ELSEVIER

Journal of Molecular Structure 482–483 (1999) 81–85

Journal of
MOLECULAR
STRUCTURE

An infrared and Raman spectroscopic study on the Hofmann-T_d-type 1,4-dioxane clathrates: $M(NH_3)_2M'(CN)_4 \cdot 2C_4H_8O_2$ (M = Mn or Cd, M′ = Hg; M = Cd, M′ = Cd)

T. Zengin, Z. Kantarci*, E. Kasap

Gazi Universitesi, Fen Edebiyat Fakültesi, Fizik Bölümü, Teknikokullar, 06500 Ankara, Turkey

Received 25 August 1998; received in revised form 9 November 1998; accepted 9 November 1998

Abstract

Three new Hofmann-T_d-type clathrates of the form $M(NH_3)_2M'(CN)_4 \cdot 2C_4H_8O_2$ (M = Mn or Cd, M′ = Hg; M = Cd, M′ = Cd) were prepared, and their IR and Raman spectra are reported. The spectral data suggest that the host frame-works of these compounds are similar to those of Hofmann-T_d-type benzene clathrates. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Inclusion compounds; Ammonia; 1,4-dioxane; Infrared and Raman spectra

1. Introduction

In our previous study [1], vibrational spectral data of $Mn(NH_3)_2M(CN)_4 \cdot 2C_6H_6$ (M = Cd or Hg) have been correlated with those of Hofmann-T_d-type clathrates $Cd(NH_3)_2Cd(CN)_4 \cdot 2C_6H_6$ [2] and $Cd(NH_3)_2Hg(CN)_4 \cdot 2C_6H_6$ [3] (Cd–Cd–Bz and Cd–Hg–Bz, respectively). In the host framework of these compounds (i.e., Cd–Hg–Bz) the Hg atom is tetrahedrally coordinated to the carbon atoms of the four cyanide groups, while the Cd atom is octahedrally surrounded by six nitrogen atoms, two are from the NH_3 molecules attached to the Cd atom in position *trans* to each other, the other four are from cyanide groups. The $Hg(CN)_4$ groups are linked by the $Cd(NH_3)_2$ moieties to form a three-dimensional network. This structure provides two kinds of cavities, α and β, for the guest molecules, the former cavity approximates to a rectangular box and the latter to a biprismatic cage, as has been illustrated in previous articles [2,3]. We have now replaced the guest benzene by 1,4-dioxane (D) and prepared three new title compounds. In this study we report the IR spectra of Mn–Hg–D, and IR and Raman spectra of Cd–Cd–D and Cd–Hg–D compounds (Raman spectra of the former beige compound could not be obtained by using the 488 or 515 nm laser line). The spectral data for the host moieties are structurally correlated with those of Mn–Hg–Bz, Cd–Cd–Bz and Cd–Hg–Bz [1]. The crystal structures of the latter two compounds are already known to be Hofmann-T_d-type clathrates [2,3].

2. Experimental

One millimole of $K_2M'(CN)_4$, 1 mmol of MCl_2 and

* Corresponding author. Fax: 00 90 312 212 2279.
E-mail address: ziya@quark.fef.gazi.edu.tr (Z. Kantarci)

0022-2860/99/$ - see front matter © 1999 Elsevier Science B.V. All rights reserved.
PII: S0022-2860(98)00839-4

Table 1
The vibrational wavenumbers (cm^{-1}) of NH_3 for Mn–Hg–D, Cd–Cd– D, Cd– Hg–D and related compounds (v = very, s = strong, m = medium, w = weak, sh = shoulder, br = broad; n.o. = not observed)

Assignment	Mn–Hg–Bz[a] IR	Cd–Cd–Bz[a]		Cd–Hg–Bz[a]		Mn–Hg–D	Cd–Cd–D		Cd–Hg–D	
		IR	R	IR	R	IR	IR	R	IR	R
ν_a (IR)	3376s	3385s	–	3383s	–	3373s,br	3356s	–	3352s	–
ν_a (R)	–	–	3370vw	–	3370vw	–	–	3340vw	–	3339vw
ν_s (R)	–	–	3290m	–	3291m	–	–	3274m	–	3273m
ν_s (IR)	3283m	3290s	–	3287s	–	3278s,br	3276s	–	3276s	–
δ_a (R)	–	–	1600m	–	1601m	–	–	1601vw	–	n.o.
δ_a (IR)	1586m	1604m	–	1587m	–	1587m	1622s	–	1620m	–
δ_s (R)	–	–	1190m	–	1192m	–	–	n.o.	–	1185w
δ_s (IR) [b]	1158w	1154w	–	–	–	1160w	–	–	–	–
δ_s (IR)	1130vs	1109vs	–	1108vs	–	1171m	1178vs	–	1182vs	–
δ_r (IR)	513s	–	530vs	528vs	–	510vs,br	–	–	566vs,vbr	–
δ_r (R)	–	–	505m	–	500m	–	–	n.o.	–	500vw

[a] Taken From Ref. [1].
[b] Band arising from decomposed lattice.

