Vibrational Spectroscopy 53 (2010) 296–306

Contents lists available at ScienceDirect

Vibrational Spectroscopy

journal homepage: www.elsevier.com/locate/vibspec

A combined DFT and vibrational spectroscopy study of the nickel and zinc O,O-diethyldithiophosphate complexes

Ferenc Billes[a,c,*], Allan Holmgren[b], Hans Mikosch[c]

[a] Department of Physical Chemistry and Material Science, Budapest University of Technology and Economics, H-1025 Budapest, Budafoki út 8, Hungary
[b] Division of Chemical Engineering, Department of Chemical Engineering and Geosciences, Luleå University of Technology, S-97187 Luleå, Porsön, Sweden
[c] Institute for Chemical Technologies and Analytics, Vienna University of Technology, A-1060 Wien, Getreidemarkt 9/164/EC, Austria

ARTICLE INFO

Article history:
Received 28 August 2008
Received in revised form 8 April 2010
Accepted 23 April 2010

Keywords:
Zinc and nickel complexes
FTIR
NIR FT Raman
Quantum chemistry
Normal coordinate analysis

ABSTRACT

Based on our earlier results on the theoretical and experimental study of potassium O,O-diethyldithiophosphate, the normal modes of nickel and zinc O,O-diethyldithiophoshate complexes were elucidated. Infrared and Raman spectra of these compounds were recorded. Quantum chemical calculations resulted in optimized structures, electric charge distributions, vibrational force constants, and fundamental frequencies. Normal coordinate analysis was applied to characterize the vibrational modes. Based on the results of these calculations vibrational spectra were simulated. The largest spectral differences between the two complexes appeared in vibrational modes encompassing the central part of the formula unit *viz.* PS_2MS_2P, where M is the metal atom. Namely, this central part of the Ni complex has D_{2h} symmetry, while that of the Zn one has D_{2d} symmetry.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Dialkylthiophosphates (DADTPs) constitute an important group of collector molecules widely used in the separation and concentration of sulfide minerals [1]. Making the valuable mineral surfaces hydrophobic facilitates the flotation operation. However, dithiophosphates have also a number of other applications. In the metal–ligand complex with zinc DADTPs have for years been used as the most common and the best antiwear and antioxidant additive in engine and industrial oil formulations [2,3]. DADTPs have also been used as one of the starting chemicals in pesticide formulations, where the organic phosphate has the role of attacking the nervous system of insects, but for example Nickel DEDTP (E for ethyl) has also been applied as analytical reagent for spectrophotometric determination of transition metals [4,5].

To better understand the interaction between the metal atom and DEDTP in Ni and Zn complexes and especially the influence of the metal atom on the vibration frequencies of DEDTP, the combination of DFT calculations and experimental spectroscopic data seems to be a promising approach. This approach may also serve as an aid to the interpretation of vibrational spectra of DEDTP adsorbed at mineral surfaces containing NiS or ZnS. However, the combination of DFT and vibrational spectroscopy is very scant in the literature. Jiang et al. [6] studied the adsorption of diethyl, diisopropyl, diisobutyl and diphenyl esters of the dithiophosphate anion onto an α-Fe_2O_3 surface utilizing the ab initio HF method. Räsänen et al. [7] studied the methyl esters applying the MP2 method and the 6-31G* basis set, but examined only the molecular geometry and the charge distribution. Hellström et al. [8,9] and Fredriksson et al. [10] have utilized ab initio DFT methods in combination with ATR-FTIR spectroscopy to examine the vibrational properties of potassium heptyl xanthate both as a free molecule and as adsorbed on a Ge surface.

However, experimental vibrational spectroscopy of DEDTP combined with quantum chemical calculation is missing in the literature with the exception of Ref. [1]. In our previous work [11], the vibrational spectroscopy of potassium O,O′-diethyldithiophosphate (KDEDTP) was investigated by measuring the infrared and Raman spectra of the solid compound and simulating the spectra of the isolated molecule by fitting the calculated frequencies and intensities to the recorded spectra. The present work is an attempt to calculate the vibrational spectra of relatively large molecules *viz.* the complexes of Ni and Zn with KDEDTP. As an intermediate result of the quantum chemical calculations the optimized molecular geometric parameters were obtained. Vibrational spectra of the adsorbed collector were recorded applying the ATR method [12–14].

