In situ IR monitoring of complexation reaction between 2,6-bis(3,5-dimethylpyrazoyl)pyridine and some metal ions

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ABSTRACT

In situ complexation reactions between 2,6-bis(3,5-dimethylpyrazoyl)pyridine (bdmpp) and some transition metals (Cu^{2+}, Co^{2+} and Ni^{2+}) were studied with a new method in liquid cell using FT-IR. In this method, the FT-IR spectrum of the solution of ligand was defined as a background, and then the changes in the FT-IR spectra by the addition of the metal salts were investigated. This method allows one to obtain the spectra of the ligand–metal complex before yielding the solid-state product. Complexation ratios (M/L) of these metals with bdmpp were found 1/1, 1/2 and 1/2, for Cu, Co and Ni, respectively. Studying with Mg^{2+} and Ca^{2+} ions showed that there were no interaction between bdmpp and these metal ions in methanol.

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1. Introduction

FT-IR spectrometry is an analytical technique that provides qualitative and also quantitative information from samples in the forms of solid, liquid, and gas. One of the advantages of IR over other spectroscopic techniques is that practically almost all of the compounds show vibrations for most of the bonds [1]. Thus, it is very useful for monitoring the bond breaking and forming reactions, and it can also be used for observing the change in bond strength. Different applications of FT-IR techniques are reported in the literature. FT-IR spectroscopy is well suited for the rapid investigation of enzymatic reactions since the recording of a complete IR spectrum takes less than a second [2,3]. In situ determination of transient pK_a changes of internal amino acids of bacteriorhodopsin by FT-IR was reported [4]. Raman spectroscopy is also used for monitoring in situ the imination reaction [5,6]. Generally, it is common to investigate the metal–ligand complexation by UV/Vis spectroscopy in solutions [7]. Aqueous solution of Cu(II) and Ni(II) complexes of macrocyclic dioxo-tetraamines were studied by using potentiometric, calorimetric, and UV/Vis spectroscopic titrations [8]. However, UV/Vis fails to make direct measurements in some cases, where no electron transition occurs on the studied molecule or no intensity change is observed at the absorption maxima. In such cases, some UV active reactants need to be added to the reaction media to acquire indirect UV measurements. Since the wavenumbers and intensities of the FT-IR vibrational bands are directly related to the bond type and its strength, it is convenient to demonstrate the change in molecule which is reacted or interacted with other species.

FT-IR spectroscopy can be efficiently used to investigate the host–guest interaction in macrocycles such as calixarenes by using FT-IR liquid cell. Calixarene complexation with some metal ions in acetonitrile was reported in the literature [9]. In that paper, all vibrational bands of ligands and complexes occurred at the same side of absorbance baseline of the IR spectra. Additionally, the observed bands were too close to each other, thus it became difficult to distinguish and identify the absorption bands corresponding to the ligand and/or complexes.

In our previous study, we have proposed a new real-time technique for imination reaction in liquid cell by FT-IR spectroscopy [10]. This method supports that the reaction of benzaldehyde and aniline is in equilibrium in chloroform [11]. The current work shows that this method could also be applicable for observing in situ reaction such as complexation by means of the interaction between ligands and metals.

2,6-Bis(3,5-dimethylpyrazoyl)pyridine (bdmpp, Scheme 1) is a terpyridine derivative ligand. Many 2,6-bis(pyrazoyl)pyridine ligands were synthesized and their metal complexes were prepared successfully [12–15].

In this work, we used IR spectroscopy to observe in situ complexation reactions of bdmpp which interacts with Cu^{2+}, Co^{2+}, and Ni^{2+}(ions). It is found that bdmpp does not interact with Mg^{2+} and Ca^{2+}.

