring}+\delta(\text{CH})$	1075	1083w	1083m	–
	18 δring	680	660	663m	664m
	19 δring	384	383	391vm	–
B_{2g}	20 $\gamma(\text{CH})$	881	867	864w	863w
	21 $\gamma(\text{CH})$	–	–	773vw	773vw
	22 γring	742	–	–	–
	23 γring	574	571	576m	575m
	24 γring	369	350	355vw	–
B_{3g}	25 $\gamma(\text{CH})$	–	–	–	–
	26 $\gamma(\text{CH})$	866	846	864vm	864vm
	27 γring	–	534	–	–

^a Taken from [7], ^b this study.

included for comparison. Our assignment is in agreement with that of Sungur *et al.* [6] and Sungur [7].

IR and Raman spectral data for 4,4'-bipyridyl in the compounds studied are consistent with all the characteristics of a coordinated ligand [1, 6, 10], that is, several modes of 4,4'-bipyridyl with B_{3u} symmetry have upward shifts in wavenumber in comparison with those of 4,4'-bipyridyl in solution (Tables Ia and Ib). Similar

shifts are observed in the $M(4,4'\text{-bipyridyl})Ni(CN)_4$ ($M=Cd$ or Ni) complexes and explained by coupling of the internal vibrations of 4,4'-bipyridyl with the M-N (4,4'-bipyridyl) stretching frequency [6]. The fact that the more pronounced upward shifts in frequencies of the host complexes (Table I) indicate that the puckering of the host framework in the absence of the guest molecule results in a stronger M-N bond, and in turn, a stronger vibrational coupling. These observations and the non-coincidences between the IR and Raman frequencies (Tables Ia and Ib), considered together, implies bidentate coordination of 4,4'-bipyridyl with a centrosymmetric planar structure in Cd-M-bipy-2G clathrates and their host complexes.

3.2. BENZENE VIBRATIONS

The assignments and the wavenumbers of the vibrational bands of benzene observed in the IR and Raman spectra of Cd-Cd-4,4'-bipy-2G and Cd-Hg-bipy-2G clathrates are tabulated in Table II, together with the wavenumbers of benzene in the liquid phase [11, 12] and in some clathrates [1, 3] on which the assignments are based. The most structurally informative spectral features which merit comment are the following: the CH out-of-plane (A_{2u}) vibrational bands of the clathrates are found to be shifted to higher frequency (695 cm^{-1}) (Table II) from that of liquid benzene (675 cm^{-1}). Similar positive frequency shifts (about 30 cm^{-1}) were observed for Hofmann-type clathrates by Akyüz *et al.* [14]. Akyüz *et al.* explained this upward shift by the presence of a weak hydrogen bond between π electrons located above and below the plane of the benzene ring and the ammonia molecules of the host lattice. Similar shifts have been found for other members of Hofmann-type compounds [15]. Therefore, we may reasonably suggest that the frequency shifts in our clathrate compounds are due to the π electron donation from the benzene ring to the hydrogen atoms of the 4,4'-bipyridyl which has a more electrophilic character caused by the bidentate coordination. These experimental observations are also consistent with the theory of orbital following during molecular vibrations [16–19]. The depletion of π -electron density of the benzene molecules by an electrophilic agent leads to a decreased ability of the carbon bonding orbitals (sp^2) to follow the out-of-plane movement of the hydrogen atoms. This results in a higher bending vibration frequency because the vibrations occur with greater difficulty as orbital overlap ($sp^2 - \pi$) decreases. Another essential feature of the out-of-plane CH bending vibration (A_{2u}) is that it appears as a very intense single band at 695 cm^{-1} in the infrared spectra of the clathrate compounds (Table II). A similar single band was observed in the infrared spectra of the Hofmann-type clathrates, $M(NH_3)_2 Ni(CN)_4 \cdot 2C_6H_6$ ($M=Mn, Fe, Ni, Cu, Zn$ or Cd) [14]. This vibrational mode splits into a doublet for Cd(pyrazine) $M(CN)_4 \cdot 2C_6H_6$ ($M=Cd$ or Hg) [1] and Cd(ethylenediamine) $Ni(CN)_4 \cdot 2C_6H_6$ [20] and a triplet for Cd(en) $M(CN)_4 \cdot 2C_6H_6$ ($M=Cd$ or Hg) [3]. In the case of clathrates with doublet or triplet features the splittings are due to the strong host-guest interactions (i.e. crystal field effects) [1]. In the case of clathrates with a single band, because of the larger cavities (α and

TABLE II

Vibrational wavenumbers (cm^{-1}) of benzene in Cd-Cd-bipy-2G, Cd-Hg-bipy-2G (G=C₆H₆) and in other host frameworks.

