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Preparation, crystal structure, vibrational spectra and thermal behavior of selenites of ethylene diamine, 1,3-propylene diamine and 1,4-butylene diamine

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Abstract

Selenites of ethylene diamine, propylene diamine and butylene diamine were prepared by crystallization from aqueous solution. The crystal structure was solved for all the substances. Ethylene diammonium(2+) selenite crystallizes in the orthorhombic space group $P2_12_12$, $a = 11.3710(2)$ Å, $b = 11.4390(5)$ Å, $c = 4.6290(4)$ Å, $V = 602.11(6)$ Å³, $Z = 4$, $R = 0.0341$ for 5729 observed reflections. 1,3-Propylene diammonium(2+) selenite dihydrate crystallizes in the monoclinic space group $C2/c$, $a = 16.241(14)$ Å, $b = 6.673(5)$ Å, $c = 17.731(14)$ Å, $\beta = 110.88(2)^\circ$, $V = 1795(3)$ Å³, $Z = 8$, $R = 0.0271$ for 12,233 observed reflections. 1,4-Butylene diammonium(2+) selenite dihydrate crystallizes in the monoclinic space group $P2_1/c$, $a = 6.686(5)$ Å, $b = 16.597(14)$ Å, $c = 9.282(8)$ Å, $\beta = 96.653(14)^\circ$, $V = 1023.2(14)$ Å³, $Z = 4$, $R = 0.0465$ for 2918 observed reflections. The FTIR and FT Raman spectra of all the compounds were recorded and interpreted. The thermoanalytical properties were studied by the TG, DTG, and DTA methods in the 293–633 K temperature range. DSC measurements were carried out in the range from 98 K to the temperature of decomposition of the compounds. No thermal effect indicating a phase transition was observed in this temperature region.

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Keywords: Ethylene diammonium selenite; 1,3-Propylene diammonium selenite dihydrate; 1,4-Butylene diammonium selenite dihydrate; Crystal structure; Vibrational spectra; Thermal behavior

1. Introduction

A wide range of salts of linear alkylene diamines with inorganic acids is known, with the greatest number of salts of ethylene diamine (e.g. chloride [1], sulfate [2], nitrate [3] and also the salts of trihydrogen phosphoric acid [4–6]). The chlorides and hydrogen phosphates of the two remaining bases (1,3-propylene diamine and 1,4-butylene diamine) are also known [7–10]; of the other salts of alkylene diamines with inorganic acids, mention should be made of, e.g., 1,3-propylene diammonium(2+) perchlorate [11]. However, the literature contains very few references to the selenites of organic nitrogen-containing bases, consisting practically only of references to piperazinium(2+) selenite monohydrate

[12] and piperazinium(2+) diselenite [12]. The salts of selenious acid and linear alkylene diamines are not known.

This work is part of an extensive project of preparation and study of substances with interesting physical properties based on the salts of oxo-acids and nitrogen-containing organic bases including short hydrogen bonds, that can be the carriers of important dielectric and optical properties or can participate in the proton conductivity of these substances.

The title compounds—ethylene diammonium(2+) selenite (*ense*), 1,3-propylene diammonium(2+) selenite dihydrate (*propse*) and 1,4-butylene diammonium(2+) selenite dihydrate (*butse*)—were prepared and studied in detail. In addition to measurement of the crystal structure, the vibration spectra were also measured and interpreted and their thermal behavior was also studied (TG, DTA, DSC).

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2. Experimental

Where not stated otherwise, the chemicals used were of p.a. purity. All the compounds (*ense*, *propse* and

Table 1
Basic crystallographic data, data collection and refinement parameters of *ense*

Empirical formula	C ₂ H ₁₀ N ₂ O ₃ Se
Formula weight	189.08
Temperature	150(2) K
Diffractometer used	Enraf–Nonius Kappa CCD
Wavelength	0.71070 Å
Crystal system, space group	orthorhombic, <i>P</i> 2 ₁ 2 ₁ 2
Unit-cell dimensions	<i>a</i> = 11.3710(2) Å, α = 90° <i>b</i> = 11.4390(5) Å, β = 90° <i>c</i> = 4.6290(4) Å, γ = 90°
Volume	602.11(6) Å ³
Z, Calculated density	4, 2.086 g/cm ³
Absorption coefficient	6.162 mm ⁻¹
<i>F</i> (0 0 0)	376
Crystal size	0.275 × 0.125 × 0.1 mm
θ range for data collection	3.99–30.03°
Index range	<i>h</i> (–12;16), <i>k</i> (–16;14), <i>l</i> (–5;6)
Reflections collected/unique	5729/1759 [<i>R</i> (int) = 0.0606]
Completeness to θ = 30.03°	99.3%
Absorption correction	Multiscan
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	1759/0/115
Goodness-of-fit on <i>F</i> ²	1.076
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0327, <i>wR</i> 2 = 0.0810
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0341, <i>wR</i> 2 = 0.0834
Largest diff. peak and hole	1.541 and –1.307 e. Å ⁻³
Weighting scheme	$w = [\sigma^2(F_o^2) + (0.0526P)^2 + 1.04P]^{-1}$ $P = [F_o^2 + 2F_c^2]/3$

butse) were prepared by mixing equimolar amounts of diluted aqueous solutions of the corresponding base (ethylene diamine (purum, Lachema) or 1,3-propylene diamine (99%, Aldrich) or 1,4-butylene diamine (99%, Aldrich)) and selenium dioxide (99.8%, Aldrich). The solution was left to crystallize in the air. The small colorless crystals formed were filtered off through an S4 frit, washed with a small amount of ice-cold distilled water and dried in the air. The purity of the substance was verified analytically (for *ense*—found 13.1% C, 4.9% H, 14.5% N and 40.4% Se, calculated 12.7% C, 5.3% H, 14.8% N and 41.8% Se, for *propse*—found 15.7% C, 6.5% H, 11.4% N and 32.2% Se, calculated 15.1% C, 6.7% H, 11.7% N and 33.0% Se and for *butse*—found 19.4% C, 6.8% H, 10.9% N and 30.6% Se, calculated 19.0% C, 7.2% H, 11.1% N and 31.2% Se).

Determination of Se(IV) was carried out iodometrically [13] in acid solution by titration of a standard solution of sodium thiosulfate (starch indicator). The end of the titration was observed visually.

X-ray structural data were obtained on an Enraf–Nonius Kappa CCD diffractometer (for *ense*) and on a Bruker AXS CCD diffractometer (for *propse* and *butse*). The intensities were corrected for the Lorentz-polarization factor and absorption. In the case of *ense* empirical absorption correction based on multiscan measurements (SORTAV software [14]) was performed. In the case of *propse* and *butse* SADABS (Bruker area detector absorption corrections) was performed [15]. Direct methods (SIR-92 [16]) were employed to solve the phase problem and the temperature parameters of the non-hydrogen atoms were refined anisotropically.

