

AN IR STUDY OF $M(1\text{-PROPANETHIOL})_2\text{Ni}(\text{CN})_4\cdot G$ ($M=\text{Cd}, \text{Ni}$ and $G=\text{BENZENE}$) CLATHRATESZ. Kartal^{1*}, D. Türköz[†], S. Bahçeli^{2†}^{*}Physics Department, Faculty of Arts and Sciences, Dumlupınar University
Kütahya, Turkey[†]Physics Department, Faculty of Arts and Sciences, Süleyman Demirel University
Isparta, Turkey

Received 3 April 2003 in final form 2 November 2003, accepted 20 January 2004

Two Hofmann-propanethiol-type clathrates of the form $M(1\text{-propanethiol})_2\text{Ni}(\text{CN})_4\cdot G$ ($M = \text{Cd}$ or Ni ; $G = \text{benzene}$) have been prepared in the powder form. The 1-propanethiol (1-PT) molecules provide the cavities in which the guest benzene molecules in clathrate structure are accommodated. The infrared investigations of the obtained clathrates indicate that these compounds are similar in structure to the other Hofmann-type clathrates.

PACS: 33.20.Ea, 33.20.Tp

1 Introduction

The infrared spectroscopy is one of the most powerful tools in order to investigate the host-guest interactions in the Hofmann-type clathrates. The general formula for the Hofmann-type clathrates is $\text{ML}_2\text{Ni}(\text{CN})_4\cdot G$ where M is a transition metal atom having the valence of +2, L is either a bidentate or two monodentates ligand molecule and G is the guest molecule. In order to produce such complexes, ammonia [1], pyridine [2] and the derivatives of pyridine [3-4] as the ligands containing the nitrogen atom; the water [5], dioxana [6], dimethylsulfoxide [7], dimethylformamide [8] as the ligands containing the oxygen atom and 1,3 thiazodin-2-thion [9], dimethylthioformamide [10] as the ligands containing the sulphur atom are used in the literature.

These remarkable compounds called clathrates are of great scientific interest because of their cage structures and inclusion behaviours. For these reasons they can use as catalysts, anti-oxidants and stabilizing agents and can give some knowledges about the formation of crystals and the the magnitude of crystal forces.

In the present study, the *n*-propyl mercaptan or 1-propanethiol (1-PT) has been used for the first time as a ligand to obtain two new Hofmann-propanethiol-type clathrates with the benzene guest molecule.

On the other hand, there are some studies for the bulk 1-PT by using IR [11-14] and Raman [15-16] spectroscopy techniques. In particular the infrared vibration modes and frequencies of 1-PT are presented by Trogrimsen and Klæboe [14].

¹E-mail address: zkartal@mail.dumlupinar.edu.tr²E-mail address: bahceli@fef.sdu.edu.tr

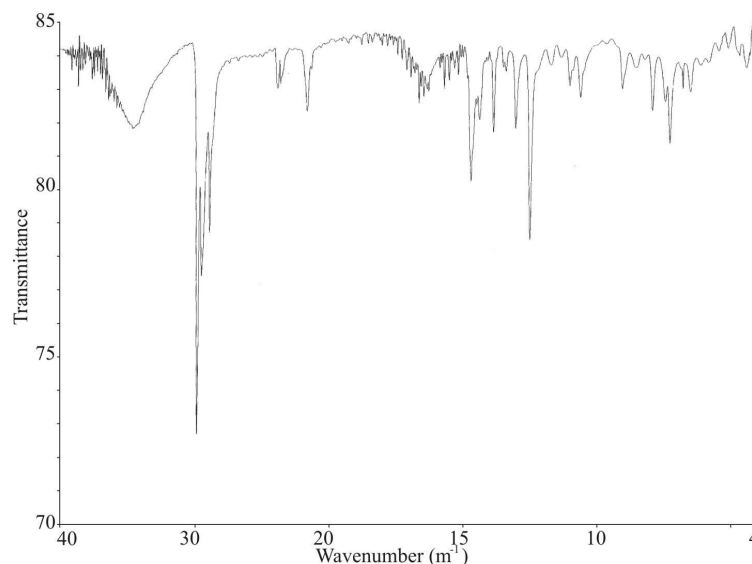


Fig. 1. The infrared spectrum of $\text{Cd(1-PT)}_2\text{Ni(CN)}_4\cdot\text{Benzene}$ clathrate.

