Host-guest Interactions in Intercalates \( \text{Zr}(\text{HPO}_4)_2 \cdot 2\text{C}_2\text{H}_5\text{OH} \) and \( \text{VOPO}_4 \cdot 2\text{C}_2\text{H}_5\text{OH} \)

Pavla Čapková, Miroslava Trchová, Pavel Matějka, Jiří Votinský, and Henk Schenk

1Faculty of Mathematics and Physics Charles University Prague, Ke Karlovu 3, CZ-12116 Prague, Czech Republic. E-mail: capkova@quantum.karlov.mff.cuni.cz; trchova@mbox.troja.mff.cuni.cz
2Laboratory of Crystallography, AIMS, University of Amsterdam, Nieuwe Achtergracht 166, NL-1018 WV Amsterdam, The Netherlands. E-mail: hs@cryschem.uva.nl; paulac@stamp.chem.uva.nl
3Department of Analytical Chemistry, Institute of Chemical Technology, Technická 5, Prague 6, CZ-16628, Czech Republic. E-mail: Pavel.Matejka@vscht.cz
4Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University Pardubice, Náměstí léti 565, CZ-53210 Pardubice, Czech Republic. E-mail: koanch@hlb.upce.cz

Received: 26 June 1998 / Accepted: 31 August 1998 / Published: 15 September 1998

Abstract Molecular mechanics simulations using Cerius² modelling environment combined with vibrational spectroscopy (IR and Raman) have been used to study the host-guest interactions in zirconium and vanadyl phosphate intercalated with ethanole. The strategy of investigation is based on the comparison of vibrational spectra for the host compound, intercalate and guest species. This comparison confirmed the rigidity of \( \text{VOPO}_4 \)- and \( \text{Zr}(\text{HPO}_4)_2 \)-layers during the intercalation and provided us with the basis for the strategy of modelling. Molecular mechanics simulations revealed the structure of intercalates and enabled to analyse the host-guest interaction energy and bonding geometry. The bilayer arrangement of ethanole molecules in the interlayer space with two differently bonded ethanole molecules has been found in both intercalates. The average interaction energy ethanole-layer for two differently bonded ethanole molecules is: 127.5 and 135.7 kcal·mol⁻¹ in \( \text{Zr}(\text{HPO}_4)_2 \cdot 2\text{C}_2\text{H}_5\text{OH} \), respectively 94.0 and 104.4 kcal·mol⁻¹ in \( \text{VOPO}_4 \cdot 2\text{C}_2\text{H}_5\text{OH} \). The Coulombic contribution to the ethanole-layer interaction energy is predominant in all cases, but the hydrogen bonding contribution is much higher in \( \text{Zr}(\text{HPO}_4)_2 \cdot 2\text{C}_2\text{H}_5\text{OH} \) than in \( \text{VOPO}_4 \cdot 2\text{C}_2\text{H}_5\text{OH} \). Present results of modelling enabled the interpretation of vibrational spectra and explanation of small changes in positions and shapes of spectral bands, in infrared and Raman spectra, proceeding from the host structure to intercalates.

Keywords Vanadyl phosphate, Zirconium phosphate, Molecular mechanics, Vibrational spectroscopy, Host-guest interaction, Intercalates

Correspondence to: P. Čapková
Introduction

Polar organic molecules can be intercalated in the layered structure of α-zirconium and vanadyl phosphate. These intercalates are attractive materials, promising a large spectrum of applications, based on their catalytic and sorption properties, ionic conductivity, and ion exchange behavior. (For the detailed review see Clearfield [1]). The phosphate-alkanole intercalates can be considered as very good starting materials for the intercalation of other, larger polar organic molecules. Intercalation of organic molecules into the layered structure of phosphates has been studied by Clearfield [1], Alberti [2], Costantino [3] and Čapková [4,5]. All these studies showed the key role of the host-guest interactions, ruling the position of the guest molecules, their ordering in the interlayer space and the stacking of layers. Due to the strong relationship between the structure and properties in intercalates, the study of the host-guest interactions is very important for the understanding and prediction of their properties.

Present work is a continuation of our recent structure analysis of two intercalates: Zr(HPO₄)₂·2C₂H₅OH [4] and VOPO₄·2C₂H₅OH [5], based on the combination of molecular mechanics simulations and X-ray diffraction. These recent works present the detailed structure analysis, including the characterization of structural disorder. Results of structure analysis confirmed the significance of the host-guest interaction for the structure-properties relationship in intercalates and showed also the importance of vibrational spectroscopy for this study. The combination of molecular mechanics simulation using Cerius² with infrared (IR) and Raman spectroscopy, has been used in the present study of host-guest interaction in vanadyl and zirconium phosphates, intercalated with ethanol. The strategy of investigation is based on the comparison of vibrational spectra for host compound, intercalate and guest species. This comparison is a good starting point for the modelling strategy. On the other hand the results of molecular simulations enable the interpretation of changes in spectral bands, proceeding from the vibrational spectra of host compounds and guest species to spectra of intercalates. Thus the combination of molecular simulations with infrared and Raman spectroscopy represents a very powerful tool for investigation of changes in structure and bonding during intercalation.

Spectroscopic measurements and modelling strategy

The method of sample preparation has already been described in our previous papers [4,5]. Infrared measurements were carried out using a NICOLET IMPACT 400 Fourier transform infrared (FTIR) spectrophotometer in a H₂O-purged environment. An ambient-temperature deuterated triglycine sulphate (DTGS) detector was used for the wavelength range from 400 to 4000 cm⁻¹. A Happ-Genzel apodization function was used in all region and the spectral resolution was 2 cm⁻¹. The Baseline Horizontal Attenuated Total Reflection (HATR)