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The Motion of the Benzene Molecules in the Host Lattices of M(NH3)2M'(CN)4·2C6H6 Clathrates*

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In our previous report[1] we discussed host-guest interactions in a series of Hofmann-type clathrates of the general formula: M(NH3)2M'(CN)4·2C6H6, where M is Ni, Fe, Co, Zn, Mn and Cd and M' is Ni. It was found that the splitting of the band due to CH out-of-plane vibration in benzene, at liquid nitrogen temperature, (at around 985 cm^{-1}), increases as the volume of the tetragonal unit cell decreases. A similar behaviour we recorded in a series of benzene clathrate compounds (isostructural with Hofmann-type clathrates) in which the M' metal was replaced by Pt or Pd, and it was interpreted as a consequence of a »free« rotation in the benzene molecules at room temperature but hindered at low temperatures. The magnitude of the splitting of this band, at liquid nitrogen temperatures, for all the clathrates studied was correlated with the volume of the tetragonal unit cell and with the effective ionic radii of the octahedrally coordinated metal M and the square-planar coordinated metal M'. The slope of $\Delta\nu$ vs, $V_{\text{(unit cell)}}$ is $\approx$−100 cm^{-1} nm^{-3}.

INTRODUCTION

A series of clathrate compounds (Hofmann-type clathrates), consisting of a metal-complex host lattice in which the benzene (guest) molecules are clathrated among the layers of polymerized diamminemetal-M(II) tetracyanometallate-M'(II) planes, has been prepared. Metal M(II) is octahedrally coordinated and metal M'(II) is square planar coordinated. The unit cell parameters of these compounds were determined by powder X-ray diffraction,[2-4] while the crystal structure of some of them was determined by X-ray diffraction methods.[5,6] They belong to the tetragonal system, space group $P4/m$ with $Z = 1$. There is no chemical bond between the host lattice and the guest molecules; the closest contact between $C_{\text{benzene}} - N_{\text{ammonia}}$ (due to van der Waals interaction) is 360 pm.

In previous infrared studies on these compounds, a host-guest interaction has been detected by us[1] as well as by other authors.[7] The magnitude of this interaction was

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* Dedicated to Prof. Dušan Hadži on the occasion of his 70th birthday.

monitored through the changes of the frequencies and shapes of the bands due to the CH out-of-plane bending vibrations of benzene (guest) molecules. There is a total of four γ(CH) benzene vibrations. Miller[8] identified the following γ(CH) vibrations in the spectra of liquid benzene (the notation, intensities and symmetry species are given according to Herzberg[9]): a very weak band at 995 cm^{-1} assigned to ν_7 (B_{2g}), a very weak band at 975 cm^{-1} assigned to ν_{19} (E_{2u}), a weak band at 849 cm^{-1} assigned to ν_{11} (E_{1g}) and a strong band at 673 cm^{-1} assigned to ν_4 (A_{2u}). In the studied clathrates, all these bands are shifted by some 10–20 cm^{-1} to higher frequencies.

We focused our attention on the weak band assigned to ν_{19} because, on cooling, this is the one that exhibits the most prominent changes in the infrared spectra of the studied clathrates. This band splits at low temperature, the magnitude of splitting being independent on the identity of the octahedrally coordinated metal M (attached to the two ammonia groups in the host lattice). Thus, the splitting was most pronounced in Ni(NH$_3$)$_2$Ni(CN)$_4\cdot$2C$_6$H$_6$. It was found that the splitting of this band at liquid nitrogen temperature increases in the order Cd < Mn < Zn < Co < Fe < Ni. The unit cell volume decreases in the same order. We interpreted this effect as a result of the mechanisms (tunneling motion[1] and hindered rotation[10]) that lead to removal of the degeneracy at liquid nitrogen temperature (LNT), but not at room temperature (RT).

In this paper, we report an infrared study of a series of Hofmann-type clathrates, in which the square-planar coordinated nickel atom is replaced by Pt or Pd. The behaviour of the observed band, due to a CH out-of-plane vibration (ν_{19}, around 985 cm^{-1}) at LNT, is similar to that in M(NH$_3$)$_2$Ni(CN)$_4\cdot$2C$_6$H$_6$: the magnitude of the splitting of this band at LNT increases as the volume of the tetragonal unit cell decreases, *i.e.* from Cd to Ni. Correlations have been derived between these parameters and the results are given below.