Table 2
Selected bond lengths (Å) and angles (°) for *ense*

Bond	Value	Angle	Value	Angle	Value
Se(1)–O(1)	1.696(2)	O(1)–Se(1)–O(3)	103.9(1)	H(11)–N(1)–H(13)	109(3)
Se(1)–O(3)	1.697(2)	O(1)–Se(1)–O(2)	102.02(9)	H(12)–N(1)–H(13)	102(3)
Se(1)–O(2)	1.707(2)	O(3)–Se(1)–O(2)	101.3(1)	C(4)–N(3)–H(31)	119(3)
				C(4)–N(3)–H(32)	111(3)
N(1)–C(2)	1.487(3)	C(2)–N(1)–H(11)	105(2)	H(31)–N(3)–H(32)	102(4)
N(3)–C(4)	1.479(4)	C(2)–N(1)–H(12)	109(3)	C(4)–N(3)–H(33)	107(2)
C(2)–C(2) ⁱ	1.503(6)	H(11)–N(1)–H(12)	121(4)	H(31)–N(3)–H(33)	108(3)
C(4)–C(4) ⁱⁱ	1.506(6)	C(2)–N(1)–H(13)	110(3)	H(32)–N(3)–H(33)	108(4)
Hydrogen bonds					
Donor–H	Donor–H	H...acceptor	Angle D–H...A	Donor–acceptor	Acceptor
N(1)–H(11)	0.97(3)	1.81(3)	173(4)	2.767(3)	O(2) ⁱⁱⁱ
N(1)–H(12)	0.79(4)	1.99(4)	170(3)	2.772(3)	O(3)
N(1)–H(13)	0.95(5)	1.79(5)	169(4)	2.724(3)	O(3) ^{iv}
N(3)–H(31)	1.07(5)	1.78(5)	164(4)	2.826(3)	O(2)
N(3)–H(32)	0.88(6)	1.87(6)	172(5)	2.740(3)	O(1) ^v
N(3)–H(33)	1.01(4)	1.74(4)	177(4)	2.748(3)	O(1) ^{vi}

Note. Equivalent positions: (i) $-x+1, -y, z$; (ii) $-x+1, -y+1, z$; (iii) $x+1/2, -y+1/2, -z$; (iv) $x, y, z-1$; (v) $-x+1/2, y+1/2, -z+1$; (vi) $-x+1/2, y+1/2, -z$.

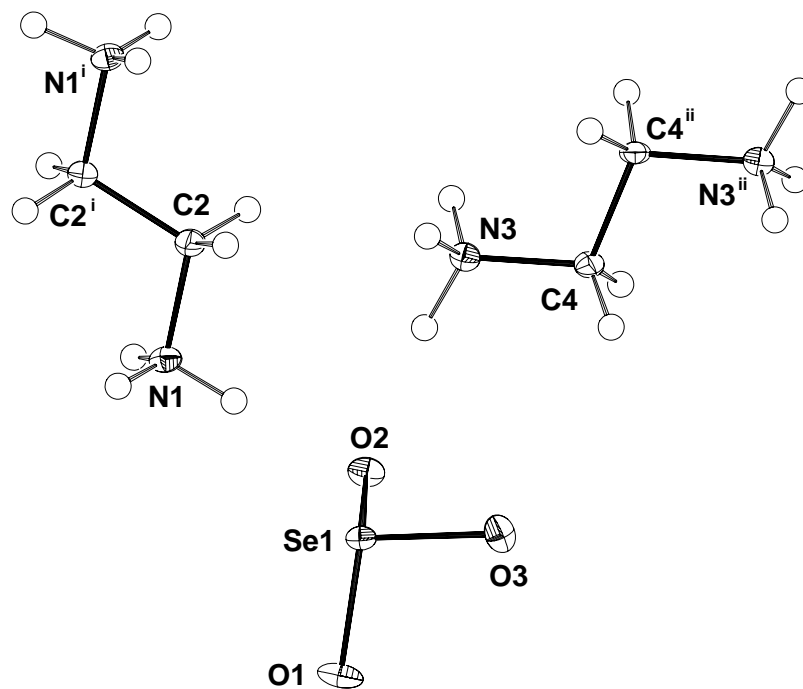


Fig. 1. Atom numbering of *ense*.

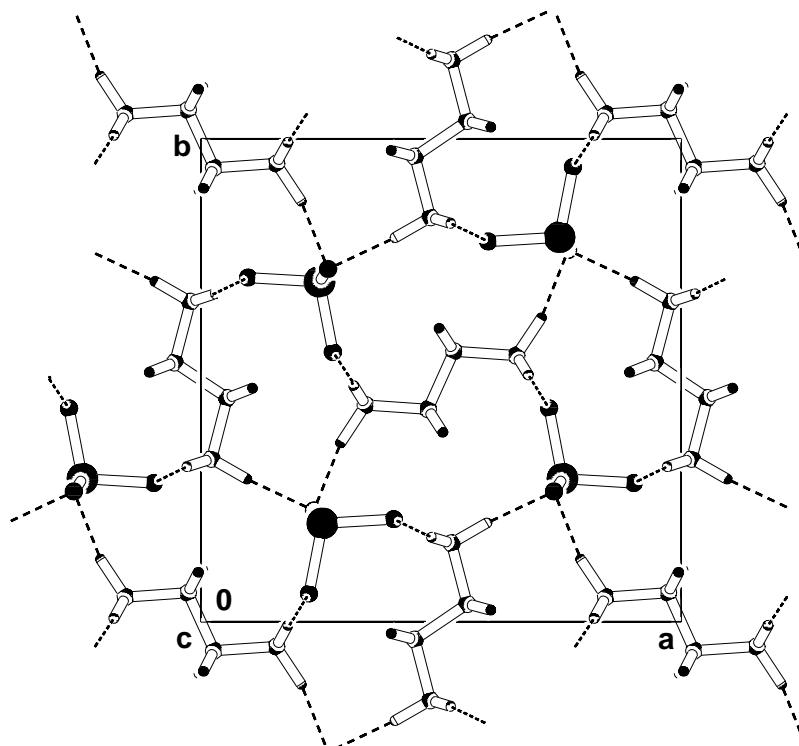


Fig. 2. Packing scheme of *ense* (projection to the xy plane, dashed lines indicate hydrogen bonds).

The coordinates, temperature parameters, and the experimental and calculated structural factors for all compounds were refined by the least-squares method

using the SHELXL-97 program package [17] and have been deposited with other crystallographic data with the Cambridge Crystallographic Data Centre (CCDC, 12

Union Road, Cambridge CB2 1EZ, UK; tel.: (44) 1223-336-408; fax: (44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk; www: <http://www.ccdc.cam.ac.uk/>) as sup-

Table 3

Basic crystallographic data, data collection and refinement parameters of *propse*

Empirical formula	C ₃ H ₁₆ N ₂ O ₅ Se
Formula weight	239.14
Temperature	158(2) K
Diffractionmeter used	Bruker AXS CCD
Wavelength	0.71073
Crystal system, space group	monoclinic, C2/c
Unit-cell dimensions	$a = 16.241(14) \text{ \AA}$, $\alpha = 90^\circ$ $b = 6.673(5) \text{ \AA}$, $\beta = 110.88(2)^\circ$ $c = 17.731(14) \text{ \AA}$, $\gamma = 90^\circ$
Volume	1795(3) Å ³
Z, Calculated density	8, 1.769 g/cm ³
Absorption coefficient	0.17 mm ⁻¹
<i>F</i> (0 0 0)	976
Crystal size	0.7 × 0.4 × 0.1 mm
θ range for data collection	2.46–28.22°
Index ranges	$h(-21;21)$, $k(-8;8)$, $l(-23;23)$
Reflections collected/unique	12233/2037 [<i>R</i> (int) = 0.0289]
Completeness to $\theta = 28.22^\circ$	91.8%
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	2037/0/140
Goodness-of-fit on <i>F</i> ²	1.089
Final <i>R</i> indices	<i>R</i> 1 = 0.0249, <i>wR</i> 2 = 0.0646
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0271, <i>wR</i> 2 = 0.0659
Largest diff. peak and hole	0.877 and -0.458 e. Å ⁻³
Weighting scheme	$w = [\sigma^2(F_o^2) + (0.0379P)^2 + 3.37P]^{-1}$ $P = [F_o^2 + 2F_c^2]/3$

plementary publications CCDC 188818, CCDC 188710 and CCDC 188711, respectively. A list of the observed and calculated structural factors can be obtained on request from the authors.