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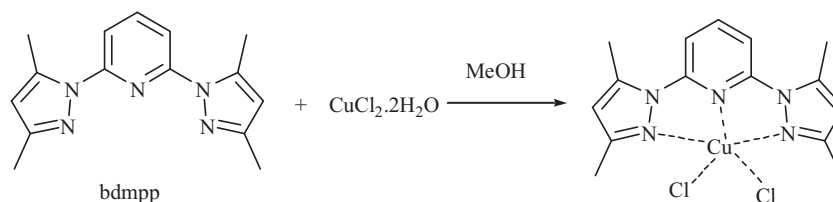
Scheme 1. Complexation of bdmpp with Cu^{2+} in methanol.

2. Materials and methods

2.1. Materials

All reagents and solvents were purchased as reagent grade from Merck, Aldrich, or Carlo Erba and used without further purification. A Perkin-Elmer Model BX 1600 instrument with a 0.015 mm pathlength CaF$_2$ liquid cell was used to collect the FT-IR spectra. 2,6-Bis(3,5-dimethylpyrazoyl)pyridine (bdmpp) was prepared from 2,6-dicholropyridine and potassium salt of 3,5-dimetyl-N-pyrazol by refluxing them in diethylene glycol dimethyl ether as described in the literature [16]. The obtained spectral data were found to be in good agreement with the literature.

2.2. Method: In situ investigation of complexation by FT-IR spectroscopy in solution

The method is summarized as follows:

1. The equivalent concentration (0.1 M) of ligand (bdmpp) and metal salts were prepared in the same solvent separately.
2. The IR spectrum of ligand (bdmpp) solution labelled BD in Table 1 was scanned in CaF$_2$ liquid cell and further used as spectral background.
3. The ligand and metal salt solutions were mixed with volume ratios listed in Table 1. The appropriate amount of methanol was added to each mixture, to preserve the constant concentration of the ligand. Finally, the IR spectra were measured with ligand spectrum as background.
4. The vibrational bands below the flat absorbance line (negative absorbance or absorption bands pointing downwards) indicate a decrease in the free ligand concentration while the vibrational bands above the baseline (positive absorbance – absorption bands pointing upwards) are due to the increase of the complex quantity in the solution.
5. In the case of no interaction between ligand and metal, no vibrational bands above or below the absorbance baseline are observed.

Table 1
Preparation of the measured solutions for bdmpp–Cu^{2+}, –Ni^{2+} and –Co^{2+}.

Volume [ml] of 0.1 M bdmpp solution (stock)	Volume [ml] of 0.1 M M^{+2} (Cu^{2+}, Co^{2+}, Ni^{2+}) solution (stock)	Volume [ml] of methanol	Mol ratios of M^{2+}/bdmpp in mixture	Entry
1.0	0.0	3.0	0/10	BD
1.0	0.1	2.9	1/10	RM 1
1.0	0.2	2.8	2/10	RM 2
1.0	0.3	2.7	3/10	RM 3
1.0	0.4	2.6	4/10	RM 4
1.0	0.5	2.5	5/10	RM 5
1.0	0.6	2.4	6/10	RM 6
1.0	0.7	2.3	7/10	RM 7
1.0	0.8	2.2	8/10	RM 8
1.0	0.9	2.1	9/10	RM 9
1.0	1.0	2.0	10/10	RM 10
1.0	1.5	1.5	15/10	RM 11
1.0	2.0	1.0	20/10	RM 12

By keeping the ligand concentration constant, vibrational bands of the ligand (bdmpp) are eliminated at the beginning. Decrease of the ligand concentration appears in the spectrum as negative bands while the formation of new ligand–metal bonds is detected as positive bands (Fig. 1).

3. Results and discussion

3.1. Monitoring of M^{2+} complexes of bdmpp by FT-IR

The complexation reaction between bdmpp and Cu^{2+} (Scheme 1) was investigated. The characteristic C=N vibrational bands of free ligand (bdmpp) are observed at 1599 and 1586 cm^{-1} as seen in Fig. 1a. The isolated solid complexes have two stretching bands at 1618 and 1569 cm^{-1} (Fig. 1c). In situ complexation spectra are given in Fig. 1b. It is clearly observed that the C=N vibrational bands of free bdmpp at 1599 and 1586 cm^{-1} are shifted to 1618 and 1569 cm^{-1} upon complexation. Methanol solution of CuCl$_2$·2H$_2$O has no explicit absorption in the range of 1500–2000 cm^{-1}.

