FT-IR Spectroscopic Study of Co(1-Propanethiol)$_2$Ni(CN)$_4$·Benzene Clathrate

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Z. Naturforsch. **59a,** 523 – 526 (2004); received April 14, 2004

By vibrational spectroscopy of the new Hofmann-propanethiol-type clathrate Co(1-propanethiol)$_2$Ni(CN)$_4$·Benzene it is shown that its structure is similar structure to those of other Hofmann-type clathrates.

Key words: IR; N-Propyl Mercaptan; Tetraciyanonickelate; Hofmann-type Clathrate.

1. Introduction

Infrared spectroscopy is one of the most powerful tools for the investigation of the host-guest interactions in Hofmann-type clathrates. The clathrates are of great interest because of their cage structure, inclusion behaviour and use as catalysts, anti-oxidants and stabilizing agents [1]. The general formula of Hofmann-type clathrates is ML$_2$Ni(CN)$_4$·G, where M is a transition metal atom having the valence +2, L is either a bidentate or two monodentates, and G is the guest molecule [2].

The ML$_2$Ni(CN)$_4$ complexes form polimeric sheets consisting of metal cyanite bridges $|\text{M- Ni(CN)}_4|_\infty$ and ligand molecules L bound to a transition metal M from the nitrogen end located above or below the sheets [3]. The Hofmann-type host provides α-type cavities (rectangular boxes) and β-type cavities (twisted biprisms) for the guest molecules [4 – 5].

For the bulk 1-propanethiol (1-PT) or n-propyl mercaptan the infrared vibration modes and frequencies were presented by Trogrimsen and Klæboe [6]. The 1-PT or n-propyl mercaptan has been used as a ligand in the M(1-PT)$_2$Ni(CN)$_4$·G (M=Cd,Ni and G=Benzene) clathrates [7]. The purpose of the present work is to offer a new Hofmann-propanethiol-type clathrate and emphasize that the host framework of this kind of compounds has a similar structure as that of conventional Hofmann-type clathrates.

2. Experimental

All chemicals were obtained from commercial sources and were used without further purification. First, KCN (Merck) of 98% purity and NiCl$_2$·6H$_2$O (Merck) of 99% purity were used for obtaining powdered K$_2$Ni(CN)$_4$. Then 1 mmole of K$_2$Ni(CN)$_4$ solved in distillated water and 2 mmoles of liquid 1-PT were mixed and stirred rapidly during 2 – 3 minutes. Then 5 mmoles of benzene were mixed together, CoCl$_2$ solved in distillated water was added by dropping, and the whole was stirred during 3 days. The precicipate formed was filtered and washed with distillated water, ethylalcohol and diethylether successively and kept in a desiccator containing molecular sieves and saturated benzene vapour. The colour of the obtained clathrate was dark brown.

The prepared samples were compressed to self-supporting pellets and introduced into an IR cell, equipped with KBr windows. The IR spectra were recorded at room temperature on a Perkin-Elmer BX FT-IR (Fourier Transformed Infrared) Spectrometer with a resolution of 4 cm^{-1} in the transmission mode.

3. Results and Discussion

The IR spectrum of Co(1-PT)$_2$Ni(CN)$_4$·Benzene clathrate is shown in Figure 1. The results obtained from the IR spectral data can be analysized for a) vi-

Table 1. IR vibrational wavenumbers (cm^{-1}) of bulk 1-PT in the $Co(1\text{-PT})_2Ni\ (CN)_4\cdot$Benzene complex.