5 ml dioxane solution in 50 ml of NH_3 solution (25%) was left overnight in the open air. The plate like crystals formed on the top of the solution were filtered washed with water, ethanol and ether, successively, and kept under ammonia vapour. The freshly prepared samples were analysed for Mn, Cd, C, H and N the following results (found %/calculated %) (note that Mn–Hg–D is very unstable; see Section 3): Mn–Hg–D : Mn(9.81/9.64), C(24.94/25.29), H(3.82/3.89), N(14.55/14.75); Cd–Cd–D: Cd(42.14/41.70); C(26.33/26.73), H(4.05/4.11), N(15.34/15.59); Cd–Hg–D : Cd(18.06/17.92), C(23.09/22.92), H(3.55/3.53), N(13.37/13.40).

IR spectra of the freshly prepared compounds were recorded between 4000 and 200 cm^{-1} on a Perkin Elmer 1330 and Mattson 1000 FTIR spectrometers, which were calibrated using polystyrene and indene. The samples were prepared as mulls in nujol and hexachlorobutadiene in a CsI cell. The Raman spectra of the Cd–Cd–D and Cd–Hg–D were excited using a Spectra-Physics 2016-4S laser and recorded on a Jobin-Yvon U1000 spectrometer which was calibrated against the laser plasma lines.

3. Results and discussion

Owing to the lack of structural data the assignments were made by treating the D, $M(NH_3)_2$ and $M'(CN)_4$ moities as isolated units. It was observed that the assignments of the vibrational bands of the ammine ligands in the IR and Raman spectra of the Hofmann-type [4–6] and Hofmann-T_d-type clathrates [1] and our compounds are consistent with the vibrational unit of $H_3N–M–NH_3$ (D_{3d}), in which the N–M–N skeleton is linear and the NH_3 moieties are staggered [1,4–6]. Based on this model we expect two components, in-phase (Raman active) and out-of-phase (IR active) for each mode of a bare ammonia molecule. The assignment and the wavenumbers of the bands attributable to the ammine in the spectra of the compounds under study are listed in Table 1. For the purposes of comparison and discussion, Table 1 also tabulates the IR and Raman spectra of the ammine ligands in Hofmann-T_d-type benzene clathrates [1] on which the assignments are based. The most notable spectral feature in the spectra of the clathrates is the considerable difference between in-phase (Raman active) and out-of-phase (IR active) $\delta(NH_3)$ vibrations. It is still not quite clear to what extent the higher frequencies in the Raman compared to the IR arise from vibrational coupling through the metal or through an interaction via the dioxane molecules. A similar observation has been made by Davies et al. for Hofmann-type benzene clathrates, and they suggested that the dominant cause is because of the hydrogen bonding interaction with benzene; as the metal M is a heavy atom, vibrational coupling through

Table 2
The vibrational wavenumbers (cm^{-1}) of $M(CN)_4$ group for Mn–Hg–D, Cd–Cd–D and related compounds

Assignment	$K_2Cd(CN)_4$[a]		$K_2Hg(CN)_4$[a]		Mn–Hg–Bz[b]	Cd–Cd–Bz[b]		Cd–Hg–Bz[b]		Mn–Hg–D	Cd–Cd–D		Cd–Hg–D	
	IR	R	IR	R	IR	IR	R	IR	R	IR	IR	R	IR	R
ν_1 (CN) A_1	–	2149	–	2149	–	–	2178vs	–	2178vs	–	–	2177vs	–	2178vs
ν_5 (CN) F_2	2145	–	2146	–	2167vs	2165vs	2165m	2168vs	2167m	2173vs	2170vs	2170m,sh	2170vs	2169s,sh
Hot band?	–	–	–	–	2154vw	2154vw	–	2155vw	–	–	–	–	–	–
ν_2 (MC) A_1	–	327	–	335	–	–	341vw	–	341vw	–	–	340w	–	337w
$\nu_6[\nu(MC) + \delta(NCM)]$ F_2	316	–	330	–	368s	360s	–	358s	–	378s	361s	–	368s	–
$\nu_7[\nu(MC) + \delta(NCM)]$ F_2	250	–	235	–	262m	264m	–	255m	–	265m	271m	269m	257m,sh	–

[a] Taken From Ref. [12].
[b] Taken From Ref. [1]. v = very, s = strong, m = medium, w = weak, sh = shoulder.