EXPERIMENTAL

All diamminemetal (Ni, Fe, Co, Zn, Mn or Cd) tetracyanonickellate(II), tetracyanopalladate(II) and tetracyanoplatinate(II) benzene clathrates were prepared by methods reported previously.[4,11] The infrared spectra were recorded with a Perkin-Elmer 580 spectrophotometer, using KBr pellets or mulls in Nujol. However, since the Nujol show weak absorption at the low frequency side of the studied band, only spectra recorded in KBr pellets will be presented.

A low temperature VLT-3 cell was used for LNT-IR studies (the low frequency part was not compensated for the KBr absorption). The instrument was calibrated against polystyrene film and water vapour. Frequencies reported for the sharp bands were recorded at 1.5 cm^{-1} resolution.

RESULTS AND DISCUSSION

The infrared spectrum of one of the studied clathrates, Ni(NH$_3$)$_2$Pt(CN)$_4\cdot$2C$_6$H$_6$ (Ni–Pt–Bz), is shown in Figure 1. The band due to a CH out-of-plane vibration (which we used to monitor the motion of guest molecules in the host lattice) is marked by an arrow. This mode ($\nu_{19} - E_{2u}$ symmetry under the D_{6h} selection rules) is infrared and Raman inactive in gaseous benzene but becomes infrared active[7] due to the lower (C_{2h}) site symmetry in the clathrate crystal.

It is known[2,3,7] that the frequencies that may be assigned to motions of benzene molecules in the clathrates are practically independent of the type of metal (M or M') attached to the NH$_3$ or CN groups. Only the CH out-of-plane modes have frequencies significantly different from the corresponding values in liquid benzene.[1,7,8,12] In addition, the band at around 985 cm^{-1} splits at LNT in some clathrates. The magnitude
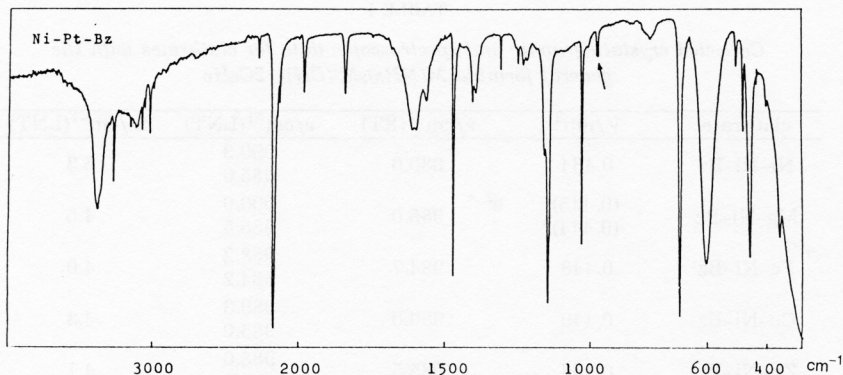
Figure 1. The IR spectra of Ni–Pt–Bz at LNT, The ν_{19} band is marked with an arrow.
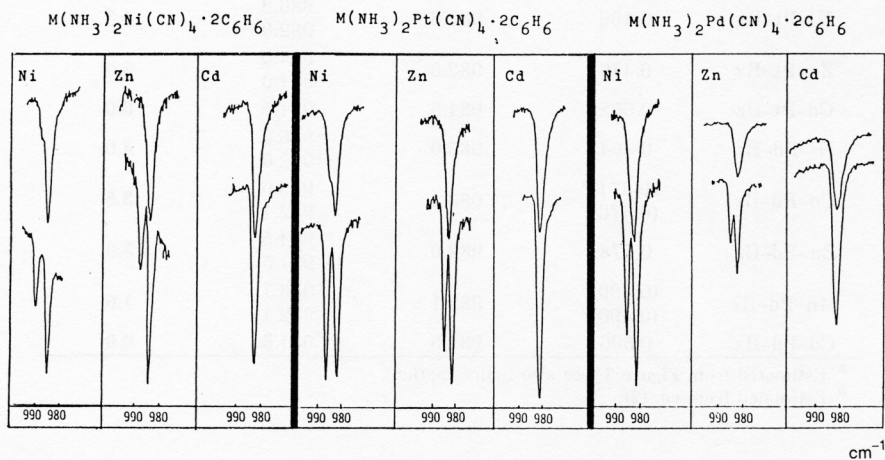

Figure 2. The CH out-of-plane vibrations in the IR spectra of various clathrates at RT (upper) and LNT (lower).

of splitting varied, depending on the type of metal M attached to the NH_3 molecules and M' attached to the CN groups in $M(NH_3)_2M'(CN_4) \cdot 2C_6H_6$ type of clathrate (Figure 2). The collected data from crystallographic ($V_{unit\ cell}$) and spectroscopic ($\Delta\nu$) measurements, for all the clathrates studied, are listed in Table I. The mean value for the slope of $\Delta\nu$ vs. V of the unit cell obtained from these data is about -100 cm^{-1} nm^{-3} (Figure 3).