Assignments	Liquid 1-PT	Co-(1-PT)-Ni-Bz
CH_3 and CH_2 stretch	2961 vs	2958 vs
CH_3 and CH_2 stretch	2930 vs	2930 s
CH_3 and CH_2 stretch	2872 s	2869 s
	2732 w	2812 vw
SH stretch	2559 m	2638 sh
CH_3 asym def	1456 s	1454 s
CH_2 scissor	1438 s	
CH_3 sym def	1376 s	1374 s
CH_2 wag	1338 m	1330 m
CH_2 wag	1297 s	1282 s
CH_2 twist	1246 s	1226 s
CC stretch	1106 s	1130 sh
CH_3rock	1085 m	1084 m
CC stretch	1055 vw	1060 sh
CC stretch	1032 vw	1032 vw
	953 vw	952 m
CH_3rock	924 w	
CH_2rock	894 m	894 m
CH_2rock	878 m	
	836 w	830 m
CSH def	792 m	783 s
CH_2rock	731 s	729 s
CS stretch	651 m	587 sh
CCC def	416 w	412 vw

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

Table 2. IR vibrational wave numbers (cm^{-1}) of the $Ni(CN)_4$ group in the $Co(1\text{-PT})_2Ni\ (CN)_4\cdot$Benzene clathrate.

Assignment	$Na_2Ni(CN)_4$[a]	Co-Ni- (1-PT)-Bz
ν(CN)	2132	2136 s
Hot band	2128	–
ν(Ni-CN)	543	554 w
π(Ni-CN)	448	477 m
δ(Ni-CN)	433	433 w

[a] Taken from [8], where s: strong, m: medium, w: weak, ν: stretching, π: out of plane bending, δ: in plane bending.

Table 3. IR vibrational wavenumbers (cm^{-1}) of benzene in the $Co(1\text{-PT})_2Ni\ (CN)_4\cdot$Benzene complex.

Assignment[b]	Liquid Benzene	Co- (1-PT)-Ni-Bz
ν_{20}, E_{1u}	3070	–
$\nu_8 + \nu_{19}$	3075	–
ν_{13}, B_{1u}	3048	–
$\nu_5 + \nu_{17}$, E_{1u}	1955	1960 b
$\nu_{10} + \nu_{17}$	1815	
ν_{19}, E_{1u}	1479	1416 s
ν_{14}, B_{2u}	1309	1329 m
ν_{15}, B_{2u}	1149	1155 m
ν_{18}, E_{1u}	1036	1071 sh
ν_{17}, E_{2u}	966	950 b
ν_{11}, A_{2u}	670	611 m

[b] Taken from [11] and where b: broad, s: strong, m: medium.

brating ligand molecules, b) $Ni(CN)_4{}^{-2}$ ion units, and c) the guest benzene molecules.

a) Ligand Vibrations: The 1-PT molecule used as a ligand in $Co(1\text{-PT})_2Ni(CN)_4\cdot$Benzene clathrate has a chain structure ($CH_3CH_2CH_2SH$). The vibrational spectroscopic results for this ligand molecule in our complex are given in Table 1. The assignments of the IR vibrational frequencies for the bulk liquid 1-PT have been referred to Trogrimsen and Klæboe [6]. As seen in Table 1, the strong bands in the interval 2958 – 2869 cm^{-1} and the weak bands (denoted with arrows) 2812 cm^{-1} and 2728 cm^{-1} can be assigned to the methyl (CH_3) and methylene (CH_2) stretching modes of 1-PT ligand molecule in our complex. On the other hand, the S-H stretching vibrations of bulk 1-PT are observed at 2559 cm^{-1}, while this mode in $Co(1\text{-PT})_2Ni(CN)_4\cdot$Benzene clathrate is shifted to the shoulder band at 2638 cm^{-1} (shown with an arrow) in the high frequency region. This upward frequency shift can be interpreted in terms of the connection between the sulphure atom of the 1-PT molecules and the metal (Co or Ni) atoms in the infinitive polymeric structure [7]. Likewise the ν(CS) stretching modes of the ligand molecule in the clathrate are shifted to 587 cm^{-1} in the low frequency region. This downward frequency shift can be regarded as the result of the increase in the ν_{sym}(SH) stretching frequency in the clathrate. We can state that the changes in the surroundings of 1-PT ligand molecules in the complex cause the frequency shifts because of the formation of a new compound.

b) $Ni(CN)_4{}^{-2}$ group vibrations: The vibrational wave numbers of the $Ni(CN)_4{}^{-2}$ anions in our investigated complex are given in Table 2 together with those found by McCullough and co-worker in the tetracyanonickelate group in the salt $Na_2Ni(CN)_4$ for comparison [8].

