



FT-IR spectroscopic study on some Hofmann-type clathrates: M(*p*-Benzoquinone)Ni(CN)₄·2G (M = Mn, Co, Ni or Hg; G = Aniline)

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ABSTRACT

Some new Hofmann type aniline clathrates in the form of M(*p*-Benzoquinone)Ni(CN)₄·2G (M = Mn, Co, Ni or Hg, *p*-Benzoquinone = pBQ and G = Aniline = An) have been obtained for the first time in powder form and their FT-IR spectra have been reported in the range of (4000–400) cm⁻¹. The thermal behavior of these clathrates has been also investigated by thermo-gravimetric analysis (TGA), differential thermal analysis (DTA) and derivative thermal gravimetric analysis (DTG). The spectral and thermal analysis results of the new Hofmann type aniline clathrates suggest that the obtained clathrates are new examples of the Hofmann-type clathrates. The Hofmann-type clathrates consist of the corrugated [M–Ni(CN)₄]_∞ polymeric layers which are held in parallel through the chain of (–M–pBQ–M–pBQ–) in our new Hofmann type aniline clathrates formed by bounding electrons of oxygen atoms of the carbonyl groups of pBQ ligand to transition metal atoms.

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1. Introduction

In various studies, the Hofmann-type clathrates given by the general formula M(II)LM'(II)(CN)₄·*n*G have been produced by using various ligands, where M is the transition metal atom having two values (Mn, Fe, Co, Ni, Cu or Cd), M' is the square-planar coordinated transition metal atom having two values (Ni, Pd or Pt), and L is either two ligand molecules having a monodentate or a ligand molecule as bidentates. G is the guest molecule and *n* is the number of guest molecules in the clathrates [1,2]. Infrared spectroscopy is one of the best ways to investigate the structure in the Hofmann-type clathrates.

In this study, we use for the first time the pBQ molecule as a ligand to produce new Hofmann-type clathrates in the of M(pBQ)Ni(CN)₄·*n*G, where M is the transition metal atom (Mn, Co, Ni or Hg) and G is aniline (An) as a guest molecule. Four new Hofmann type aniline clathrates have been synthesized in powder form. These clathrates were investigated by FT-IR and thermal analysis in the infrared range of (4000–400) cm⁻¹ and in the temperature range of (20–700) °C.

2. Experimental

2.1. Materials and syntheses of the compounds

In this study, all chemicals, namely pBQ; C₆H₄O₂ (Fluka), MnCl₂ (Fluka, 99%, anhydrous), CoCl₂·6H₂O (Fluka, 98%), NiCl₂·6H₂O

(Fluka, 99%), HgCl₂ (Fluka, 99.5%), K₂[Ni(CN)₄] (Fluka, 98%), and An; C₆H₅NH₂ (Sigma–Aldrich, 99.5%), were used without further purification. The clathrates were prepared as follows: first, 1 mmol K₂[Ni(CN)₄] was dissolved in distilled water and 1 mmol pBQ molecules were added to the solution under stirring; second 3 mmol guest molecule An were added to the solution under rapidly stirring for 3 min; finally, 1 mmol of the MCl₂ (M = Mn, Co, Ni and Hg) dissolved in distilled water was added to this mixture. The whole mixture was stirred during five days. The obtained compounds were filtered, washed with pure water, ethanol and diethyl ether, and kept in desiccators containing vapor of guest molecule and silica gel.

2.2. Instrumentation

The FT-IR spectra of these clathrates were recorded in the range of (4000–400) cm⁻¹ at the room temperature on a Bruker Optics Vertex 70 FT-IR Spectrometer having the resolution of 2 cm⁻¹ using an ATR attachment which was calibrated using CO₂ bands. The TGA and DTA curves of the clathrates were recorded under air at a heating rate of 10 °C/min in the temperature area (20–700) °C using platinum crucibles on a SII EXSTAR 6000 TG/DTA 6300 thermal analyzer. The clathrates were analyzed for metals with Perkin-Elmer optima 4300 DV ICP-OES and for C, H and N amounts with CHNS-932 (LECO) elemental analyzer. The results of elemental analyses are given in Table 1. According to the elemental analysis results, there are two aniline (An) molecules in the present clathrates as guest molecules (*n* = 2). Same results have been observed for the other Hofmann type aniline clathrates [3–5].

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Table 1
Elemental analysis of the M-(pBQ)-Ni-G (M = Mn, Co, Ni or Hg and G = An) clathrates.

Abbreviations of clathrates and M_r (g)	Elemental analysis, Found (%)/(Calculated) (%)						
	Mn	Co	Ni	Hg	C	H	N
Mn-pBQ-Ni-An $M_r = 512.05$	10.52 (10.73)	– (–)	11.52 (10.46)	– (–)	51.33 (51.60)	3.41 (3.54)	16.46 (16.41)
Co-pBQ-Ni-An $M_r = 516.05$	– (–)	11.19 (11.42)	11.14 (11.37)	– (–)	50.96 (51.21)	3.44 (3.52)	15.92 (16.29)
Ni-pBQ-Ni-An $M_r = 515.80$	– (–)	– (–)	22.55 (22.76)	– (–)	50.97 (51.23)	3.41 (3.52)	16.03 (16.29)
Hg-pBQ-Ni-An $M_r = 657.70$	– (–)	– (–)	8.76 (8.92)	30.21 (30.50)	39.91 (40.18)	2.55 (2.76)	12.93 (12.78)

All the analyses of these clathrates were carried out immediately to avoid any declathration.

3. Results and discussion

The FT-IR spectra of all clathrates are compatible with each other and are shown in Fig. 1. The assignments have been made by treating the ligand the pBQ molecule, the $[\text{Ni}(\text{CN})_4]^{2-}$ ions as isolated units and guest aniline molecule to determine the possible shifts for each clathrates.