2 Experimental

All chemicals used in this study were obtained from the commercial sources and were used without any purification. First, KCN (Merck) of 98% purity and $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ (Merck) of 99% purity were used for obtaining the powdered $\text{K}_2\text{Ni(CN)}_4$ compound. Then, 1 mmole of $\text{K}_2\text{Ni(CN)}_4$ solution in distilled water and 2 mmoles of liquid 1-PT was dropped into the mixture and stirred rapidly during 2-3 minutes. Then, 6 mmoles of benzene were mixed together and all MCl_2 ($\text{M}=\text{Cd}$ or Ni) solution in the distilled water were added by dropping to this mixture and all were stirred during 3 days. The precipitate formed was filtered and washed with distilled water, ethylalcohol and ether successively and kept in a desiccator containing molecular sieves and saturated benzene vapour. The colour of the obtained clathrate containing Cd was cream while the other including Ni is light green.

The prepared samples were compressed into self-supporting pellet and introduced into an IR cell equipped with KBr windows. IR spectra were recorded at room justified temperature on a Perkin-Elmer BX FT-IR (Fourier Transformed Infrared) Spectrometer with a resolution of 0.04 cm^{-1} in the transmission mode.

3 Results and Discussion

The IR spectra of $\text{Cd(1-PT)}_2\text{Ni(CN)}_4\cdot\text{Benzene}$ and $\text{Ni(1-PT)}_2\text{Ni(CN)}_4\cdot\text{Benzene}$ clathrates are given in Figs. 1 and 2, respectively. The analysis of the obtained data from IR spectra can be achieved at three different parts by considering the vibrations of ligands, Ni(CN)_4^{2-} ion units which form the polymeric structure and the guest benzene molecules.

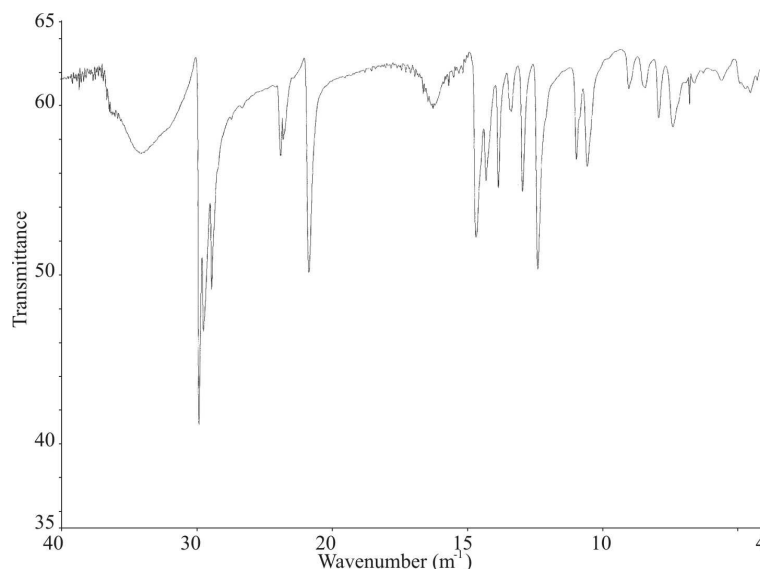


Fig. 2. The infrared spectrum of $\text{Ni}(1\text{-PT})_2\text{Ni}(\text{CN})_4 \cdot \text{Benzene}$ clathrate.

3.1 Ligand Vibrations

IR spectra of 1-PT used as a ligand in $M(1\text{-PT})_2\text{Ni}(\text{CN})_4 \cdot G$ clathrates and bulk liquid 1-PT indicate the existence of some frequency shifts (Tab. 1). The assignments of IR vibrational frequencies for the liquid 1-PT have been taken from reference [14]. These frequency shifts observed in IR spectra of 1-PT molecules at the investigated complexes are arisen from mainly two reasons. One of the reasons is the change in the surrounding conditions of 1-PT due to the formed compound. The second reason can be explained by considering the explicit form of 1-PT which is $\text{CH}_3\text{CH}_2\text{CH}_2\text{SH}$.

As seen in its explicit form, 1-PT has a chain structure. We expect that 1-PT molecules as a ligand are connected to the metal atom of the infinite polymeric structure by via its own sulphure atom. Thus there is a pairing between the vibrations of M-S bond and the internal vibrations of 1-PT. A similar pairing exists between the M-O bonding vibrations and the internal vibrations of ligand molecules [2].