The infrared spectra were measured on a Nicolet Magna 760 FTIR spectrometer. The measurements were carried out by the nujol and fluorolube mull methods in the range 400–4000 cm⁻¹ (Happ–Genzel apodization, 2 cm⁻¹ resolution) at the temperature of 298 K.

The Raman spectra were measured using a Bruker Equinox 55/S FTIR spectrometer with a FRA 106/S Raman module. The measurement was carried out from 90 to 4000 cm⁻¹ (Blackman-Harris 4-Term apodization, 2 cm⁻¹ resolution, 1064 nm NdYAG laser excitation) at the temperature of 298 K. The spectra were processed using the WinFIRST program [18].

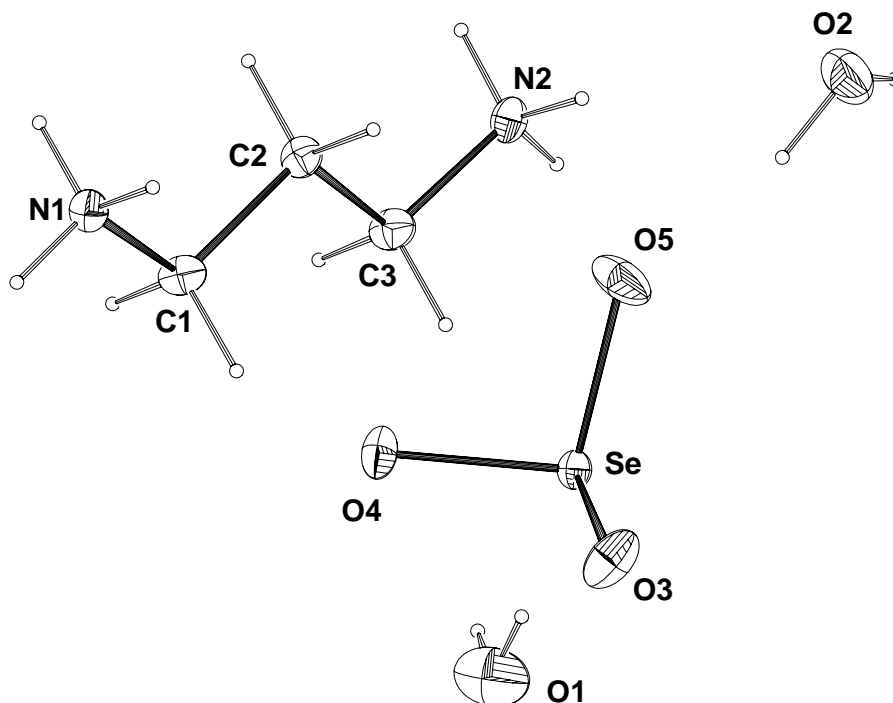
The DSC measurements were carried out on a Perkin-Elmer DSC 7 calorimeter between 98 K (cooling accessory limit) and the decomposition (dehydration) temperature of each particular compound. Powdered samples (10–30 mg) were sealed in Al pans. Above room temperature, the calorimeter was calibrated using the extrapolated onsets of melting of indium and zinc and the melting enthalpy of indium. Below room temperature, melting and a solid-state phase transition of cyclohexane were used for the calibration. A scanning rate of 10 K/min was employed. N₂ atmosphere (25 ml/min) and He atmosphere (20 ml/min) were used above and below room temperature, respectively.

Table 4

Selected bond lengths (Å) and angles (°) for *propse*

Bond	Value	Angle	Value	Angle	Value
Se–O(5)	1.714(2)	O(3)–Se–O(4)	106.5(1)	H(1A)–N(1)–H(1B)	110(3)
Se–O(3)	1.680(2)	O(3)–Se–O(5)	101.8(1)	H(1A)–N(1)–H(1C)	106(3)
Se–O(4)	1.682(2)	O(4)–Se–O(5)	99.48(9)	H(1B)–N(1)–H(1C)	108(3)
				C(3)–N(2)–H(2A)	112(2)
N(1)–C(1)	1.478(4)	H(11)–O(1)–H(12)	102(5)	C(3)–N(2)–H(2B)	103(2)
N(2)–C(3)	1.478(3)	H(21)–O(2)–H(22)	106(5)	C(3)–N(2)–H(2C)	113(3)
C(1)–C(2)	1.516(4)			H(2A)–N(2)–H(2B)	110(3)
C(2)–C(3)	1.520(4)	C(1)–N(1)–H(1A)	113(2)	H(2A)–N(2)–H(2C)	109(3)
		C(1)–N(1)–H(1B)	108(2)	H(2B)–N(2)–H(2C)	110(3)
		C(1)–N(1)–H(1C)	112(2)		
Hydrogen bonds					
Donor–H	Donor–H	H...acceptor	Angle D–H...A	Donor–acceptor	Acceptor
N(1)–H(1A)	0.87(3)	1.96(3)	171(3)	2.824(4)	O(4) ⁱ
N(1)–H(1B)	0.98(3)	1.86(3)	165(3)	2.818(4)	O(4) ⁱⁱ
N(1)–H(1C)	0.92(3)	1.92(3)	165(3)	2.817(4)	O(3) ⁱⁱⁱ
N(2)–H(2A)	0.87(3)	2.08(3)	161(3)	2.924(4)	O(3) ^{iv}
N(2)–H(2B)	0.93(5)	1.79(5)	178(2)	2.712(4)	O(5)
N(2)–H(2C)	0.80(4)	2.29(4)	161(4)	3.053(4)	O(4) ^v
O(1)–H(11)	0.78(5)	2.07(5)	138(5)	2.706(4)	O(3) ^{vi}
O(1)–H(12)	0.72(3)	2.08(3)	159(4)	2.760(5)	O(2) ⁱⁱⁱ
O(2)–H(21)	0.90(5)	1.74(5)	165(4)	2.615(4)	O(5) ^{vii}
O(2)–H(22)	0.77(5)	1.97(5)	157(5)	2.697(5)	O(1) ^{viii}

Note. Equivalent positions: (i) $x-1/2, y-1/2, z$; (ii) $-x+1/2, -y+1/2, -z+2$; (iii) $x-1/2, y+1/2, z$; (iv) $-x+1/2, y+1/2, -z+3/2$; (v) $-x+1/2, y-1/2, -z+3/2$; (vi) $x, y+1, z$; (vii) $-x+1, y, -z+3/2$; (viii) $-x+1, -y+1, -z+2$.

Fig. 3. Atom numbering of *propse*.

The thermal properties (DTA, DTG and TG curves) of *ense*, *propse* and *butse* were measured on a Derivatograph 1500 instrument (heating rate 1.25 K/min, temperature range 293–633 K).