In our opinion, there are at least two possible explanations for the interdependence found between $\Delta\nu$ and V:

(1) Free rotation of guest molecules at RT but hindered at LNT.[1,10] At room temperature, higher symmetry is preserved due to »isotropisation« of the force constants.[10] However, the hindered rotation at low temperature may lead to a lowering of the effective symmetry of the force field around the C_6H_6 entities. As a result, the degeneracy

TABLE I

Collected crystallographic and spectroscopic data for clathrates with the general formula $M(NH_3)_2M'(CN)_4 \cdot 2C_6H_6$

clathrate	V/nm^3	ν/cm^{-1}(RT)	ν/cm^{-1}(LNT)	$\Delta\nu/cm^{-1}$(LNT)
Ni–Ni–Bz	0.434	986.0	990.3 985.0	5.3
Mg–Ni–Bz	(0.445)[a] (0.444)[b]	985.0	990.0 985.5	4.5
Fe–Ni–Bz	0.448	984.7	988.2 984.2	4.0
Co–Ni–Bz	0.449	986.0	989.3 985.0	4.3
Zn–Ni–Bz	0.453	985.5	988.6 984.5	4.1
Mn–Ni–Bz	0.460	984.5	986.5 983.5	3.0
Cd–Ni–Bz	0.488	983.5	983.5	0.0
Ni–Pt–Bz	0.456	982.8	986.3 982.0	4.3
Zn–Pt–Bz	0.476	982.5	984.0 981.0	3.0
Cd–Pt–Bz	0.502	981.5	981.5	0.0
Ni–Pd–Bz	0.464	983.0	986.0 982.0	4.0
Co–Pd–Bz	(0.471)[a] (0.476)[b]	983.1	985.6 982.1	3.5
Zn–Pd–Bz	0.478	982.0	984.5 981.5	3.0
Mn–Pd–Bz	(0.490)[a] (0.490)[b]	982.1	983.7 982.1	1.6
Cd–Pd–Bz	0.506	981.5	981.5	0.0

[a] Estimated from Figure 3 (see also figure caption).
[b] Estimated from eq. (2).

of the CH out-of-plane vibration is removed at LNT and splitting of the band (site--group splitting) is observed*. The splitting is directly dependent upon the size of the unit cell. The host-guest interactions, which are not only due to the existence of van der Waals forces but also to the presence of a weak hydrogen bond between the π-electrons of the aromatic guest and the ammonia molecules of the host lattice,[7,12] are obviously strongly dependent on the volume of the unit cell.

(2) It is known from the crystallographic data[5,6] that the two benzene molecules in the unit cell of the clathrates can occupy two possible orientations, which are mirror images of each other with respect to the *a*-axis of the unit cell. It is possible that the splitting of the band due to CH out-of-plane vibration, at 985 cm^{-1}, may appear as a result of »freezing« of the benzene molecules at LNT (some sort of flip-flop motion is

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* No crystal data at LNT are available. Most probably, the space group symmetry is the same at RT and LNT because in some cases (*cf.* Ni–Ni–Bz and Ni–Pt–Bz in Figure 2) splitting is present even at room temperature. Another candidate in which similar splitting may be expected is the ν_{11} band. However, in most cases this band could not be identified in the iR spectra of the studied clathrates.
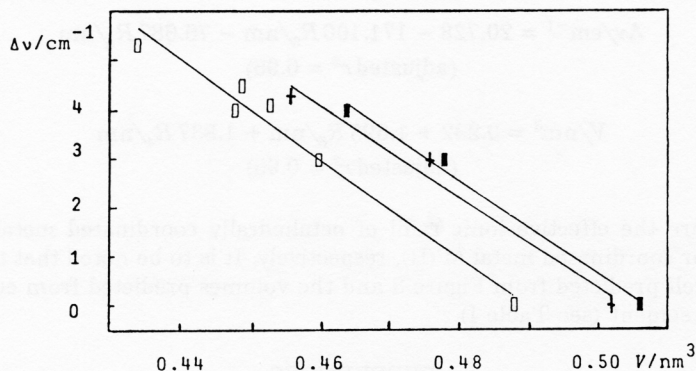
Figure 3. A plot of $\Delta\nu$ vs. $V_{\text{unit cell}}$ (cf. Table I) for:
(1) □ – $M(NH_3)_2NI(CN)_4 \cdot 2C_6H_6$; $\Delta\nu/cmP^{-1}$ = 49.6 – 101.3 V/nm^3
(2) + – $M(NH_3)_2Pt(CN)_4 \cdot 2C_6H_6$; $\Delta\nu/cm^{-1}$ = 47.6 – 94.6 V/nm^3
(3) ■ – $M(NH_3)_2Pd(CN)_4 \cdot 2C_6H_6$; $\Delta\nu/cm^{-1}$ = 49.1 – 06.9 V/nm^3
(adjusted r^2 = 0.99, for all three correlations)