Table 3
The vibrational wavenumbers (cm^{-1}) of 1,4-dioxane for Mn–Hg–D, Cd–Cd–D, Cd–Hg–D clathrates and related compounds. (v = very, s = strong, m = medium, w = weak, sh = shoulder; n.o. = not observed.)

Assignment	Liquid dioxane [a]		Cd–Ni–G [bc]	Mn–Hg–D	Cd–Cd–D		Cd–Hg–D	
	IR	R	IR	IR	IR	R	IR	R
$\nu_1(a_g)$, $\nu_{20}(b_g)$	–	2968s	–	–	–	2979vs	–	2980vs
$\nu_{11}(a_u)$, $\nu_{28}(b_u)$	2960vs	–	2982m	2981s	2981s	–	2980s	–
$\nu_2(a_g)$, $\nu_{21}(b_g)$	–	2856s	–	–	–	2860vs	–	2862vs
$\nu_{12}(a_u)$, $\nu_{29}(b_u)$	2852vs	–	2860s	2862s	2860s	–	2860s	–
$\nu_{22}(b_g)$	–	1459m,sh	–	–	–	1460m	–	1459m
$\nu_{30}(b_u)$	1454s	–	1457m 1455m	1454m	1452m	–	1454m	–
$\nu_{13}(a_u)$	1446s,sh	–	–	1442m	1442m	–	1443m	–
$\nu_3(a_g)$	–	1444s	–	–	–	1445m	–	1445m
$\nu_4(a_g)$	–	1397w	–	–	–	1398w	–	1396w
$\nu_{31}(b_u)$	1374m,sh	–	1378w	1375m	1377m	–	1377m	–
$\nu_{14}(a_u)$	1366s	–	1367m	1367m	1367m	–	1367m	–
$\nu_{23}(b_g)$	–	1335w	–	–	–	n.o.	–	n.o.
$\nu_5(a_g)$	–	1305s	–	–	–	1305s	–	1307s
$\nu_{32}(b_u)$	1289s	–	1291m	1294s	1292s	–	1292s	–
$\nu_{15}(a_u)$	1256s	–	1257s	1257s	1257s	–	1255m,sh	–
$\nu_{16}(a_u)$	1125vs	–	1116s	1117vs	1117vs	–	1116vs	–
$\nu_{24}(b_g)$	–	1217m	–	–	–	1217m	–	1217m
$\nu_6(a_g)$	–	1128m	–	–	–	1126w	–	1126w
$\nu_{25}(b_g)$	–	1110m	–	–	–	1100m	–	1098m
$\nu_{17}(a_u)$	1083s	–	1079m	1080s	1080s	–	1082s	–
$\nu_{33}(b_u)$	1049s	–	1044m	1043s	1045s	–	1043s	–
$\nu_7(a_g)$	–	1015s	–	–	–	1016s	–	1016s
$\nu_{34}(b_u)$	888s	–	892m	895s	891s	–	893s	–
$\nu_{18}(a_u)$	874s	–	868vs	870vs	868vs	–	868vs	–
$\nu_{26}(b_g)$	–	853m,sh	–	–	–	853w	–	854w
$\nu_8(a_g)$	–	837vs	–	–	–	833vs	–	834vs
$\nu_{35}(b_u)$	614s	–	608m	615m	613m	–	617m	–
$\nu_{27}(b_g)$	–	490m	–	–	–	488m	–	487m
$\nu_9(a_g)$	–	435m	–	–	–	446m	–	444m
$\nu_{10}(a_g)$	–	424m	–	–	–	424w	–	423w
$\nu_{19}(a_u)$	283m,sh	–	–	278m	282m,sh	–	285m,sh	–
$\nu_{36}(b_u)$	273s	–	–	–	–	272w	–	273w

[a] Taken From Ref. [11].
[b] Taken From Ref. [10].
[c] $Cd(NH_3)_2Ni(CN)_4 \cdot 2$dioxane.

this atom should be rather weak and the δ_s mode is strongly affected by a hydrogen bonding interaction with benzene [4].