---

* Corresponding author at: Department of Physical Chemistry and Material Science, Budapest University of Technology and Economics, H-1521 Budapest, Budafoki út 8, Hungary. Tel.: +36 1 463 1267; fax: +36 1 463 3767.
E-mail address: fbilles@mail.bme.hu (F. Billes).

0924-2031/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.vibspec.2010.04.011

2. Experimental

The nickel and zinc DEDPT compounds were prepared from the potassium salt of O,O′-diethyldithiophosphoric acid and $NiCl_2$ and $ZnCl_2$, respectively. The potassium salt was provided by CHEMINOVA. It is the major component of the commercial collector applied in sulfide ores flotation.

Infrared spectra were recorded using a Bruker IFS v/S spectrometer equipped with a DTGS detector and a diffuse reflectance accessory. The sample was diluted to 4% by weight in oven-dried spectroscopic grade potassium bromide and 200 scans were collected at 4 cm^{-1} resolution. The DRIFT spectra were transformed to Kubelka–Munk units.

Raman spectra were recorded using a Perkin Elmer NIR FT Raman 1700X spectrometer. The scattering was excited with intensity-stabilized 1064 nm emission from a Spectron SL 301 Nd:YAG laser, and the scattered light collected with a 180° backscattering-geometry lens. The laser power was 400 mW and 64 accumulations at 4 cm^{-1} resolution were detected by an indium gallium arsenide detector.

3. Calculations

For the quantum chemical calculations the Gaussian 03 program package [15] was used. The applied DFT functional was Becke3LYP [16,17]. The 6-311++G(df,p) basis set was used considering the nickel, zinc, phosphorus and the sulfur atoms.

The first step of the calculations was the optimization of the molecular structure. This step gave in addition to the optimized geometry (parameters and Cartesian coordinates) also the atomic net and NBO charges. During the second step the molecular energy function was differentiated twice with respect to the Cartesian coordinates. This step gave vibrational force constants, normal frequencies, atomic amplitudes in the normal modes, and molecular dipole moments.

The next step was the fit of the calculated entries to the experimental frequencies. At first the Cartesian coordinates were transformed to internal coordinates. The calculated force constants were also transformed into the new coordinate system. This natural internal coordinate system was chosen according to [18]. Performing the normal coordinate analysis the force constants were fitted to the experimental normal frequencies. For this fit identical scale factors were used for the force constants of the chemically similar coordinates. Subsequently, the potential energy distribution was calculated to describe the normal modes. The programs for all the calculations involved in this step were home-made ones.

In order to compare the experimental spectra with the calculated frequencies, infrared and Raman spectra were simulated using Lorentzian type bands with 15 cm^{-1} FWHH. This simulation is merely to get the frequency lines obtained from the calculations to appear like a real spectrum and should of course not be mixed up with an advanced simulation of the real line shapes. For the elaboration of the quantum chemical results our home-made programs were applied.

4. Results and discussion

The presented work is a possible model for the interaction between transition metal ions (like Ni and Zn) and dialkyldithiophosphates.

4.1. Molecular structures

The optimized molecular structures of the Ni and Zn DEDTP derivatives are shown in Fig. 1, where Fig. 1a1 shows the Ni$(DEDTP)_2$ complex and Fig. 1b1 the Zn$(DEDTP)_2$ complex in general view. Fig. 1a2 and a3 present two projections of Fig. 1a1, while Fig. 1b2 and b3 are similarly two projections of Fig. 1b1. Apparently, the PS_2MS_2P structures of the two complexes are quite different. As it can be seen, the space around the Ni atom is planar, whilst the structure around the Zn atom is tetrahedral, the two S_2M planes are perpendicular to each other.

