FTIR SPECTROSCOPIC EVIDENCE OF NICKEL–CARBOXYLATE COORDINATION IN A Ni-MOF-74-TARGETED MATERIAL

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Abstract. The interaction of nickel ions with 2,5-dihydroxyterephthalic acid (H4DOBDC) was evaluated through comparison of the FTIR spectra of the initial ligand and a nickel-containing product prepared by solvothermal treatment. The material was obtained from nickel nitrate hexahydrate and H4DOBDC in a DMF–ethanol–water system at 100 °C for 24 h. Spectra were recorded on a Bruker ALPHA II spectrometer. The ligand showed a carbonyl-related band near 1680 cm−1, while the final material exhibited prominent features at 1556 and 1411 cm−1, tentatively assigned to asymmetric and symmetric carboxylate stretching. Additional bands at 1455, 1361, 1240, 1200, 1118, 889 and 815 cm−1 support changes in the ligand environment and retention of its aromatic backbone. FTIR evidence favors nickel–ligand coordination but cannot, by itself, establish crystallographic phase purity.

Keywords: Ni-MOF-74; FTIR; nickel–ligand coordination; carboxylate stretching; H4DOBDC; vibrational spectroscopy.

Introduction

Fourier-transform infrared (FTIR) spectroscopy is widely employed to examine the functional groups of metal–organic coordination materials. In a carboxylate-

containing ligand, coordination to a metal center may change the vibrational frequencies associated with protonated carboxyl groups, carboxylate anions and the aromatic skeleton. Such changes are especially informative when the spectrum of the starting ligand is available for direct comparison [1, 2].

Materials and methods

The nickel-containing product was synthesized from 6.72 mmol H4DOBDC and 9.52 mmol Ni(NO3)2·6H2O, corresponding to a nominal Ni:ligand ratio of 1.42:1. The reaction medium was DMF, absolute ethanol and distilled water in a volume ratio of 15:1:1. After mixing the reagents, the reaction was conducted at 100 °C for 24 h in a sealed autoclave. The isolated solid was washed with DMF, treated with methanol, vacuum-dried at 80 °C and activated at 150 °C.

FTIR spectra of the initial H4DOBDC ligand and the synthesized sample were registered using a Bruker ALPHA II spectrometer. The ligand spectrum covers approximately 4000–400 cm−1 and the product spectrum approximately 2000–600 cm−1. The wavenumbers and assignments follow the measured spectra. Quantitative intensity ratios, replicate statistics and peak-fitting results were not reported.

Results and discussion

The initial H4DOBDC spectrum contains a broad absorption feature near 3420 cm−1, attributed to O–H stretching and hydrogen bonding. A strong feature near 1680 cm−1 is assigned to the carbonyl stretching of protonated carboxylic-acid groups. The band at about 1625 cm−1 is associated mainly with aromatic C=C stretching. Additional reported features around 1420 and 1385 cm−1 involve coupled carboxyl-related and skeletal vibrations. Lower-frequency signals near 780 and 650 cm−1 are associated with out-of-plane aromatic-ring and C–H modes (Figure 1).

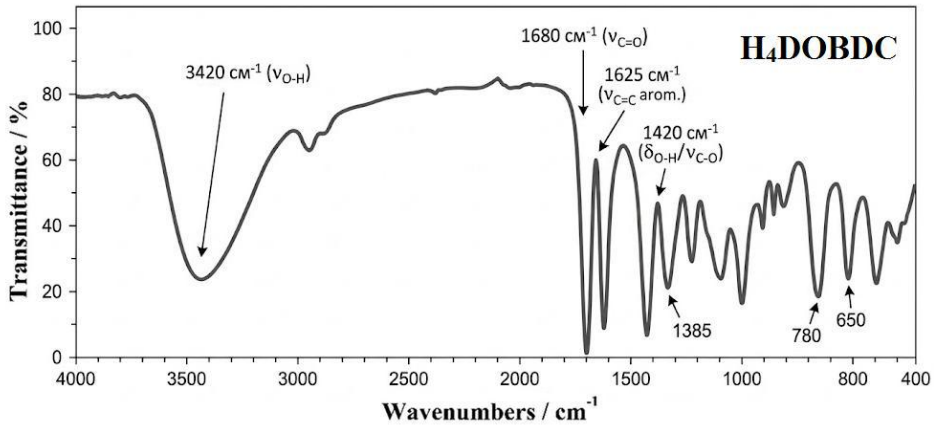


Figure 1. FTIR spectrum of the H4DOBDC ligand.