However, the considerable frequency shifts has been observed at the S-H stretching mode of the bulk 1-PT. For instance, the S-H stretching vibrations of $\text{Cd}(1\text{-PT})_2\text{Ni}(\text{CN})_4 \cdot \text{Benzene}$ and $\text{Ni}(1\text{-PT})_2\text{Ni}(\text{CN})_4 \cdot \text{Benzene}$ clathrates are assigned at 0.77 m^{-1} and 1.19 m^{-1} , respectively, while this band was at 25.59 m^{-1} in the bulk 1-PT as seen in Tab. 1. These downward frequency shifts show that the sulphure atoms of 1-PT molecules in the complexes are directly connected to the metal (Cd or Ni) atoms in the infinite polimeric structures. This decreasing in $\nu_{\text{sym}}(\text{SH})$ stretching frequency causes an increase in the $\nu_{\text{asym}}(\text{CS})$ stretching frequencies between C and S atoms. In this framework, the $\nu(\text{CS})$ stretching modes at 7.04 m^{-1} and 6.50 m^{-1} for the bulk 1-PT have been shifted to the bands at 7.17 m^{-1} and 6.40 m^{-1} in the $\text{Cd}(1\text{-PT})_2\text{Ni}(\text{CN})_4 \cdot \text{Benzene}$ and 7.18 m^{-1} and 6.51 m^{-1} in the $\text{Ni}(1\text{-PT})_2\text{Ni}(\text{CN})_4 \cdot \text{Benzene}$ clathrates in the upward fre-

Tab. 1. The IR vibrational wavenumbers (m^{-1}) of the bulk 1-PT and the $\text{M}(1\text{-PT})_2\text{Ni}(\text{CN})_4\cdot\text{Benzene}$ ($\text{M}=\text{Cd}, \text{Ni}$) complexes.

Assignments	Liquid 1-PT	Cd-(1-PT)-Ni-Bz	Ni-(1-PT)-Ni-Bz
CH_3 and CH_2 stretch	29.61 vs	29.59 vs	29.57 s
CH_3 and CH_2 stretch	29.30 vs	29.30 s	29.27 m
CH_3 and CH_2 stretch	28.72 s	28.70 s	28.68 m
	27.32 w	27.26 w	27.31 w
	26.62 w	26.59 w	26.50 w
SH stretch	25.59 m	24.82 w	24.40 w
	23.59 w	23.69 m	23.76 w
	23.34 w	23.47 m	23.45 w
		19.62 vw	19.50 vw
CH_3 asym def	14.56 s	14.58 s	14.56 s
CH_2 scissor	14.38 s	14.39 w	14.30 w
		14.24 m	14.20 m
CH_3 sym def	13.76 s	13.75 s	13.74 s
CH_2 wag	13.38 m	13.29 w	13.29 m
CH_2 wag	12.97 s	12.92 s	12.84 s
CH_2 twist	12.46 s	12.37 s	12.26 s
CH_2 twist	12.16 vw	12.10 sh	12.14 sh
CC stretch	11.06 s	11.26 w	11.26 w
CH_3 rock	10.85 m	10.89 m	10.86 m
CC stretch	10.55 vw		
CC stretch	10.32 vw	10.30 vw	
	9.53 vw	9.50 vw	9.64 vw
CH_3 rock	9.24 w		9.27 vw
CH_2 rock	8.94 m	8.97 m	8.94 m
CH_2 rock	8.78 m		
	8.36 w	8.46 w	8.35 w
CSH def	8.14 w	8.12 vw	
CSH def	7.92 m	7.83 m	7.82 m
CH_2 rock	7.31 s	7.35 w	7.30 m
CS stretch	7.04 m	7.17 m	7.18 sh
CS stretch	6.50 m	6.40 m	6.51 w
CCC def	4.16 w	4.18 vw	4.22 w

where s: strong, vs: very strong, m: medium, w: weak, vw: very weak, sh: shoulder

Tab. 2. The IR vibrational wavenumbers (m^{-1}) of $\text{Ni}(\text{CN})_4$ group in the $M(1\text{-PT})_2\text{Ni}(\text{CN})_4 \cdot \text{Benzene}$ ($M=\text{Cd}, \text{Ni}$) clathrates.

Assignment	$\text{Na}_2\text{Ni}(\text{CN})_4^a$	Cd-Ni-(1-PT)-Bz	Ni-Ni-(1-PT)-Bz
$\nu(\text{CN})$	21.32	21.55 s	21.48 s
Hot band	21.28	21.18 sh	20.85 sh
$\nu(\text{Ni-CN})$	5.43	5.33 w	5.47 w
$\pi(\text{Ni-CN})$	4.48	4.63 w	4.64 w
$\delta(\text{Ni-CN})$	4.33	4.33 m	4.41 w

^aTaken from ref.[17], where s: strong, vs: very strong, m: medium, w: weak, sh: shoulder, ν : stretching, π : out of plane bending, δ : in plane bending.

quency region.