3. Results and discussion

3.1. Crystal structure of ethylene diammonium (2+) selenite

The conditions of data collection and basic crystallographic data are given in Table 1 and selected bond lengths and bonding angles are given in Table 2. The positions of the hydrogen atoms were found on the differential Fourier map and their temperature parameters were refined isotropically. The atom numbering can be seen in Fig. 1, and the packing scheme is depicted in Fig. 2 (PLATON software [19]). The SeO_3^{2-} and $\text{C}_2\text{H}_{10}\text{N}_2^{2+}$ moieties are arranged in a three-dimensional network, where each of the oxygen atoms participates in two $\text{N-H}\cdots\text{O}$ hydrogen bonds (with a length of 2.73–2.83 Å). The selenite anion exhibits almost ideal C_{3v} symmetry (all the Se–O distances are almost identical—1.696 to 1.707 Å), which corresponds well with the model in which almost identically long hydrogen bonds are formed with all the oxygen atoms of the selenite anion (with a length of 2.72–2.77 Å); only one hydrogen bond $\text{N}(3)\text{—H}(31)\cdots\text{O}(2)$ is somewhat longer (2.83 Å). The NCCN chain is planar, similar to most common salts of ethylene diamine [1, 3–6]. The chain is deformed

Table 5
Basic crystallographic data, data collection and refinement parameters of *butse*

Empirical formula	$\text{C}_4\text{H}_{18}\text{N}_2\text{O}_5\text{Se}$
Formula weight	253.17
Temperature	158(2) K
Diffractometer used	Bruker AXS CCD
Wavelength	0.71073
Crystal system, space group	monoclinic, $P2_1/c$
Unit-cell dimensions	$a = 6.686(5) \text{ \AA}$, $\alpha = 90^\circ$ $b = 16.597(14) \text{ \AA}$, $\beta = 96.653(14)^\circ$ $c = 9.282(8) \text{ \AA}$, $\gamma = 90^\circ$
Volume	$1023.1(15) \text{ \AA}^3$
Z, Calculated density	4, 1.644 g/cm ³
Absorption coefficient	3.66 mm^{-1}
$F(000)$	520
Crystal size	$0.2 \times 0.15 \times 0.1 \text{ mm}$
θ range for data collection	$2.53\text{--}26.37^\circ$
Index ranges	$h(-8;3)$, $k(-17;15)$, $l(-11;4)$
Reflections collected/unique	2843/1442 [$R(\text{int}) = 0.0385$]
Completeness to $\theta = 26.37^\circ$	68.6%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1442/0/146
Goodness-of-fit on F^2	1.008
Final R indices	$R1 = 0.0352$, $wR2 = 0.0918$
R indices (all data)	$R1 = 0.0406$, $wR2 = 0.0980$
Largest diff. peak and hole	0.428 and $-0.550 e. \text{ \AA}^{-3}$
Weighting scheme	$w = [\sigma^2(F_o^2) + (0.0553P)^2 + 2.2326P]^{-1}$ $P = [F_o^2 + 2F_c^2]/3$

and the torsion angle attains a value of 63.7° only in the crystal structure of ethylene diamine sulfate [2]. The bond lengths of C–C and C–H and the magnitude of the relevant angles lie in the usual ranges.

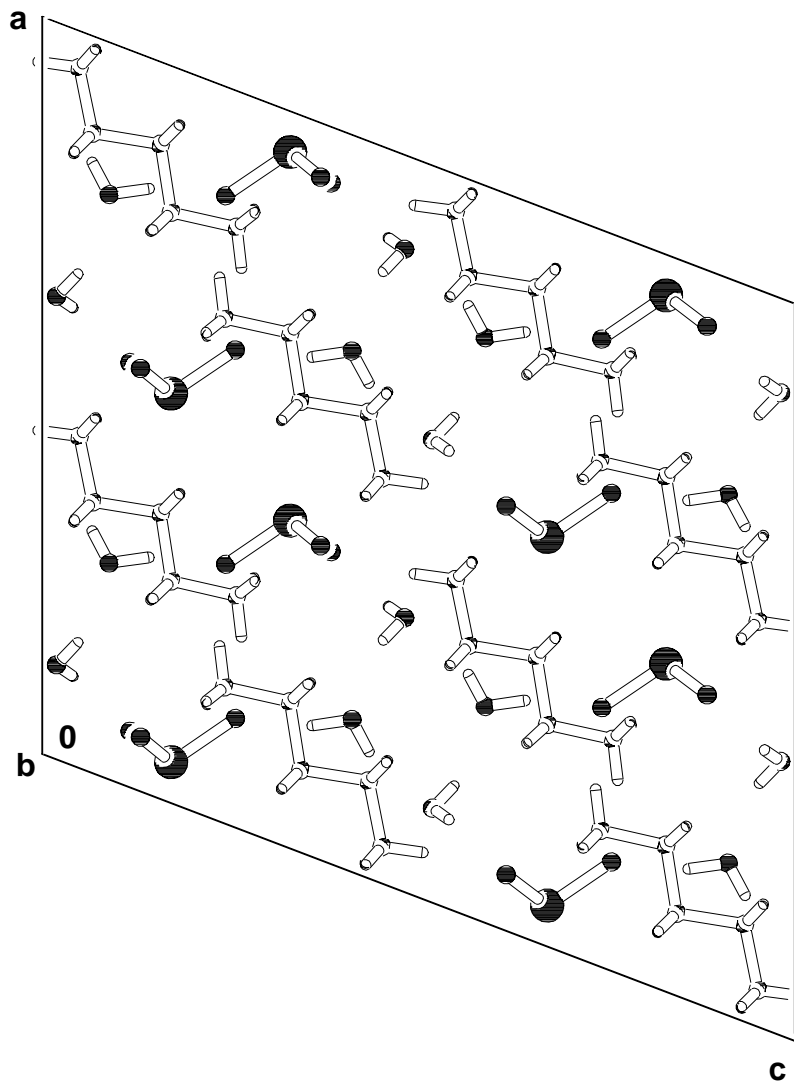


Fig. 4. Packing scheme of *propse* (projection to *xz* plane, hydrogen bonds are omitted for clarity).

3.2. Crystal structure of 1,3-propylene diammonium (2+) selenite dihydrate

The conditions of data collection and the basic crystallographic data are given in Table 3 and selected bond lengths and bonding angles are given in Table 4. The hydrogen atoms in the CH₂ groups were located in the calculated positions; the positions of the hydrogen atoms of the nitrogen atoms of 1,3-propylene diammonium (2+) ion and the water molecules were found on the differential Fourier map and were refined isotropically. The atom numbering is shown in Fig. 3, and packing scheme is depicted in Fig. 4.