In Fig. 1b, the vibrational bands observed at 1599 and 1586 cm^{-1} related to the bdmpp in solution appeared below the absorbance line exactly overlap with the vibrational bands of free bdmpp (Fig. 1a) indicating that a decrease in bdmpp concentration in solution is clearly monitored in FT-IR spectra. On the other hand, the increasing vibrational bands (above the absorbance baseline), which are at the same frequency with the isolated complex, show the formation of complex in the reaction media.

For observing the complex formation in methanol solution, M^{2+}/bdmpp solution mixtures were prepared at 12 different concentration ratios. Table 1 shows the different concentration ratios (M/L) of the reaction mixtures. While the amount of bdmpp was kept constant in all reaction mixtures, the amount of metal salts added to each mixture was changed. FT-IR spectra of all reaction mixtures having different metal/ligand ratios were obtained under the same condition as the background.

The same analysis method was applied to determine the complexation ratios of Ni^{+2} (Fig. 2) and Co^{2+} (Fig. 3) with bdmpp (Scheme 2). Complexation with these metal ions exhibit similar series of spectra as for Cu^{2+}–bdmpp, discussed above. The location of bands of the ligand is the same in these systems, but the characteristic vibrational bands of Ni^{2+}, Co^{2+} and Cu^{2+} complexes are different from those of the bdmpp ligand (Figs. 1b, 2b and 3b).

The interaction of bdmpp with Mg^{2+} and Ca^{2+} prepared at five different ratios of M/L in the mixtures (as given in Table 2) was also studied by the presented technique.