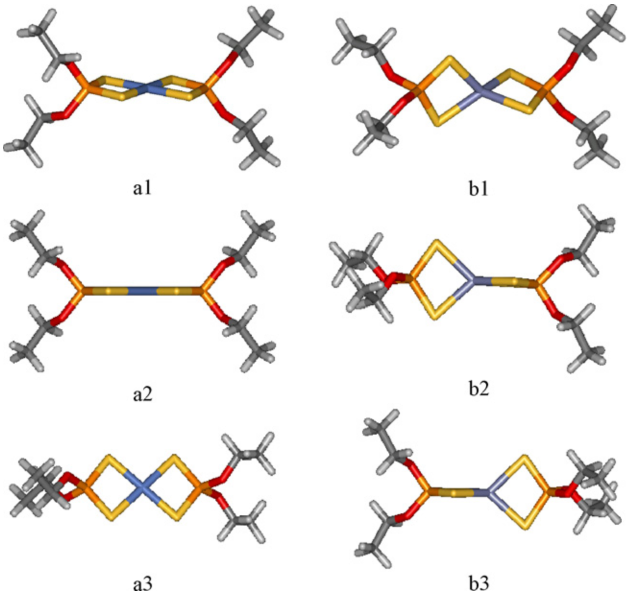

Fig. 1. Optimized structures of *a*: Ni$(DEDTP)_2$ and *b*: Zn$(DEDTP)_2$; a1, b1 are general views, a2 is the projection of the general view to the PS_2NiS_2P plane; a3 it its projection to the plane perpendicular to the PS_2NiS_2P plane; b2 is the projection of the general view to the PS_2Zn plane; b3 is its projection to the ZnS_2P plane.

The reason for this structural difference must be the difference in the electronic structures of the two atoms. The electronic ground state of the Ni atom is $Ar3d^84s^2$, whilst the electronic structure of the Zn atom is $Ar3d^{10}s^2$. During the complex formation each of the four sulfur atoms donate two electrons to the Ni^{2+} ion ($Ar3d^8$) saturating its 3d subshell to d^{10}, two electrons build the 4s subshell, the remaining four ones occupy 4p orbitals. The resulting Ni structure in its complex is $Ar3d^{10}4s^2p^4$ corresponds the dsp^2 hybrid and implying therefore the observed planar structure. According to Fig. 1a2 and a3 and the dsp^2 hybridization and the central part of the complex (PS_2NiS_2P) has three mutually perpendicular twofold rotational axes crossing each other in the Ni atom, and three mutually perpendicular symmetry planes. Therefore the central part has D_{2h} symmetry.

The Zn^{2+} ion (Ard^{10}) is donated on similar way by the four sulfur atoms and the Zn electron structure in the formed Zn$(DEDTP)_2$ complex is $Ar3d^{10}4s^2p^6$. This sp^3 hybrid structure should have to form a tetrahedral space around it. However, the four sulfur atoms are symmetrically not equivalent. They belong by pairs (S4, S5 and S24, S25, respectively) to their own DEDTP groups (see Fig. 2). Therefore the expected T_d symmetry around the Zn atom is distorted, the PS_2ZnS_2P central group stretches along the P–Zn–P line. So this group has a fourfold rotation–reflection symmetry axis (the P–Zn–P line), two symmetry planes, each of them contains one of the ZnS_2P rings and intersect in the P–Zn–P line, and twofold rotational symmetry axes in the bisectors of the symmetry planes, perpendicular to each other and also the rotation–reflection axis. These symmetry elements correspond to D_{2d} symmetry.

That is, the central parts of these compounds have relatively high symmetry. Table 1 shows the molecular parameters of the compounds. Regarding to their symmetry, only half of the bond lengths and valence angles are shown, with the exclusion of those

Download English Version:

https://daneshyari.com/en/article/1249682

Download Persian Version:

https://daneshyari.com/article/1249682

Daneshyari.com