The structure of (NH₃(CH₂)₃NH₃)SeO₃·2H₂O consists of 1,3-propylene diammonium(2+) cations, selenite anions and water molecules. The bond lengths and

angles of the dications lie in the usual ranges, the NCCCN chain is almost planar (with torsion angles N(1)–C(1)–C(2)–C(3) 179.3° and C(1)–C(2)–C(3)–N(2) –178.7°). Similar parameters were found, e.g., for 1,3-propylene diammonium(2+) dihydrogen phosphate [20]. The chain is usually more or less deformed in the other salts of this base [7,9] and is deformed most in the perchlorate [11], where the N–C–C–C torsion angle equals 76.8°. This substance (1,3-propylene diammonium(2+) perchlorate) also contains relatively long N–H···O hydrogen bonds in its structure (with a length of 2.98–3.21 Å). The selenite anion is deformed and tends to exhibit C_s symmetry rather than C_{3v}. The Se–O(5) distance is about 0.3 Å longer than the Se–O(3) and Se–O(4) distances (approx. 1.68 Å), which corresponds well with the fact that the O(5) oxygen atom is bonded by two relatively strong hydrogen bonds to the

Table 6
Selected bond lengths (Å) and angles (°) for butse

Bond	Value	Angle	Value	Angle	Value
Se(1)–O(3)	1.685(3)	O(3)–Se(1)–O(4)	102.1(2)	H(1A)–N(1)–H(1B)	106(5)
Se(1)–O(4)	1.696(3)	O(3)–Se(1)–O(5)	102.9(2)	H(1A)–N(1)–H(1C)	104(5)
Se(1)–O(5)	1.687(3)	O(4)–Se(1)–O(5)	104.0(2)	H(1B)–N(1)–H(1C)	114(5)
N(1)–C(4)	1.494(6)	H(11)–O(1)–H(12)	95.4(4)	C(1)–N(2)–H(2A)	115(3)
N(2)–C(1)	1.485(6)	H(21)–O(2)–H(22)	90.8(4)	C(1)–N(2)–H(2B)	106(3)
C(1)–C(2)	1.525(7)			C(1)–N(2)–H(2C)	111(2)
C(2)–C(3)	1.530(7)	C(4)–N(1)–H(1A)	112(3)	H(2A)–N(2)–H(2B)	114(4)
C(3)–C(4)	1.524(7)	C(4)–N(1)–H(1B)	109(4)	H(2A)–N(2)–H(2C)	102(4)
		C(4)–N(1)–H(1C)	111(3)	H(2B)–N(2)–H(2C)	109(4)
Hydrogen bonds					
Donor–H	Donor–H	H...acceptor	Angle D–H...A	Donor–acceptor	Acceptor
N(1)–H(1A)	0.87(5)	2.05(5)	165(5)	2.897(5)	O(5)
N(1)–H(1B)	1.01(7)	1.70(7)	177(2)	2.708(5)	O(3) ⁱ
N(1)–H(1C)	0.83(5)	1.99(5)	174(5)	2.813(5)	O(4) ⁱⁱ
N(2)–H(2A)	0.88(5)	1.94(5)	170(5)	2.812(6)	O(5) ⁱⁱⁱ
N(2)–H(2B)	1.01(5)	1.73(5)	174(4)	2.736(5)	O(4) ^{iv}
N(2)–H(2C)	0.83(4)	2.13(4)	157(3)	2.913(6)	O(4) ^v
O(1)–H(11)	0.953(4)	2.0503	150.47	2.918(6)	O(5) ^{vi}
O(1)–H(12)	0.721(5)	2.1941	158.14	2.875(7)	O(2) ^{iv}
O(2)–H(22)	0.892(4)	1.7949	162.88	2.661(6)	O(3) ^{vii}
O(2)–H(21)	0.816(5)				

Note. Equivalent positions: (i) $-x+1, -y+2, -z+1$; (ii) $x+1, y, z$; (iii) $x, -y+3/2, z-1/2$; (iv) $-x+1, y-1/2, -z+3/2$; (v) $x+1, -y+3/2, z-1/2$; (vi) $x, y-1, z$; (vii) $x, -y+3/2, z+1/2$.

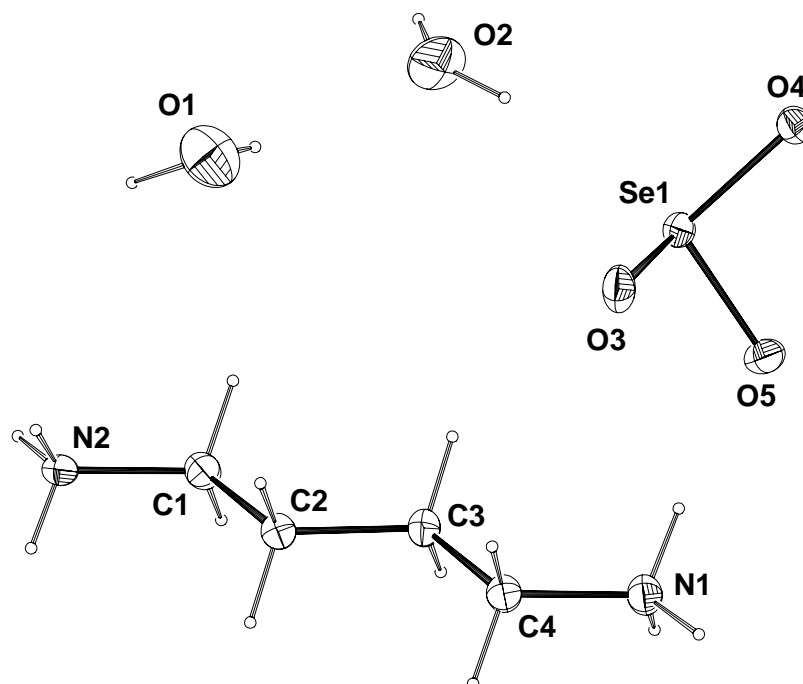


Fig. 5. Atom numbering of butse.

N(2) nitrogen atom (2.71 Å) and to the O(2) oxygen atom of water (2.61 Å). The remaining oxygen atoms of the selenite anion are bonded by hydrogen bonds to the nitrogen atoms of the amine, although these

bonds are somewhat longer (2.82–3.05 Å). The water molecules are bonded through hydrogen bonds (with a length of 2.69–2.76 Å) together and to the selenite anions (2.62–2.71 Å).

Table 7
Correlation analysis of SeO_3^{2-} internal modes in *ense* crystals

Free ion modes	Degree of freedom	Free ion symmetry C_{3v}	Site symmetry C_1	Factor group symmetry D_2	Vibrational modes	Activity	
						IR	Raman
ν_1	4	A_1	A	A	$\nu_1, \nu_2, 2\nu_3, 2\nu_4$	z	$\alpha_{xx}, \alpha_{yy}, \alpha_{zz}$
ν_2	4	A_2		B_1	$\nu_1, \nu_2, 2\nu_3, 2\nu_4$		α_{xy}
ν_3	4	E		B_2	$\nu_1, \nu_2, 2\nu_3, 2\nu_4$		α_{xz}
ν_4	4	E		B_3	$\nu_1, \nu_2, 2\nu_3, 2\nu_4$		α_{yz}

Table 8
Correlation analysis of SeO_3^{2-} internal modes in *propse* and *butse* crystals

Free ion modes	Degree of freedom		Free ion symmetry C_{3v}	Site symmetry C_1	Factor group symmetry C_{2h}	Vibrational modes		Activity	
	Propse	butse				propse	butse	IR	Raman
ν_1	8	4	A_1	A	A_g	$2\nu_1, 2\nu_2, 4\nu_3, 4\nu_4$	$\nu_1, \nu_2, 2\nu_3, 2\nu_4$	z	$\alpha_{xx}, \alpha_{yy}, \alpha_{zz}, \alpha_{xy}$
ν_2	8	4	A_2		A_u	$2\nu_1, 2\nu_2, 4\nu_3, 4\nu_4$	$\nu_1, \nu_2, 2\nu_3, 2\nu_4$		α_{xz}, α_{yz}
ν_3	8	4	E		B_g	$2\nu_1, 2\nu_2, 4\nu_3, 4\nu_4$	$\nu_1, \nu_2, 2\nu_3, 2\nu_4$		x, y
ν_4	8	4	E		B_u	$2\nu_1, 2\nu_2, 4\nu_3, 4\nu_4$	$\nu_1, \nu_2, 2\nu_3, 2\nu_4$		