3.2 $\text{Ni}(\text{CN})_4^{-2}$ group vibrations

It is well known that $\text{Ni}(\text{CN})_4^{-2}$ anion has D_{4h} symmetry group and it is expected seven normal modes in vibrational spectrum. Four of them, that is, $E_u \nu(\text{CN})$, $E_u \nu(\text{Ni-CN})$, $A_{2u} \pi(\text{Ni-CN})$ and $E_u \delta(\text{Ni-CN})$ modes are infrared active modes at the other modes are active in Raman spectroscopy. First four modes are observed in our study. For this reason we accept that the $\text{Ni}(\text{CN})_4^{-2}$ ions have an square-planar arrangement.

The assignments of IR vibrational frequencies of $\text{Ni}(\text{CN})_4^{-2}$ groups in our complexes are based on the work done by McCullough and co-workers in the tetracyanonickelate groups in the salt $\text{Na}_2\text{Ni}(\text{CN})_4$ [17]. For the aim of comparison IR spectral results of $\text{Ni}(\text{CN})_4$ groups in our clathrates and in the reference [17] are given in Tab. 2.

This comparison shows that the vibration frequencies $\nu(\text{CN})$ are shifted to the bands at 21.55 m^{-1} and 21.48 m^{-1} in the higher frequency region for $\text{Cd}(1\text{-PT})_2\text{Ni}(\text{CN})_4 \cdot \text{Benzene}$ and $\text{Ni}(1\text{-PT})_2\text{Ni}(\text{CN})_4 \cdot \text{Benzene}$ clathrates, respectively. The similar shifts are observed at the out of plane bending vibration frequencies $\pi(\text{Ni-CN})$ for both complexes. These shifts arise from the pairing between the CN stretching vibrations and the metal-nitrogen bond stretching vibration. At the same time, the frequencies of the CN stretching vibrations depend on the electronegativity, oxidation states and the coordination numbers of the metal connected [18]. On the other hand the weak bands at 5.33 m^{-1} and 5.47 m^{-1} for $\text{Cd}(1\text{-PT})_2\text{Ni}(\text{CN})_4 \cdot \text{Benzene}$ and $\text{Ni}(1\text{-PT})_2\text{Ni}(\text{CN})_4 \cdot \text{Benzene}$ clathrates, respectively, are mainly the $\nu(\text{Ni-CN})$ stretching modes of $\text{Ni}(\text{CN})_4^{-2}$ groups. These characteristic IR frequencies denote the laminated Ni-CN-M structure for our complexes and are in good agreement with those of the Hofmann-type complexes which have the polymeric layer structure. It can be considered that these polymeric layers are held in the parallel by Wan der Waals interactions between the methyl (CH_3) groups in the 1-PT ligand molecules [9]. The 1-PT molecules take place in the above and below of the planar layers. In this kind of complexes the M (metal) atoms are surrounded in the square-planar environment by four carbon atoms of cyanone groups and 1-PT molecules.

Tab. 3. The IR vibrational wavenumbers (m^{-1}) of benzene in the $\text{M}(\text{1-PT})_2\text{Ni}(\text{CN})_4\cdot\text{Benzene}$ ($\text{M}=\text{Cd}, \text{Ni}$) complexes.

Assignment ^b	Liquid Benzene	Cd-(1-PT)-Ni-Bz	Ni-(1-PT)-Ni-Bz
ν_{20}, E_{1u}	30.70	-	-
$\nu_8 + \nu_{19}$	30.75	-	-
ν_{13}, B_{1u}	30.48	-	-
$\nu_5 + \nu_{17}, \text{E}_{1u}$	19.55	19.66 vw	19.59 w
$\nu_{10} + \nu_{17}$	18.15	18.45 w	18.45 w
ν_{19}, E_{1u}	14.79	14.89 m	14.90 m
ν_{14}, B_{2u}	13.09	13.29 w	13.29 s
ν_{15}, B_{2u}	11.49	11.63 m	
ν_{18}, E_{1u}	10.36	10.49 m	10.45 s
ν_{17}, E_{2u}	9.66	9.66 w	9.63 sh
ν_{11}, A_{2u}	6.70	6.69 m	6.69 m

^bTaken from ref. [19] and where s: strong, vs: very strong, m: medium, w: weak, sh: shoulder, ν : stretching.