The spectrum of the synthesized nickel-containing product differs substantially from that of the free ligand. Notable bands at 1556 and 1411 cm−1 are consistent with the asymmetric and symmetric stretching of carboxylate groups, respectively. This comparison suggests deprotonation of the carboxylic acid groups and their participation in nickel–oxygen coordination. The difference between the two reported carboxylate stretching positions is 145 cm−1. The value alone is insufficient to determine a unique carboxylate binding geometry without independent structural data.

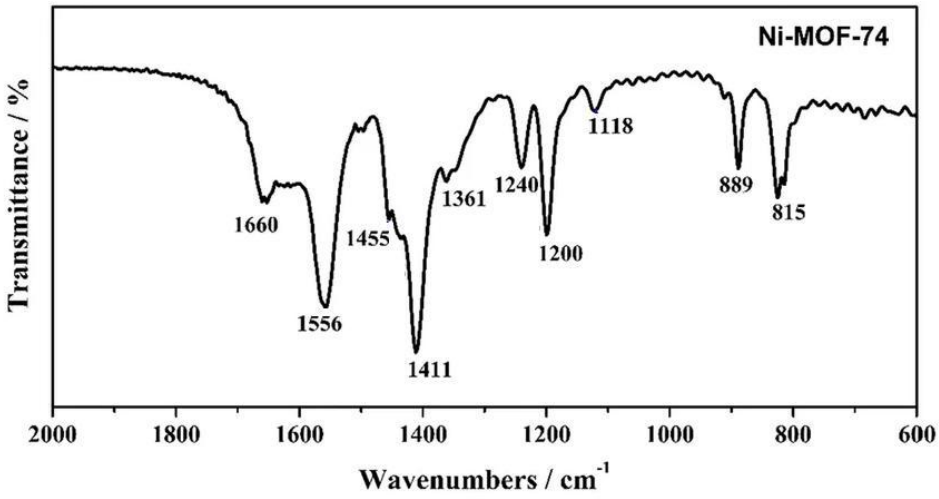


Figure 2. FTIR spectrum of the synthesized Ni-containing material.

The product displays further bands at 1455 and 1361 cm−1, consistent with contributions from carboxylate-related and aromatic-skeletal vibrations. Absorptions

around 1240, 1200 and 1118 cm−1 are attributed to C–O and ligand-skeleton vibrations, whereas those at 889 and 815 cm−1 are assigned to out-of-plane modes of aromatic C–H groups. Their presence supports retention of the ligand's organic backbone in the obtained material.

A band near 1660 cm−1 requires particular caution because residual DMF from synthesis can absorb in this region. It should therefore not be presented as independent proof of coordination. Likewise, the available product spectrum does not cover the 3420 cm−1 region; the absence of this region from the plot cannot be interpreted as disappearance of hydroxyl groups. Spectral positions support an interpretation of nickel–ligand interaction, but additional powder X-ray diffraction, elemental analysis and surface-area measurement would be required to verify crystalline identity and porosity.

Conclusion

Comparative FTIR measurements indicate a change from the carbonyl features of the free H4DOBDC ligand toward carboxylate-related bands in the nickel-containing product. The signals at 1556 and 1411 cm−1, together with retained aromatic-skeletal vibrations, support formation of nickel–ligand coordination bonds. The possibility of residual solvent absorption at 1660 cm−1 and the different spectral windows shown for the two samples limit stronger conclusions. FTIR provides chemical evidence compatible with the Ni-MOF-74 preparation route, while phase identity and purity still require crystallographic confirmation.

References

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