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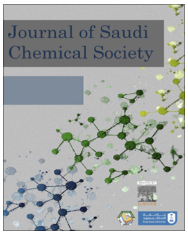

ORIGINAL ARTICLE

Crystal structure, Hirshfeld surface analysis, thermal behavior and IR investigation of a new organic selenate-selenide $[C_3H_{12}N_2]_2(SeO_4)(SeO_3)\cdot 4H_2O$

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Hybrid selenate-selenide;
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Abstract The new hybrid compound called propane-1,3-diammonium selenate-selenide tetrahydrate **(PDASe)** was obtained by slow evaporation and characterized by X-ray diffraction, NMR and IR spectroscopies, TGA and DSC analysis and UV–visible transmittance.

This compound contains both Se^{IV} in the form of selenide (SeO_3^{2-}) trigonal pyramids and Se^{VI} as selenate (SeO_4^{2-}) tetrahedra. The structure is built up from tunnels containing all the components of the structure and oriented along b axis. The organic and inorganic groups are linked together by two types of hydrogen bonds, O–H···O and N–H···O. Crystal structure and Hirshfeld surfaces analysis revealed that the compound were mainly supported by N–H···O and O–H···O intermolecular interactions and the uncoordinated water molecules play a key role in the construction of the 3D stacking motif.

The dehydration and the decomposition of the title compound are confirmed by the thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The analysis by the UV visible spectroscopy confirmed the transparency of our compound in the visible region.

1. Introduction

Selenium (Se) occurs in a variety of oxidation states, like selenate (SeO_4^{2-}) and selenide (SeO_3^{2-}) oxyanions, where in the oxidation states are +6 and +4; elemental selenium (Se), and selenide (Se^{2-}). During a systematic study of the interaction

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between selenic acid with organic amino entities, there was a formation of more compounds organic group with selenate as we can see from (SeO_4) of $[C_5H_6N_5]_2SeO_4{\cdot}2H_2O$ [1], $[C_3H_7N_6]_4(SeO_4)_2{\cdot}3H_2O$ [2] and $C_6H_8NO.SeO_4{\cdot}2H_2O$[3]. Rarely, we observed organic chain with Selenide (SeO_3) as an example of $C_2H_7N_4O.HSeO_3$ [4]. Except in our case, the presence of the two types of units, SeO_4 and SeO_3, in one compound was not yet observed and is herein reported for the first time. In this arrangement, the structure is formed of organic entities, anionic groups: SeO_4^{2-} tetrahedra and trigonal pyramids SeO_3^{2-} and water molecules crystallographically independent. These groups are interconnected by two types of bonds O–H···O and N–H···O giving a new hybrid (**PDASe**). Water molecules are omnipresent in nature and play a significant role in the stabilization of supramolecular systems. In the title compound, the water molecule is included as indispensable part of the structure [5–7].

The present paper describes for the first time the crystallographic description of a new hybrid, rarely encountered in the literature, associated to selenate and selenide groups with propane-1,3-diammonium. It concerns the characterization of this compound as infrared spectrum and optical absorption studies. In the thermal part, we present thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC) between 30 and 600 °C.

These analyses have helped to highlight the wealth of structural types of hybrid compounds mainly due to the diversity of organic molecules added to inorganic groups.

2. Materials and method

2.1. General

Single-crystal X-ray diffraction intensity data were obtained on a Bruker APEX-II area detector diffractometer using MoKα radiation ($\lambda = 0.71073$ Å).

Molecular Hirshfeld surface calculation was performed using the CrystalExplorer [8–13] program. The distance from Hirshfeld surface to the nearest nucleus inside and outside the surface was marked by d_i and d_e respectively, whereas d_{norm} is a normalized contact distance, which is defined in turns of d_i, d_e and the van der Wals (vdW) radii of atoms: [14]

$$d_{norm} = \frac{d_i - r_i^{vdW}}{r_i^{vdW}} + \frac{d_e - r_e^{vdW}}{r_e^{vdW}}$$

d_{norm} was visualized using a red – white – blue scheme. If the atoms make intermolecular contacts closer than the sum of their vdW radii, these contacts were represented as red spots on the surface. Longer contacts were blue, while white was used for contacts around the sum of the van der Waals radii [14].