The FT-IR spectra of Mg^{2+} and bdmpp ligand mixtures are shown in Fig. 4. As seen from the figure, there is only one vibrational band appeared at 1670 cm^{-1} due to the water of MgCl$_2$·2H$_2$O in the mixtures. There are no vibrational bands observed below the zero absorbance line indicating that the free ligand concentrations do not change in solution and thus no complexation occurs in the mixtures. Similar results were obtained for Ca^{2+} and bdmpp ligand mixtures. Only the vibrational band at 1670 cm^{-1} for Mg^{2+} appeared at 1675 cm^{-1} which was assigned as due to the associated water to the CaCl$_2$·2H$_2$O in the mixture.
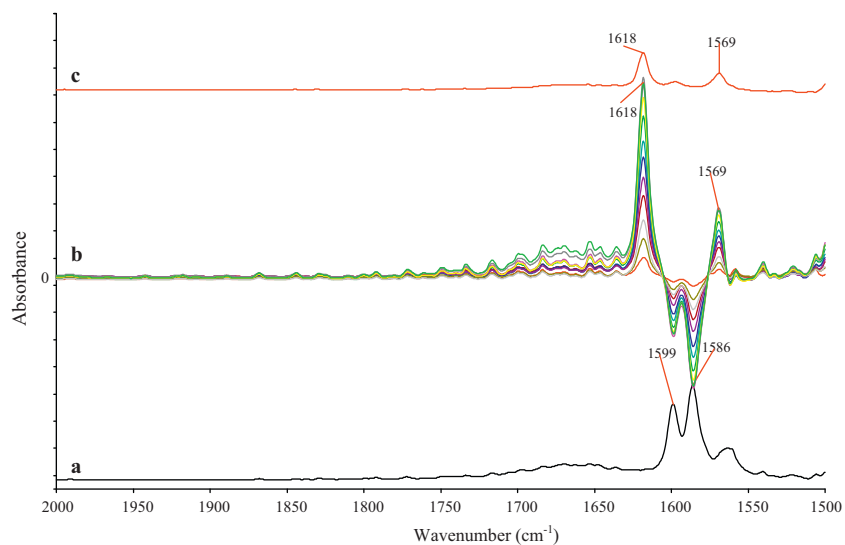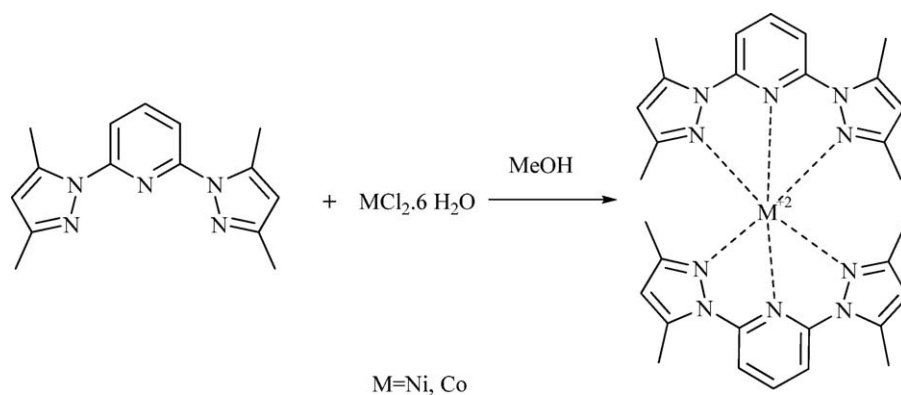
Fig. 1. FT-IR spectra of bdmpp (a), 12 bdmpp + Cu²⁺ mixtures at different concentration ratios (with the bdmpp solution spectrum used as background) (b), Cu–bdmpp complex (c), all dissolved in methanol. Curves a and c are offset along the absorbance scale for clarity.
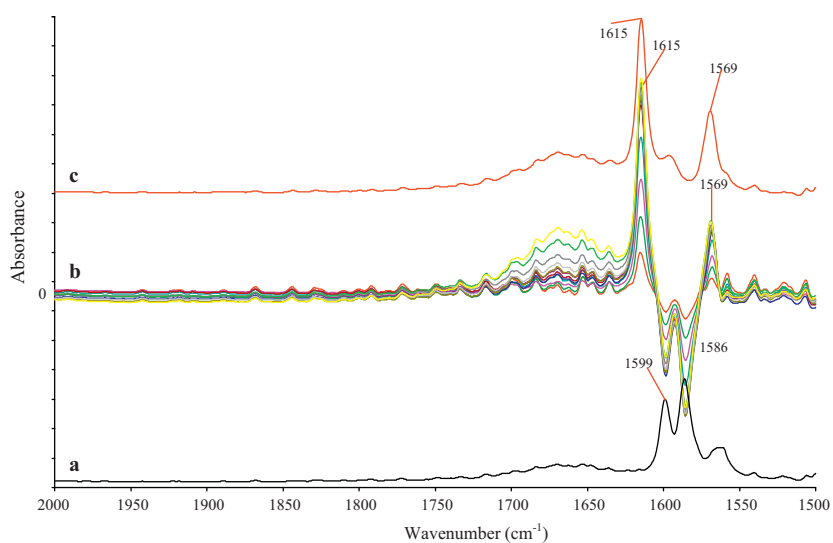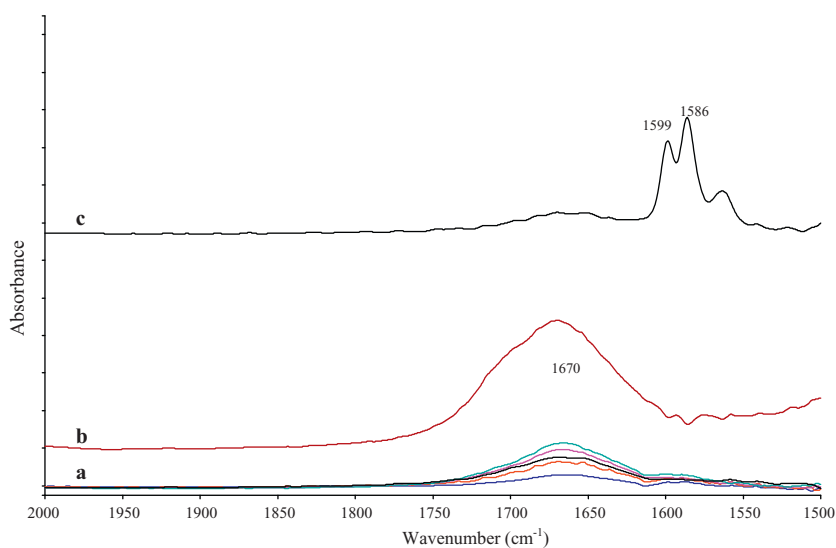