The characteristic wave numbers of the (CN) and (Ni-CN) modes are similar to those of Hofmann-type clathrates, indicating that the $\{M\text{-}Ni(CN)_4\}_\alpha$ layers were preserved [7]. The ν(CN) E_u and δ(Ni-CN) E_u modes are both observed as strong and medium bands at 2136 cm^{-1} and 433 cm^{-1} in the IR spectra of the clathrate, respectively. On the other hand, the ν(Ni-CN) and π(Ni-CN) modes of the $Ni(CN)_4{}^{-2}$ groups are shifted to higher frequencies for $Co(1\text{-PT})_2Ni(CN)_4\cdot$Benzene clathrate, as seen in Table 2. These upward frequency shifts can arise from the pairing between the CN stretching vibrations and the metal-nitrogen bond stretching vibration. In fact, the frequencies of the CN streching vibrations of the

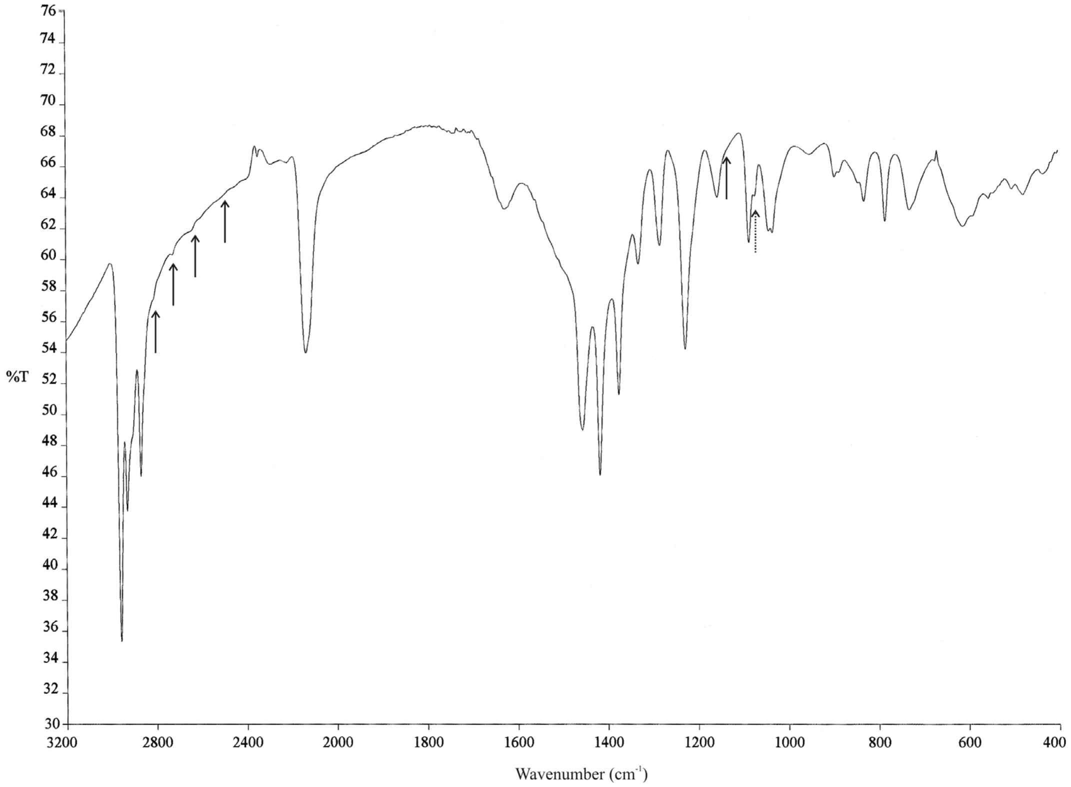

Fig. 1. The infrared spectrum of Co(1-PT)$_2$Ni(CN)$_4$·Benzene clathrate.