All NMR spectra were recorded on a Bruker DSX-300 spectrometer operating at 300 MHz for ^1H and 75.49 MHz for ^{13}C with a classical 4 mm probe head allowing spinning rates up to 10 kHz. ^1H and ^{13}C NMR. A proton spectrum was recorded under classical MAS conditions while the carbons were recorded using the cross-polarization from protons (contact time 5 ms). In the present study, NMR was used to determine the chemical shifts of the atoms.

The infrared spectrum was recorded at room temperature on a Perkin Elmer Spectrum™ 100 FT-IR spectrometer in the 4000–650 cm^{-1} region.

The Thermal stability was measured using Thermogravimetric Analysis (Perkin Elmer, Model: Pyris 6 TGA) in alumina crucible under a nitrogen flow of 20 ml min^{-1} with a heating scan rate of 10 °C min^{-1} over the temperature range [30–600 °C]. The analyses were performed by Perkin Elmer software.

Thermal properties were measured using differential scanning calorimetry (Perkin Elmer, Model: Pyris Diamond) in aluminum caps under a nitrogen flow at a heating/cooling rate of 10 °C min^{-1} over the temperature range [45–250 °C]. The analyses were performed by Perkin Elmer software.

The optical absorption spectrum of **PDASe** was recorded at room temperature using a PerkinElmer Lambda 950 spectrometer within a 200–1300 nm wavelength range. H_2O was used as a reference material ($C_{PDASe} = 0.0596$ mol l^{-1}). The optical absorption of the solution was determined from the direct transmission measurements performed using a conventional UV–visible spectrophotometer.

2.2. Chemical preparation

The single crystal of $[C_3H_{12}N_2]_2(SeO_4)(SeO_3){\cdot}4H_2O$ was obtained by slow evaporation at room temperature (≈25 °C) of aqueous solution containing a 2:2 stoichiometric mixture of propane-1,3-diaminium (Water Solubility at 25 °C (mg/L) and selenic acid (Solubility 1.3 g mol^{-1} (water, 30 °C)) with the following reaction:

$$2C_3H_{10}N_2 + 2H_2SeO_4 \xrightarrow{H_2O} [C_3H_{12}N_2]_2(SeO_4)(SeO_3) \cdot 4H_2O$$

After several days, colorless transparent parallelepiped single crystal of $[C_3H_{12}N_2]_2(SeO_4)(SeO_3){\cdot}4H_2O$ was obtained.

2.3. Structure determination

The unit cell parameters, optimized by least-squares refinement were calculated and refined using indexation of collected intensities. The total number of measured reflections was 4599 among which 2748 were independent and 2439 had intensity $I > 2\sigma(I)$.

The selenic atoms were located using the direct methods with program SHELXS-97 [15]. The oxygen and the organic moieties were found from successive Fourier calculations using SHELXL-97 [16].

The water H atoms were located in a difference map and refined with O–H distance restraints of 0.88(2) Å and H-H restraints of 1.5(2) Å so that the H-O–H angle would fit to the ideal value of a tetrahedral angle. Next, the hydrogen atoms of the C(N)H and NH_2 groups were fixed geometrically by the appropriate instructions of the SHELXL-97 program (HFIX 43, HFIX33, and HFIX 93, respectively) [15]. The final cycle of refinement leads to the final discrepancy factors $R_1 = 0.028$ and $wR_2 = 0.070$. The drawings were made with Diamond [17].

3. Results and discussion

3.1. Crystal structure

Structural determination at room temperature shows that **PDASe** crystallizes in the triclinic system, space group $P\bar{1}$,

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