It is known that Hofmann-type [7–10] and Hofmann-T_d-type clathrates [1] are unstable under ambient conditions and sensitive to grinding; even on mild grinding they decompose with liberation of benzene, resulting in the $M(NH_3)_2M'(CN)_4$ host complex [1,4–10]. In our case, however, the decomposition is in the manner of replacement of NH_3 host moities by the guest dioxane molecules, resulting in the $M(dioxane)_2M'(CN)_4$ complex [9] and liberated NH_3 molecules. Similar observations have also been made for Hofmann-type dioxane clathrates [10]. On vigorous grinding, spectra exhibit signs of sample decomposition. Mn–Hg–D is very unstable, even on mild grinding it decompose almost completely (Table 3). For example, several dioxane bands are split into doublets assignable to guest and ligated dioxane molecules, a feature which also occurs in Hofmann-type dioxane clathrates, $M(NH_3)_2Ni(CN)_4 \cdot 2C_4H_8O_2$ (M = Ni or Cd) [10]. These bands were readily

identified by making a comparison between the IR spectra of several nujol mulls of clathrate obtained with different extents of grinding and the corresponding $MD_2M'(CN)_4$ complex [9].

In assigning the bands attributable to $M(CN)_4$ (M = Cd or Hg) ions in the spectra of our clathrates, we refer to the work of Jones [12] who presented vibrational data for the $Cd(CN)_4$ and $Hg(CN)_4$ ions with T_d symmetry in the solid $K_2Cd(CN)_4$ and $K_2Hg(CN)_4$ salts, respectively (Table 2). The assigned bands of the $M(CN)_4$ unit in the clathrates appear to be much higher than those for isolated $M(CN)_4$ ions (Table 2). Such upward frequency shifts have been observed for T_d-type [1] and Hofmann-type [4–7] compounds, in which both ends of the CN group are coordinated, and explained as the mechanical coupling of the internal modes of $M(CN)_4$ with the Cd–NC vibrations. It follows that the N ends of the $M(CN)_4$ units are also bound to an M atom in the compounds.

Vibrational studies [13] show that dioxane has a chair conformation with a centre of symmetry (C_{2h}) in the gas and liquid phases, in the metal halide complexes [14] and in Hofmann-type dioxane clathrates [15]. As a result of mutual exclusion between infrared and Raman bands of dioxane in the spectra of our compounds (Table 3), it can be concluded that the dioxane molecule is centro-symmetric and is thus most likely in a chair configuration (Table 3).

The preceeding discussion considered as a whole leads us to the conclusion that the host lattices of our clathrates are similar to those of the Hofmann-T_d-type clathrates [1–3].

References

[1] E. Kasap, Z. Kantarci, J. Incl. Phenom. 20 (1995) 33.
[2] H. Yuge, T. Iwamoto, J. Incl. Phenom. 14 (1992) 217.
[3] R. Kuroda, Inorg. Nucl. Chem. Lett. 9 (1973) 13.
[4] J.E.D. Davies, A.B. Dempster, S. Suzuki, Spectrochim. Acta 30A (1974) 1183.
[5] S. Akyüz, A.B. Dempster, L. Morehouse, Spectrochim. Acta 30A (1974) 1989.
[6] S. Suzuki, W. J. Orville-Thomas, A. Sopková, J. Skorsepa, J. Mol. Struct. 54 (1979) 1.
[7] S. Akyüz, A.B. Dempster, J.E.D. Davies, K. T. Holmes, J. Mol. Struct. 38 (1977) 43.
[8] T. Iwamoto, Y. Ohtsu, Chem. Lett. (1972) 463
[9] S. Sağlam, private comminication, unpublished spectral data
[10] B. Dempster, H. Uslu, Spectrochim. Acta 34A (1978) 71.
[11] A. Sopková, J. Bubanec, J. Therm. Anal. 12 (1977) 97.
[12] H. Jones, Spectrochim. Acta 17 (1961) 188.
[13] O.H. Ellestad, P. Klaboe, Spectrochim. Acta 27A (1971) 1025.
[14] G.W. Fowles, D.A. Rice, R.A. Walton, Spectrochim. Acta 26A (1970) 143.
[15] E. Kendi, D. Ülkü, Z. Kristallogr. 144 (1976) 91.