Ni(CN)$_4$$^{-2}$ groups depend on the electronegativity, oxidation states and coordination numbers of the metal connected [9]. Considering these data, we can state that, because the Ni(CN)$_4$$^{-2}$ ions have a square-planar arrangement and the metals atoms are surrounded by four carbon atoms of cyanone groups in the clathrates, the polymeric layers are hold in the paralel by Van der Waals interactions between the methyl (CH$_3$) groups in the 1-PT ligand molecules [10].

c) Benzene (guest molecule) Vibrations: The assignments and the frequencies of the vibrational bands arising from the enclathrated benzene observed in the spectrum of Co(1-PT)$_2$Ni(CN)$_4$·Benzene are given in Table 3 along with the wave numbers of benzene in the liquid phase found by Painter and Koening for comparison [11]. It is expected that the benzene molecules loose their intrinsic (D$_{6h}$) symmetries due to the changes of their surroundings in the clathrates [12].

Structurally the most informative spectral features are as follows. The A$_{2u}$ (the CH –out-of plane) mode is observed to be shifted to lower frequency (the medium band at 611 cm^{-1}), whereas this band is observed at 670 cm^{-1} for the bulk benzene, as seen in Table 3. Similarly, the ν_{19} mode of the guest benzene molecules in the complex appears in a strong band at 1416 cm^{-1}, which is shifted to the lower frequencies. On the other hand, the E$_{1u}$(ν_{18}) mode is observed as a shoulder at 1071 cm^{-1} (denoted with a pointed arrow in Fig. 1) in the higher frequency region. These frequency shifts for the guest benzene molecule in the Co(1-PT)$_2$Ni(CN)$_4$·Benzene complex are explained by considering their interactions with the host molecules of this compound.

As a conclusion we can state that the Co(1-PT)$_2$Ni(CN)$_4$·Benzene compound is a novel Hofmann-type clathrate.

Acknowledgements

This work was supported by the TÜBİTAK (Turkish Scientific and Technical Research Council) within the project No. TBAG-AY/301 (103T003) and the Süleyman Demirel University, The Unit of the Management of Scientifical Research Projects within the project No. 621.

[1] M. Hagan, Clathrate Inclusion Compounds, Reinhold Publising Corporation, Chapman & Hall Ltd., New York 1962, p. 5.

[2] T. Iwamoto: 'Inclusion Compounds', in J. L. Atwood, J. E. D Davies, and D. D. Mc Nicol (eds.), Vol. I, Academic Press, London 1984, p. 29.

[3] T. Iwamoto: 'Inclusion Compounds' in J. L. Atwood, J. E. D. Davies, and D. D. Mc Nicol (eds.), Vol. 5, Oxford University Press, London 1991, p. 177.

[4] R. Kurada, Inorg. Nucl. Chem. Lett. **9**, 13 (1973).

[5] T. Iwamoto and D. F. Shriver, Inorg. Chem. **11**, 2570 (1972).

[6] T. Trogrimsen and P. Klæboe, Acta Chemica Scandinavica **24**, 1139 (1970).

[7] Z. Kartal, D. Türköz, and S. Bahçeli, Acta Phys. Slovaca **54**, 97 (2004).

[8] R. L. McCullough, L. H. Jones, and G. A. Crosby, Spectrochim. Acta **16**, 929 (1960).

[9] M. Davies, Infrared Spectroscopy and Molecular Structure, Elsevier, Amsterdam 1963.

[10] N. Karacan and Y. Tufan, Spect. Lett. **28**, 773 (1995).

[11] P. C. Painter and J. L. Koening, Spectrochim Acta **33**A, 103 (1977).

[12] E. Kasap and Z. Kantarcı, J. Incl. Phenom. and Mol. Recog. in Chem. **28**, 117 (1997).