possible at RT). Here again, like in the above interpretation, this »freezing« is expected to be strongly dependent on the size of the tetragonal unit cell.

The slope $\Delta\nu$ vs. V (around –100 cm^{-1} nm^{-3}, Figure 3) can be used for predicting the volumes of the tetragonal unit cells in Hofmann-type clathrates. We made these predictions for clathrates such as Mg–Ni–Bz, Co–Pd–Bz and Mn–Pd–Bz, for which the crystallographic data are unavailable. The predicted volumes of these clathrates (based on different splittings of the γ_{CH} band) are given in Table I in parentheses.

We have made two more correlations for $M(NH_3)_2M'(CN)_4 \cdot 2C_6H_6$ type compounds, inspired by the paper of Petruševski and Aleksovska:[13] the effective ionic radii (cf. Table II) of the octahedrally coordinated metal M attached to the NH$_3$ groups and the square-planar coordinated metal M' attached to the CN groups were correlated (1) with the magnitude of the splitting of the band at around 985 cm^{-1} (eq. 1) and (2) with the volumes of the tetragonal unit cells (eq. 2). The results are presented below. The values for the effective ionic radii were taken from literature.[14] Multiple linear regression analyses were performed on an IBM-PC computer, using a program written in BASIC.

TABLE II

Effective ionic radii[14] for M and M', used in the multiple linear regression analyses[a]

M or M'	R_6/nm	R_4/nm
Ni	0.069	0.049
Pt		0.060
Pd		0.064
Mg	0.072	
Zn	0.074	
Co	0.0745	
Fe	0.078	
Mn	0.083	
Cd	0.095	

[a] Only relevant values are given.

$$\Delta\nu/\mathrm{cm}^{-1} = 20.728 - 171.100\,R_6/\mathrm{nm} - 76.687\,R_4/\mathrm{nm}$$
$$\text{(adjusted}\,r^2 = 0.96) \tag{1}$$

$$V/\mathrm{nm}^3 = 0.232 + 1.695\,R_6/\mathrm{nm} + 1.837\,R_4/\mathrm{nm}$$
$$\text{(adjusted}\,r^2 = 0.95) \tag{2}$$

R_6 and R_4 are the effective ionic radii of octahedrally coordinated metal M(II) and square-planar coordinated metal M'(II), respectively. It is to be noted that the volumes of the unit cell predicted from Figure 3 and the volumes predicted from eq. (2) are in excellent agreement (see Table I).

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SAŽETAK

Gibanje molekula benzena u domicilnoj rešetki klatrata M(NH₃)₂M'(CN)₄.2C₆H₆

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U prethodnom radu[1] razmatrali smo interakciju domaćin-gost u seriji klatrata Hofmannova tipa opće formule: $M(NH_3)_2M'(CN)_4.2C_8H_8$, gdje je M = Ni, Fe, Co, Zn, Mn i Cd, a M' je Ni. Utvrđeno jer da cijepanje vrpce uslijed deformacijske OH vanravninske vibracije benzena, koja se pri temperaturi tekućeg dušika nalazi na oko 985 cm⁻¹, raste s padom volumena tetragonske jedinične ćelije u slijedu Cd, Mn, Zn, Fe, Co i Ni. Slično ponašanje utvrđeno je i u nizu klatratnih spojeva benzena (izostrukturni s klatratima Hofmannova tipa) u kojima je metal M' zamijenjen s Pt i Pd, te je interpretirano kao posljedica »slobodne« rotacije molekula benzena na sobnoj temperaturi, odnosno zapriječene rotacije pri temperaturi tekućeg dušika. Veličina cijepanja te vrpce pri temperaturi tekućeg dušika za sve je proučene klatrate korelirana s volumenom tetragonske jedinične ćelije i efektivnim radijusima kristala oktaedarski heksakoorodiniranog metala M i kvadratno-planarno tetrakoordiniranog metala M'. Nagib $\Delta\nu$ prema ν (jedinične ćelije) približno iznosi -100 cm⁻¹/nm³.