Fig. 2. FT-IR spectra of bdmpp (a), 12 bdmpp + Ni²⁺ mixtures at different concentration ratios (with the bdmpp solution spectrum used as background) (b), Ni–bdmpp complex (c), all in methanol. Curves a and c are offset for clarity.
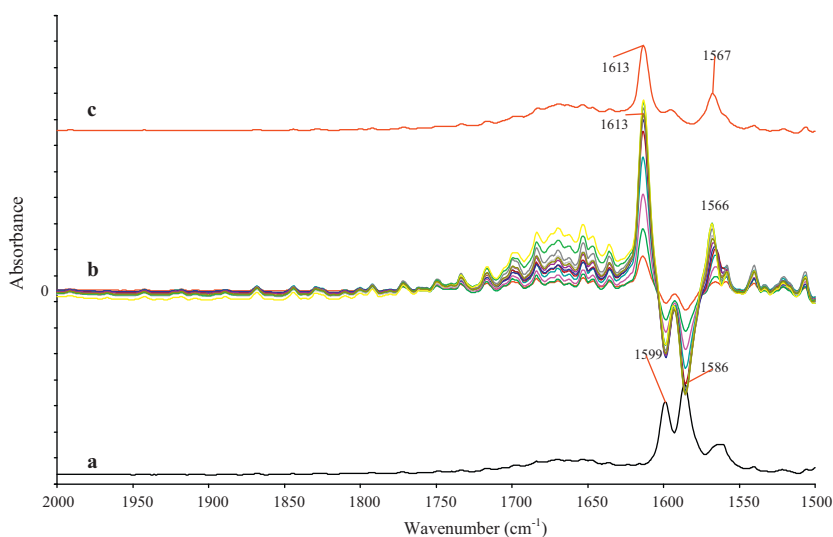
Fig. 3. FT-IR spectra of bdmpp (a), 12 bdmpp + Co²⁺ mixtures at different concentration ratios (with the bdmpp solution spectrum used as background) (b), Co–bdmpp complex (c), all in methanol. Curves a and c are offset for clarity.

Scheme 2. Complexation of bdmpp with Ni^{2+} and Co^{2+} in methanol.

Fig. 4. FT-IR spectra of five bdmpp + Mg^{2+} mixtures at different concentration ratios (with the bdmpp solution spectrum used as background) (a), $MgCl_2 \cdot 2H_2O$ (b), bdmpp (c), all in methanol. Curves b and c are offset for clarity.