Assignment ^a	Liquid benzene		Cd-Cd-pyz-G ^b		Cd-Hg-pyz-G ^b		Cd-Cd-en-2G ^c		Cd-Cd-bipy-2G		Cd-Hg-bipy-2G	
	IR ^d	R ^c	IR	R	IR	R	IR	R	IR	R	IR	R
$\nu_8 + (\nu_1 + \nu_6)$	-	3187	-	3183	-	-	-	-	-	-	-	-
2 ν_8	-	3166	-	3163	-	-	-	-	-	3172m	-	3172m
$\nu_{20}E_{1u}$	3073	-	3088	-	3088	-	3076	-	-	-	-	-
$\nu_{13}B_{1u}$	3062 ^f	-	3068	-	3086	-	-	-	-	-	-	-
ν_2A_{1g}	-	3062	-	3062	-	3062	-	-	-	3066 ^g m	-	3066m
ν_7E_{2g}	-	3050	-	3053	-	3053	-	-	-	-	-	-
$\nu_3 + \nu_1 + \nu_6$	-	2949	-	2950	-	2950	-	-	-	2953w	-	2953w
$(\nu_5 + \nu_{17})E_{1u}$	1955	-	1951	-	1951	-	1961	-	1980w	-	1980	-
$\nu_1 + \nu_6$ in	-	1606	-	1603	-	1604	-	-	-	1605m	-	1605m
ν_8E_{2g} resonance	-	1586	-	1586	-	1586	-	-	-	1587m	-	1587m
$\nu_{19}E_{1u}$	1479	-	1479	-	1479	-	1478	-	1482w	-	1482w	-
$\nu_{14}B_{2u}$	1309	-	-	-	-	-	1315	-	1315 ^g	-	1315 ^g m	-
$(\nu_{10} + \nu_{16})E_{1u}$ ^d	1251	-	-	-	-	-	-	-	1291m	-	1291m	-
ν_9E_{2g}	-	1177	-	1177	-	1177	-	-	-	1178w	-	1178m
$\nu_{15}B_{2u}$	1149	-	1147	-	1147	-	1147	-	1149w	-	1149w	-
$\nu_{18}E_{1u}$	1036	-	1035	-	1035	-	1036	-	1035s	-	1039s	-
ν_1A_{1g}	-	991	-	991	-	991	-	-	-	992s	-	992m
$\nu_{17}E_{2u}$	966	-	-	-	-	-	-	-	-	-	-	-
$\nu_{10}E_{1g}$	-	850	-	855	-	854	-	-	-	-	-	855w
$\nu_{11}A_{2u}$	670	-	685	-	685	-	688	-	695vs	-	695vs	-
			681		681		682					677

^a Using the numbering system of Wilson [13].^{b,c,d,e} Taken from [1, 3, 11, 12], respectively, ^f calculated value, ^g overlapped with bipy. band.

β) due to the ligands, the host-guest interactions are not expected to be effective for splitting.

Owing to the lack of X-ray structural study on Cd-M-4,4'-bipy-2G clathrates, the location of the benzene molecules are unknown. However, based on the vibrational spectroscopic results, we tentatively propose that each of the two cavities (α and β) accommodates a benzene molecule. A complete single crystal study is required to shed light on this proposal.