Table 9
FTIR and FT Raman spectra of *ense*

Assignment	IR	Raman	Assignment	IR	Raman
?		3130 (1)	ρNH_3^+	1177 m	
νCH_2		2979 (14)		1155 m	
	2950 w	2965 (14)		1100 sh	1101 (1)
	2920 w	2913 (24)	$\rho \text{NH}_3^+, \nu \text{C-N}, \nu \text{C-C}$	1085 m	
	2868 m	2837 (8)	$\nu \text{C-N}, \nu \text{C-C}$		1073 (15)
$\nu \text{N-H}\cdots\text{O}$		2805 (6)	ρNH_3^+	1034 m	
	2769 sb		$\nu \text{C-N}, \nu \text{C-C}$	1005 w	1005 (3)
	2753 sb	2753 (5)		991 w	993 (2)
	2682 s	2690 (5)		977 w	971 (8)
	2591 sb	2598 (4)		964 w	
	2515 sb	2520 (4)	ρNH_3^+	838 m	
	2440 mb		$\nu_1 \text{SeO}_3^{2-}$	790 s	785 (100)
	2215 sb	2215 (3)	$\nu_3 \text{SeO}_3^{2-}$	737 s	752 (3)
?	1980 mb				718 (14)
	1916 w			702 s	698 (23)
	1812 w		?	638 m	640 (2)
	1741 w			624 sh	627 (2)
$\delta_{as} \text{NH}_3^+$	1664 m		$\delta \text{C-C-N}$	508 w	
	1650 m	1656 (2)		487 w	487 (8)
	1618 w	1628 (2)	$\nu_2 \text{SeO}_3^{2-}$	444 s	439 (6)
	1574 m		$\nu_4 \text{SeO}_3^{2-}$		396 (10)
	1562 m	1564 (1)			364 (7)
$\delta_s \text{NH}_3^+$	1500 m				351 (8)
$\delta_s \text{NH}_3^+, \text{sciss } \text{CH}_2$	1494 m	1493 (6)	External modes		242 (5)
?	1413 w	1414 (2)			222 (4)
	1378 w				204 (8)
	1367 sh				161 (9)
ωCH_2		1347 (5)			140 (3)
		1329 (4)			110 (7)
?		1294 (3)			
	1277 w	1285 (3)			
		1265 (1)			

Note. Abbreviation: s, strong; m, medium; w, weak; b, broad; sh, shoulder; ν , stretching; δ , deformation or in-plane bending; ω , wagging; sciss, scissoring; ρ , rocking; s , symmetric; as , antisymmetric.

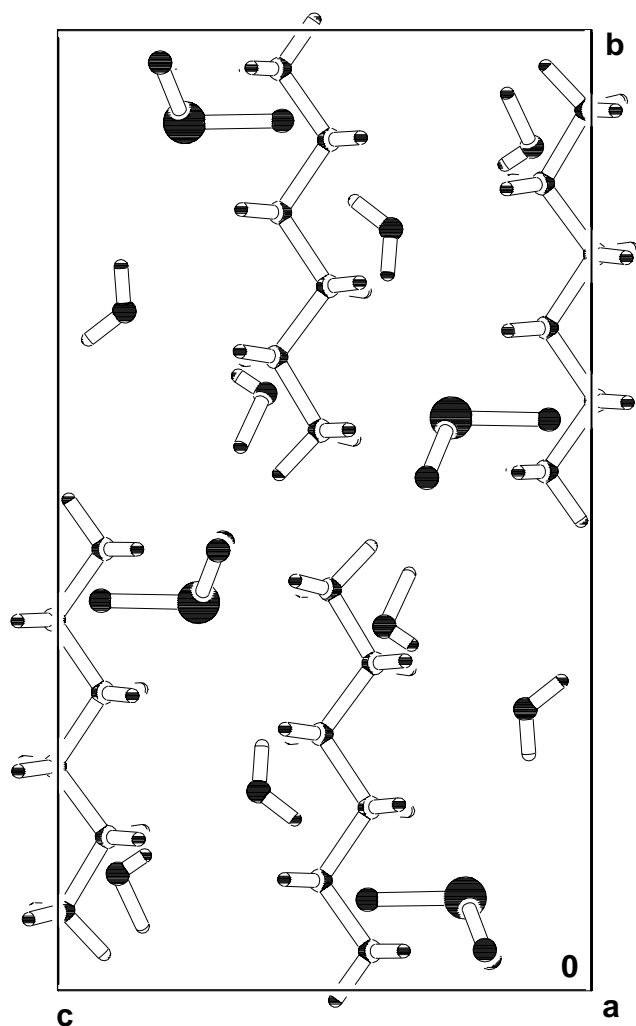


Fig. 6. Packing scheme of *butse* (projection to yz plane, hydrogen bonds are omitted for clarity).

3.3. Crystal structure of 1,4-butylene diammonium (2+) selenite dihydrate

The conditions of data collection and the basic crystallographic data are given in Table 5, while Table 6 gives selected bond lengths and bonding angles. The hydrogen atoms in the CH_2 groups were located in the calculated positions; the positions of the hydrogen atoms of the nitrogen atoms of the 1,4-butylene diammonium (2+) ion and water molecules were found on the differential Fourier map and refined isotropically. The atom numbering is shown in Fig. 5 and the packing scheme is depicted in Fig. 6.

The structure of $(\text{NH}_3(\text{CH}_2)_4\text{NH}_3)\text{SeO}_3 \cdot 2\text{H}_2\text{O}$ consists of 1,4-butylene diammonium (2+) cations, selenite anions and water molecules. The bond lengths and bonding angles of the dications lie within the usual limits, the NCCCCN chains are almost planar (with torsion angles $\text{N}(2)-\text{C}(1)-\text{C}(2)-\text{C}(3)$ 179.4° ; $\text{C}(1)-\text{C}(2)-$

$\text{C}(3)-\text{C}(4)$ 177.1° and $\text{C}(2)-\text{C}(3)-\text{C}(4)-\text{N}(1)$ -176.7°) and thus this structure is one of the few structures of 1,4-butylene diamine salts in which the NCCCCN chain is also planar [8,10]. The longer the carbon chain, the easier it is for the molecule to twist and assume positions with various torsion angles, e.g. as in the nitrate of this base [21].

The selenite anion is almost not deformed and exhibits approximately C_{3v} symmetry (all the Se–O distances are in the range 1.685–1.697 Å). The oxygen atoms of the selenite anion are bonded by hydrogen bonds to the amine nitrogen atoms (2.71–2.91 Å) and to water molecules (2.66–2.91 Å). Both water molecules are also mutually bonded by a single hydrogen bond with a length of 2.90 Å.