3.1. pBQ vibrations

The pBQ molecule contains two carbonyl groups having oxygen atoms which can donate electrons. The molecular structure of the pBQ is shown in Fig. 2.

The pBQ is used as a polymerization inhibitor in petrochemical, dyestuff pharmaceutical, pesticide intermediate, fungicide, reagent in photography, medicine, herbicide, and chemicals [6]. The pBQ molecule has a regular symmetrical structure. Its dimension is smaller than that of many other macro molecules (lengthwise 5.32745 Å) and it possesses a superior electron transfer property in chemical reactions. Because of these properties, the pBQ molecules are preferred for the production of the chemical compounds [7]. The types of interaction of the pBQ with other molecules were defined by Hunter [8]. The interaction regions were determined through the rules of Hunter–Sander [9]. The polarization of the pBQ provides four (π – π) interactions to become effective from edge to surface. Yet, the oxygen of the carbonyl groups in the pBQ molecule, compared to the (π – π) interactions [8], is more effective in order to have hydrogen bond or exchange of electrons with metal.

The electron density of the pBQ was calculated at the Restricted Hartree–Fock (R–HF) level using PM3 method in MOPAC 97 program package. The calculations indicate that oxygen atoms numbered as 7 and 8 have higher electron density than that of the carbon atoms with numbered 2, 3 and 5, 6. Hence, it expects that the binding takes place with the oxygen atoms of the carbonyl groups. There are various Raman and infrared studies reported for the pBQ molecule [10–14].

The pBQ has a planar structure and belongs to the D_{2h} point group. It has 30 normal vibrations, among which 5 b_{1u} , 5 b_{2u} and 3 b_{3u} vibrations are IR active [11]. The assignments and wavenumbers of the infrared bands for the pBQ molecule observed in the FT-IR spectra of the clathrates are given in Table 2, together with the vibrational wavenumbers of bulk the pBQ.

The observed small frequency shifts are due to the changes of the surround of the pBQ molecule and the pairing of the internal vibration of the pBQ molecule with the vibrations of (M–O) bond. Such small frequency shifts were also reported in other studies [15,16]. The noticeable frequency shifts were observed at frequencies of the CH str, b_{2u} ; CH str, b_{1u} ; C=O str, b_{1u} . The frequencies of

the CH str, b_{2u} and CH str, b_{1u} in the bulk pBQ molecules at 3030 and 2980 cm^{-1} shifted to low frequency region around 48–55 and 30–55 cm^{-1} in clathrates, respectively.

The observed frequency of the C=O str, b_{1u} at 1740 cm^{-1} for the bulk pBQ molecule shifted to low frequency region around 101–122 cm^{-1} in the clathrates. The infrared spectral data for the pBQ in the clathrates are consistent with all the vibrational features the CH and C=O groups of a coordinated ligand. The CH and C=O stretching frequency should decrease due to the consecutive effects and coordination [17]. Hence, the CH and C=O bonds should become weaker. This shift shows that pBQ molecule is connected directly to transition metals atoms through the oxygen of the carbonyl groups. These observed frequencies shifts may be interpreted as a weakening of the C=O bonds resulting from the electron draining of the two oxygen atoms on account of their bridging coordination between the metal atoms (M = Mn, Co, Ni and Hg).

The frequency shifts to higher frequencies were also observed for the clathrates. For example, the (C=O) wag, b_{3u} frequencies shifted to the higher frequency around 7–14 cm^{-1} . The reason is that the bonding of the (CO–M) makes difficult the C–O deformation motion for the C=O. Similar shifts were observed in Şenyel's study [18].

The non covalent Ni– π binding force among the Ni ions with aromatic systems of the pBQ ligand and aniline guest molecules should be too much weak to be seen by spectroscopic techniques; however, these types of interactions were observed in a similar study including crystallographic technique [19]. This non covalent Ni– π binding force is very important in stabilizing the polymeric layers of the clathrates.

3.2. $[\text{Ni}(\text{CN})_4]^{2-}$ vibrations

If a unit cell has the symmetry D_{4h} , then seven normal modes are expected to be in a vibration spectrum. Four of them must be active in the IR spectrum and the remaining ones in the Raman spectrum. The IR active vibrational modes are $\nu(\text{CN}) E_u$, $\nu(\text{NiCN}) E_u$, $\pi(\text{NiCN}) A_{2u}$ and $\delta(\text{NiCN}) E_u$. Since we have observed these four bands in the infrared spectrum, our clathrates have a square planar environment. The frequencies of the $\text{Ni}(\text{CN})_4$ group vibrations in clathrates are assigned on the basis of the work of McCullough et al. [20], who presented vibrational data for the ion $\text{Ni}(\text{CN})_4$ in $\text{Na}_2\text{Ni}(\text{CN})_4$. The vibrational wavenumbers of the $\text{Ni}(\text{CN})_4$ in our clathrates are given in Table 3, together with McCullough data and the data for the complex of Ni–CPN–Ni [21] for comparison.

As the stretched vibrations of the CN group of the $\text{K}_2\text{Ni}(\text{CN})_4$ were observed in 2122 cm^{-1} region, the band $\nu(\text{CN}) E_u$ for the clathrates of M-pBQ-Ni-An shifted to a higher frequency range around 31–43 cm^{-1} . The same shift around 15–25 cm^{-1} appeared also in the plane bending of $\delta(\text{NiCN}) E_u$, of the $\text{K}_2\text{Ni}(\text{CN})_4$ were observed in 414 cm^{-1} region for clathrates. The shifts show that both bands are connected to the transition metal atoms. The stretched

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