The complexation reaction of bdmpp with Cu^{2+}, Co^{2+}, and Ni^{2+} was studied in methanol by FT-IR spectroscopy using this method. Although complexation reactions do not include any breaking or formation of covalent bonds, the ligand and metal share the ligand's lone pair electrons.
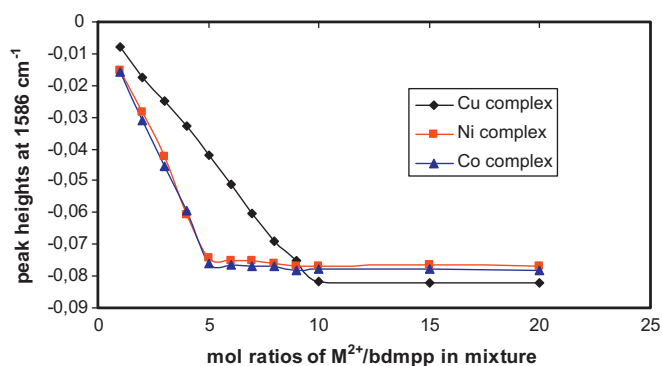
Job's method and the Mole Ratio method are also commonly used methods that are employed for the determination of stoichiometry of complexes [17–20]. Since the vibrational band heights and the vibrational band areas are related to the concentration of compound in solution, we can obtain data about concentrations of ligand and complexes in any equilibrium state of the complexation reaction. The 1/10 to 20/10 ratios of M^{2+}/bdmpp in mixture were studied (Table 1). Since the concentration of free ligand is kept

constant in all mixtures, the increase in the heights of vibrational bands of free ligand can be directly attributed to the complex formation and its type such as ML, ML_2 and so on. The spectral changes observed for various Cu/bdmpp, Ni/bdmpp, and Co/bdmpp reaction mixtures are shown in Figs. 1b, 2b and 3b, respectively. Respective plots of the 1586 cm^{-1} band height against M/L ratio are shown in Fig. 5.

Since there are no changes in the absorption band heights over the 10/10 reaction mixture of M/L, it is clear that the Cu–bdmpp

Table 2
Preparation of the measured solutions for bdmpp–Mg^{2+} and –Ca^{2+}.

Volume [ml] of 0.1 M bdmpp solution (stock)	Volume [ml] of 0.1 M M^{+2} (Mg^{2+}, Ca^{2+}) solution (stock)	Volume [ml] of methanol	Mol ratios of M^{2+}/bdmpp in mixture	Entry
0.5	0.0	1.5	0/5	BD
0.5	0.1	1.4	1/5	RM 1
0.5	0.2	1.3	2/5	RM 2
0.5	0.3	1.2	3/5	RM 3
0.5	0.4	1.1	4/5	RM 4
0.5	0.5	1.0	5/5	RM 5

Fig. 5. Variation of peak intensity of the 1586 cm^{-1} (negative) band of bdmpp in the studied reaction mixtures.

complexation ratio is 1/1. It is also comparable with the decrease of the free ligand from the vibrational bands below the absorbance line (Fig. 1b).

Co–bdmpp and Ni–bdmpp complexes were produced as much as the same ratios of concentration, but quite different from the Cu^{2+} (Fig. 5). Both Co–bdmpp and Ni–bdmpp complexation were terminated at 5/10 concentration ratio of M/L. Although the metal ion concentrations were increased to the concentration ratio of up to 20/10 no change at any vibrational bands have been observed for the concentration ratio over 5/10. In other words, bdmpp is used up after 5/10 concentration ratio. The resultant complexation reactions are suggested in Scheme 2.

4. Conclusion

The presented method is based on the definition of the free ligand solution FT-IR spectrum as a background for similar measurements of solutions containing ligand and metal at different concentration ratios. When there is no complexation, the ligand bands do not appear. When complexation occurs, the increase of the complex bands above the base absorbance line is observed with simultaneous appearance of ligand bands below the base line ("negative absorbance"). The method eliminates the necessity to obtain the solid metal-ligand complex for investigation.

The complexation ratio of M/L is also monitored easily by this method.

Consequently, it has been found that Cu^{2+}, Ni^{2+} and Co^{2+} yield complexation reaction with bdmpp at 1/1, 1/2, 1/2 ratios, respectively. However, Ca^{2+} and Mg^{2+} did not form complex with bdmpp in methanol solution.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.vibspec.2011.01.002.

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