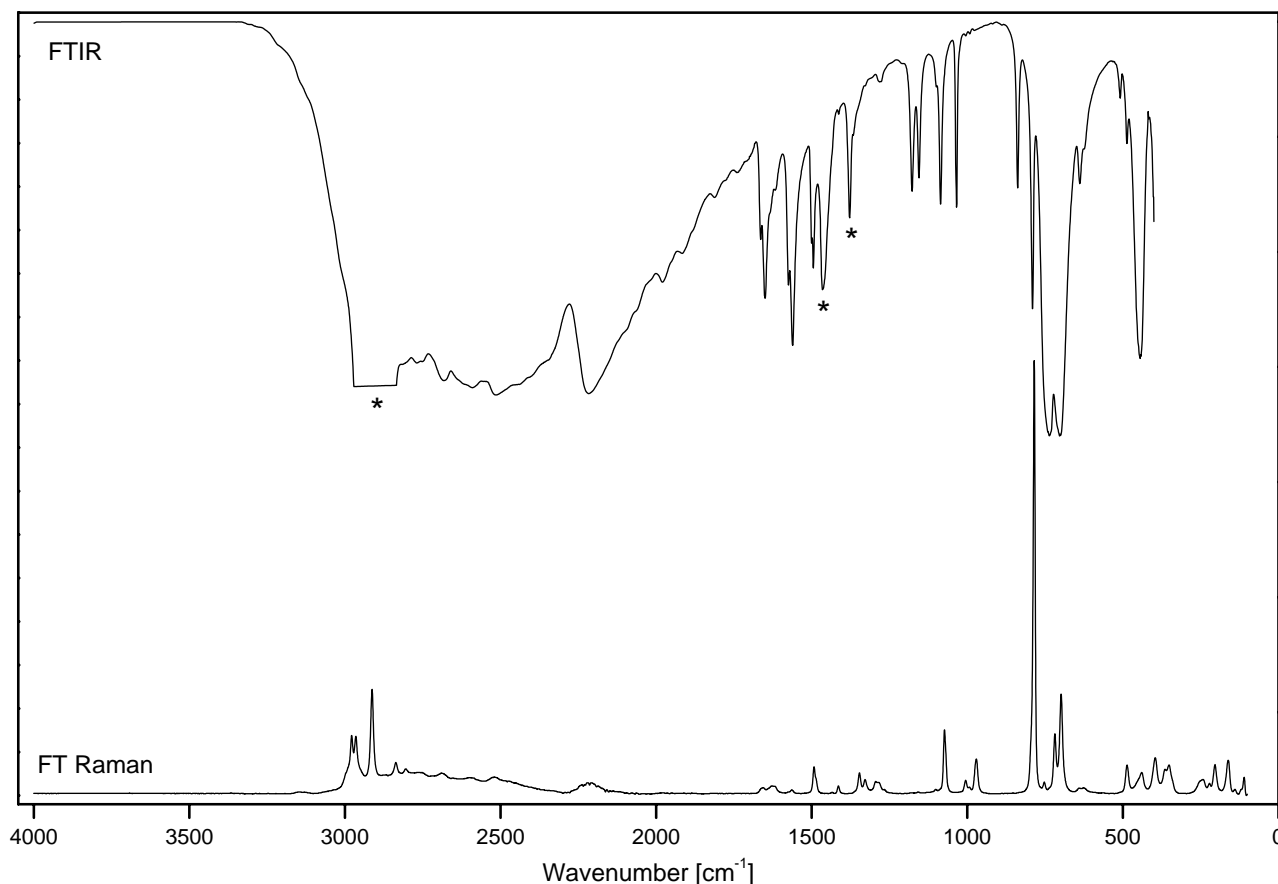
3.4. Analysis of the vibrational spectra

The number of normal modes of the *ense*, *propse* and *butse* crystals were determined by nuclear site group analysis [22].

The *ense* crystals belong in the $P2_12_12$ (D_2^3) space group with 18 atoms per asymmetric unit ($Z=4$). All the atoms occupy four-fold positions $c(C_1)$. Two types of species present in the unit cell, ethylene diammonium(2+) cation and SeO_3^{2-} anion, occupying four-fold positions $c(C_1)$, were considered in more detailed calculations of the internal and external modes. The results are representations $12A$ (RA) + $11B_1$ (IR, RA) + $11B_2$ (IR, RA) + $11B_3$ (IR, RA) for external modes (excluding acoustic modes), and $42A$ (RA) + $42B_1$ (IR, RA) + $42B_2$ (IR, RA) + $42B_3$ (IR, RA) for internal modes.

The *propse* crystals belong in the $C2/c$ (C_{2h}^6) space group with 27 atoms per asymmetric unit ($Z=8$). All the atoms occupy eight-fold positions $f(C_1)$. Four types of species present in the unit cell, propylene diammonium(2+) cation, SeO_3^{2-} anion and two water molecules, occupying eight-fold positions $f(C_1)$, were considered in more detailed calculations of the internal and external modes. The results are representations $24A_g$ (RA) + $23A_u$ (IR) + $24B_g$ (RA) + $22B_u$ (IR) for external modes (excluding acoustic modes), and $57A_g$ (RA) + $57A_u$ (IR) + $57B_g$ (RA) + $57B_u$ (IR) for internal modes.

The *butse* crystals belong in the $P2_1/c$ (C_{2h}^5) space group with 30 atoms per asymmetric unit ($Z=4$). All the atoms occupy four-fold positions $e(C_1)$. Four types of species present in the unit cell, butylene diammonium(2+) cation, SeO_3^{2-} anion and two water molecules, occupying four-fold positions $e(C_1)$, were considered in more detailed calculations of the internal and external modes. The results are representations $24A_g$ (RA) + $23A_u$ (IR) + $24B_g$ (RA) + $22B_u$ (IR) for external modes (excluding acoustic modes), and $66A_g$

Fig. 7. FTIR (nujol mull) and FT Raman spectra of *ense*. Nujol bands are indicated by asterisk.Table 10
FTIR and FT Raman spectra of *propse*

Assignment	IR	Raman	Assignment	IR	Raman
ν O–H...O	3297 sb		ω CH ₂		1350 (5)
ν O–H...O, ν N–H...O	3080 sb				1333 (21)
ν CH ₂		3011 (18)		1308 w	1299 (13)
		2989 (26)	ρ NH ₃ ⁺	1224 w	1226 (6)
	2968 w	2973 (22)		1150 w	1144 (3)
	2933 w	2932 (61)	ν C–N, ν C–C	1052 w	1051 (21)
	2910 w	2915 (35)	γ O–H...O, γ N–H...O	995 w	
		2892 (24)	ρ NH ₃ ⁺ , ν C–N, ν C–C	979 w	981 (29)
	2862 w	2864 (24)	ρ NH ₃ ⁺	954 w	
ν O–H...O, ν N–H...O	2771 s	2778 (15)	ν_1 SeO ₃ ²⁻	813 s	822 (100)
	2690 s		ν_3 SeO ₃ ²⁻	746 vs	735 (22)
	2603 s	2605 (8)	?	639 m	
	2537 s	2532 (8)		627 m	
	2369 m			567 sh	
	2155 m	2160 b (3)	ν_2 SeO ₃ ²⁻	462 m	459 (8)
δ H ₂ O	1696 w			445 s	
δ_{as} NH ₃ ⁺ , δ H ₂ O	1625 m	1640 b (1)	ν_4 SeO ₃ ²⁻	420 w	418 (14)
δ_{as} NH ₃ ⁺	1568 m				376 (28)
δ_s NH ₃ ⁺	1522 m				361 (23)
sciss CH ₂	1475 m	1485 (16)	External modes		266 (3)
	1464 m	1453 (23)			236 (3)
?	1404 m	1397 (2)			205 (6)
	1377 sh				120 (13)

Note. Abbreviation: s, strong; vs, very strong; m, medium; w, weak; b, broad; sh, shoulder; ν , stretching; δ , deformation or in-plane bending; γ , out-of-plane bending; ω , wagging; sciss, scissoring; ρ , rocking; s_s , symmetric; as_s , antisymmetric.