3.3 Guest (Benzene) Vibrations

IR spectral data of guest benzene molecules in the clathrates are given in Tab. 3. For the assignments we referred to the works done on the free benzene molecules in the liquid state and benzene molecules in some other clathrates [19-20]. In IR spectra of our clathrates, several vibration bands of isolated benzene molecules are observed as seen in Tab. 3. By considering the fact that the benzene molecules lost their intrinsic D_{6h} symmetries due to the changes of their surroundings in the clathrates [20]. We can state that the bands due to the γ_{CH} (out of plane bending) modes are of the key importance for deriving conclusions about the guest-host interactions in the clathrates. As seen in Tab. 3 the band at 6.70 m^{-1} in the liquid benzene remains practically unchanged at the medium bands at 6.69 m^{-1} for both clathrates, but the ν_{19} mode at 14.79 m^{-1} in the liquid benzene is shifted to the bands at 14.89 m^{-1} and 14.90 m^{-1} in the $\text{Cd}(\text{1-PT})_2\text{Ni}(\text{CN})_4\cdot\text{Benzene}$ and $\text{Ni}(\text{1-PT})_2\text{Ni}(\text{CN})_4\cdot\text{Benzene}$ clathrates, respectively.

4 Conclusion

According to the above discussion the guest benzene molecules interact with their own surroundings in the large cavities of clathrates.

As a conclusion, we can state that the $\text{M}(\text{1-PT})_2\text{Ni}(\text{CN})_4\cdot\text{Benzene}$ ($\text{M}=\text{Cd}$ or Ni) compounds are two novel Hofmann-type clathrates.

Acknowledgement: This work was supported by Süleyman Demirel University, The Unit of the Management of Scientific Research Projects within the project No:621.

References

- [1] J. H. Rayner, H. M. Powell: *J. Chem. Soc* **28** (1952) 319
- [2] S. Akyüz, A.B. Depster, R.L. Morehous, S.Suzuki: *J. Mol. Struct.* **17** (1973) 105
- [3] S. Akyüz, J.E.D. Davies, Y. Demir, N. Varman: *J. Mol. Struct.* **79** (1982) 267
- [4] Ş. Ağustoslu, S. Akyüz, J.E.D. Davies: *J. Mol. Struct.* **114** (1984) 437
- [5] R.S. Drago, J.T.Kwan, R.D. Archer: *J. Am. Chem. Soc.* **80** (1958) 2667
- [6] A.B. Dempster, H. Uslu: *Spectrochim. Acta. Part A* **34** (1978) 71
- [7] S. Bayari, Z.Kantarci, S.Akyüz: *J. Mol. Struct.* **351** (1995) 19
- [8] M. Şenyel: *Bull. Of Pure and Appl. Sci.* **20 D** (2001) 61
- [9] N. Karacan, Y.Tufan: *Spect. Lett.* **28** (1995) 773-782
- [10] M. Şenyel, G.S. Kürkçüoğlu: *J. Appl. Spec.* **68** (2001) 5862
- [11] R.E. Pennington, D.W. Scott, H.L. Finke, J.P. McCullough, J.F. Messerly, I.A. Hossenlopp, G. Waddington: *J. Am. Chem. Soc.* **78** (1956) 3266
- [12] M. Hayashi, Y. Shiro, H. Murata: *Bull. Chem. Soc. Japan* **39** (1966) 112
- [13] D.W. Scott, M.Z. El-Sabban: *J. Mol. Spectry.* **30** (1969) 317
- [14] T. Trogrimsen, P.Klæboe: *Acta Chemica Scandinavica* **24** (1970) 1139
- [15] S. Ventakeswaran: *Ind. J. Phys* **5** (1930) 219
- [16] G. Radinger, H.Z. Wittek: *Physik. Chem. B* **45** (1940) 329
- [17] R.L. McCullough, L.H.Jones, G.A. Crosby: *Spectrochim. Acta* **16** (1960) 929
- [18] M. Davies: *Infrared Spectroscopy and Molecular Structure*. Elsevier, Amsterdam (1963)
- [19] P.C. Painter, J.L. Koenig: *Spectrochim Acta* **33 A** (1977) 103
- [20] E. Kasap, Z. Kantarci: *J. of Incl. Phenom and Mol. Recog. in Chem.* **28** (1997) 117