3.3. $\text{Cd}(\text{CN})_4$ AND $\text{Hg}(\text{CN})_4$ GROUP VIBRATIONS

The fact that in the host framework of the Td-type clathrates [1, 4] and the Td-type host complexes [5] the metal atom M in $\text{M}(\text{CN})_4$ is tetrahedrally surrounded by the carbon ends of four CN ions suggests that the clathrates and their host complexes studied here also have tetrahedral $\text{M}(\text{CN})_4$ units. In order to assign the bands attributable to the $\text{M}(\text{CN})_4$ (M=Cd or Hg) ion in the spectra of our clathrate compounds, we refer to the work of Jones who presented vibrational data for the salts $\text{K}_2\text{Cd}(\text{CN})_4$ and $\text{K}_2\text{Hg}(\text{CN})_4$ in the solid state [21]. The structural studies on these salts have shown that the K-NC distance is ca. 2.9 Å in $\text{K}_2\text{Cd}(\text{CN})_4$ [22] and $\text{K}_2\text{Hg}(\text{CN})_4$ [23], while the Cd-NC distance is ca. 2.3 Å in Td-type host frameworks [5, 24, 25]. 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 $\text{M}(\text{CN})_4$ groups in the compounds studied are given in Table III, together with the vibrational wavenumbers of $\text{K}_2\text{Cd}(\text{CN})_4$ and $\text{K}_2\text{Hg}(\text{CN})_4$. In Table III is also listed the wavenumbers of the infrared and Raman spectra of the benzene clathrate compound $\text{Cd}(\text{pyrazine})\text{Cd}(\text{CN})_4 \cdot \text{C}_6\text{H}_6$ and $\text{Cd}(\text{pyrazine})\text{Hg}(\text{CN})_4 \cdot \text{C}_6\text{H}_6$ for comparison. The assigned wavenumbers for the $\text{M}(\text{CN})_4$ group in the compounds studied appear to be much higher than those for isolated $\text{M}(\text{CN})_4$ units (Table III). Such frequency shifts have been observed for other Td-type clathrates, $\text{Cd}(\text{pyrazine})\text{Cd}(\text{CN})_4 \cdot \text{C}_6\text{H}_6$ and $\text{Cd}(\text{pyrazine})\text{Hg}(\text{CN})_4 \cdot \text{C}_6\text{H}_6$ [1] (Table III) and Td-type host complexes, $\text{Cd}(\text{pyridine})_2\text{M}(\text{CN})_4$ (M=Cd or Hg) [26], in which both ends of the CN group are coordinated and explained as the mechanical coupling of the internal modes of $\text{M}(\text{CN})_4$ (M=Cd or Hg) with the metal (Cd)-NC vibrations [1, 26]. It follows that the N-ends of the $\text{M}(\text{CN})_4$ groups are also bound to a Cd atom in our clathrates, $\text{Cd}(4,4'\text{-bipy})\text{M}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$, and host complexes, $\text{Cd}(4,4'\text{-bipy})\text{M}(\text{CN})_4$.

The preceding discussion of the spectral data is based on the presumption that the host framework of the compounds studied are similar to those of regular Td-type clathrate compounds. However, in view of the long span length of the 4,4'-bipyridyl molecule, a word may be in order, too, at this point regarding the structure of our compounds. The Ni-(4,4'-bipyridyl)-Ni span length is 11.8 Å in the $\text{Ni}(4,4'\text{-bipyridyl})\text{Ni}(\text{CN})_4 \cdot 0.8\text{C}_6\text{H}_6$ clathrate [27]. This suggests that the straight Cd-(4,4'-bipyridyl)-Cd span may be estimated to be ca. 11–12 Å. This length appears to be too long to keep the host framework of $\text{Cd}[\text{M}(\text{CN})_4]$ similar to

TABLE III
Cyanide group vibrational wavenumbers (cm^{-1}) for Cd-Cd-bipy-2G and Cd-Hg-bipy-2G ($G=C_6H_6$) and their host complexes.

Symmetry and assignment ^a	K ₂ Cd(CN) ₄ ^a		K ₂ Hg(CN) ₄ ^a		Cd-Cd-pyz-G ^b		Cd-Cd-bipy-2G		Cd-Hg-bipy-2G		Cd-Cd-bipy		Cd-Hg-bipy	
	IR	R	IR	R	IR	R	IR	R	IR	R	IR	R	IR	R
$\nu_1(\text{CN})A_1$	-	2149	-	2149	-	2180vs	-	2179vs	-	2179vs	-	2179vs	-	2179vs
$\nu_5(\text{CN})F_2$	2145	-	2146	-	2176vs	2172sh	2165vs	2166s	2165vs	2166s	2162ms	2163s	2163s	2163s
Hot band	-	-	-	-	2164vw	2162w	2150w	-	2149w	-	-	-	-	-
$\nu_2(\text{MC})A_1$	-	327	-	335	-	-	-	355vw	-	355vw	-	-	-	-
$\nu_6[\nu(\text{MC})+\delta(\text{NMC})]F_2$	316	-	330	-	365vs	-	350vs	-	350vs	-	348vs	348vs	348vs	348vs
$\nu_7[\nu(\text{MC})+\delta(\text{MMC})]F_2$	250	-	330	-	-	-	270m	-	273m	-	-	-	-	-

^{a,b} Taken from [21, 1], respectively.

those found in $\text{Cd}(\text{NH}_3)_2 \text{Hg}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ [2], $\text{Cd}(\text{NH}_3)_2 \text{Cd}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ [24] and $\text{Cd}(\text{ethylenediamine})_2 \text{Cd}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ [5, 24]. Therefore, the framework of $\text{Cd}[\text{M}(\text{CN})_4]$ in Cd-Cd-2G, Cd-Hg-2G, Cd-Cd and Cd-Hg seems to be distorted about the coordination spheres of Cd(octahedral) and M(tetrahedral) (M=Cd or Hg) to some extent. Such distortions have been observed in other Td-type host structures [24, 25]. In this context, the fact to be noted is that a number of papers have suggested that similar compositions never support similar structures for the cyanometallate inclusion and complex systems [25, 28–33]. Hence, it should be emphasized that our proposal for the structure of the clathrate and complex compounds studied here is tentative and possibly speculative, but it appears consistent with the available data.

Acknowledgements

The authors wish to thank Prof. Dr. L. Zor (University of Anatolia) and Miss. N. Akkuş (Hacettepe University) for chemical analysis and two referees for very useful comments and correcting the English of the manuscript. One of us (Z.K.) is grateful to the Gazi University Research Fund for purchase of the Jobin Yvon U1000 spectrometer.

References

1. N. Ekici, Z. Kantarcı, and S. Akyüz: *J. Incl. Phenom.* **10**, 9 (1991).
2. R. Kuroda: *Inorg. Nucl. Chem. Lett.* **9**, 13 (1973).
3. T. Iwamoto and D.F. Shriver: *Inorg. Chem.* **11**, 2570 (1972).
4. T. Iwamoto: *J. Mol. Struct.* **75**, 51 (1981).
5. S. Nishikiori and T. Iwamoto: *J. Incl. Phenom.* **3**, 283 (1985).
6. A. Sungur, S. Akyüz, and J.E.D. Davies: *J. Incl. Phenom.* **5**, 491 (1987).
7. A. Sungur: Ph.D. Thesis, Physics Department, Faculty of Science, Hacettepe University, Beytepe, Ankara, Turkey.
8. H. Kiharo and Y. Gondo: *J. Raman Spectrosc.* **17**, 263 (1986).
9. V.P. Gupta: *Indian J. Pure App. Phys.* **11**, 775 (1973).
10. J. Metz, O. Schneider and M. Hanack: *Spectrochim. Acta* **38A**, 1265 (1982).
11. P.C. Painter and J.L. Koening: *Spectrochim. Acta* **33A**, 103 (1977).
12. J.E.D. Davies, A.B. Dempster and S. Suzuki: *Spectrochim. Acta* **30A**, 1183 (1974).
13. E.B. Wilson: *Phys. Rev.* **45**, 706 (1934).
14. S. Akyüz, A.B. Dempster, and R.L. Morehouse: *Spectrochim. Acta* **30A**, 1989 (1974).
15. S. Suzuki, W.J. Orville-Thomas, A. Sopkova, and J. Skorsepa: *J. Mol. Struct.* **54**, 1 (1979).
16. R.D. Kross, V.A. Fassel, and M. Margoshes: *J. Am. Chem. Soc.* **78**, 1332 (1956).
17. C.A. Coulson: *V. Henri Mem. Not.: Desoer, Liège*, p. 15 (1948).
18. J. Duchesne: *Bull. Acad. Roy. Belg.* **38**, 197 (1952).
19. J.W. Linnett and P.J. Wheatley: *Nature* **161**, 971 (1948); *Trans. Faraday Soc.* **45**, 33 (1949).
20. T. Iwamoto and Y. Otsu: *Chem. Lett.*, 463 (1972).
21. L.H. Jones: *Spectrochim. Acta* **17**, 188 (1961).
22. B. Ziegler and D. Babel: *Z. Naturforsch.* **46B**, 47 (1991).
23. P.N. Gerlach and B.M. Powell: *J. Chem. Phys.* **85**, 6004 (1986).
24. H. Yuge and T. Iwamoto: *J. Incl. Phenom.* **14**, 217 (1992).
25. H. Yuge and T. Iwamoto: *J. Chem. Soc. Dalton Trans.*, 2841 (1993).
26. Z. Kantarcı: *Commun. Fac. Sci. Univ. Ankara* **37**, 53 (1988).
27. Y. Mathey, C. Mazieres and R. Setton: *Inorg. Nucl. Chem. Lett.* **13**, 1 (1977).

28. T. Kitazawa, S. Nishikiori, R. Kuroda, and T. Iwamoto: *Chem. Lett.*, 459 (1988).
29. T. Kitazawa, S. Nishikiori, R. Kuroda, and T. Iwamoto: *Chem. Lett.*, 1729 (1988).
30. T. Kitazawa, S. Nishikiori, A. Yamagishi, R. Kuroda, and T. Iwamoto: *J. Chem. Soc. Chem. Commun.*, 413 (1990).
31. B.F. Abrahams, B.F. Hoskins, and R. Robson: *J. Chem. Soc. Chem. Commun.*, 60 (1990).
32. B.F. Abrahams, B.F. Hoskins, J. Liu, and R. Robson: *J. Am. Chem. Soc.* **113**, 3045 (1991).
33. J. Kim, D. Whang, J.I. Lee, and K. Kim: *J. Chem. Soc. Chem. Commun.*, 1400 (1993).