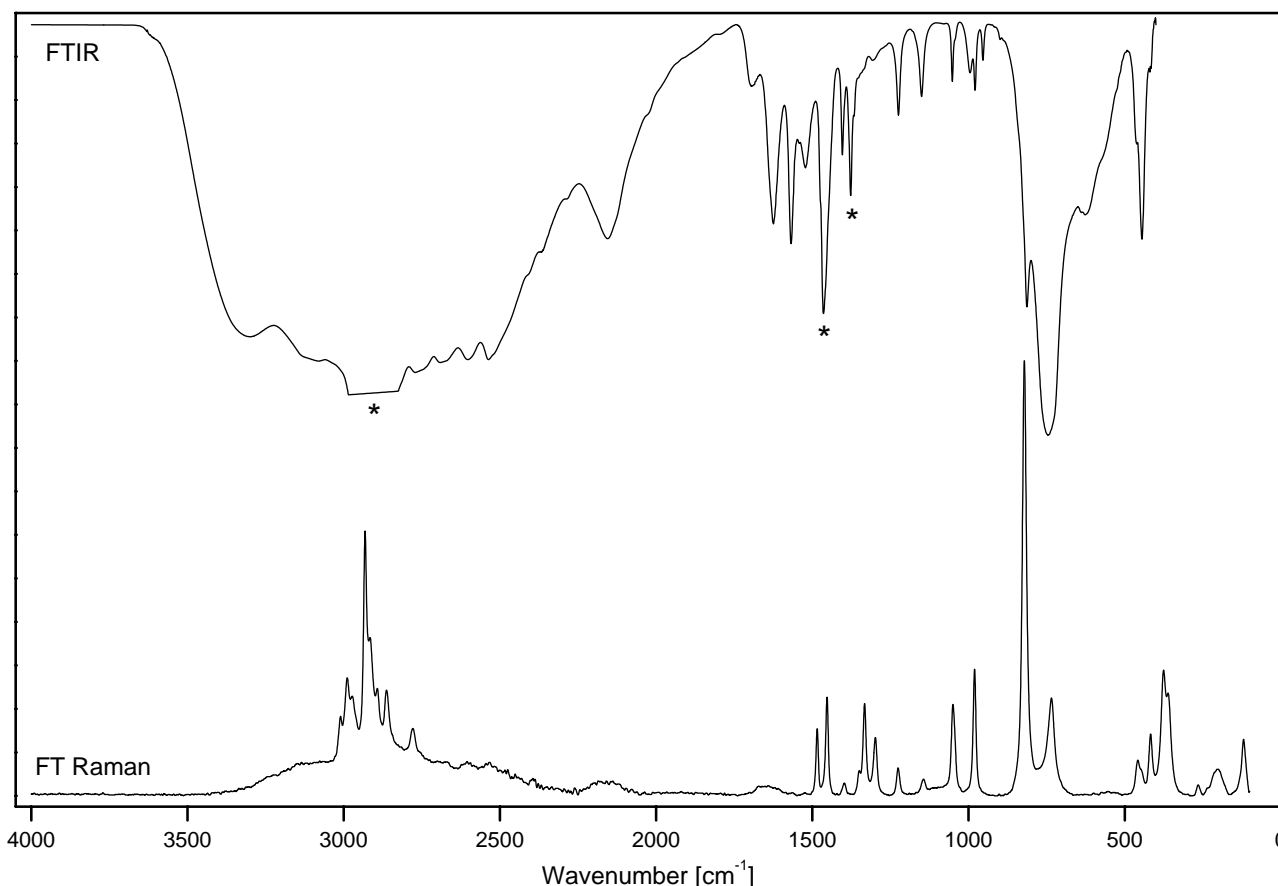


Fig. 8. FTIR (nujol mull) and FT Raman spectra of *propse*. Nujol bands are indicated by asterisk.

(RA) + 66A_u (IR) + 66B_g (RA) + 66B_u (IR) for internal modes.

Standard correlation method [23] was used for detailed study of the expected vibrational features of the SeO₃²⁻ groups in all the structures. The results obtained are presented in Tables 7 and 8.

3.5. Vibrational spectra

The vibrational spectra of all compounds are depicted in Figs. 7–9 and the wavenumbers of the maxima are given in Tables 9–11. The assignment of the vibrational spectra is based on previous studies of alkylene diamines [24–26] and the selenite anion [27].

Broad intense bands in the IR spectra of all compounds with maxima in the 3600–2100 cm⁻¹ region can be assigned to the stretching vibration of the O–H...O and N–H...O hydrogen bonds. The positions of these maxima depend on the length of these hydrogen bonds and correspond quite well (according to Refs. [28, 29]) to the hydrogen bonds found in the crystal structures. For example—only hydrogen bonds of the N–H...O type were found in the structure of the *ense* compound (with a length 2.73–2.83 Å). The broad bands corresponding to the stretching vibrations of the

hydrogen bonds with this length (2.73–2.83 Å) were found in the 2770–2200 cm⁻¹ region. Another example consists in the presence of the vibrations of long hydrogen bonds the O–H...O and N–H...O types (between water molecules and anions or mutually between water molecules) in the compounds *propse* and *butse* (with lengths of over 2.75 Å—see also Tables 4 and 6) that can be found in the 3600–3100 cm⁻¹ region in the IR spectra.

The 3020–2800 cm⁻¹ region corresponds to symmetric and antisymmetric stretching vibrations of the CH₂ group, which are more intense in the Raman spectra and are partly overlapped by stretching vibrations of the hydrogen bonds in the infrared spectra. Scissoring and wagging vibrations of CH₂ group were observed in the 1480–1450 and 1350–1300 cm⁻¹ regions, respectively.

Bands in the 2000–1750 cm⁻¹ region can be assigned to overtones and combination vibrations of fundamental vibrations.

The broad bands with wavenumber around 1650 cm⁻¹ (compounds *propse* and *butse*) correspond to the deformation vibrations of water molecules and, together with presence of strong stretching O–H...O bands, demonstrate that both structures certainly contain molecules of the water of crystallization.

Table 11
FTIR and FT Raman spectra of *butse*

Assignment	IR	Raman	Assignment	IR	Raman
ν O–H...O	3610 m 3450 m 3410 m 3265 m		?	1403 m 1377 sh 1345 w 1310 w	1399 (3) 1339 (8) 1314 (32)
ν O–H...O, ν N–H...O	3025 sh		?		1287 (2)
ν CH ₂		3001 (16) 2986 (20) 2974 sh 2960 w 2943 w	ρ NH ₃ ⁺	1162 m 1128 w	1219 (3)
		2922 (76) 2896 (32) 2874 w 2858 w	ν C–N, ν C–C	1055 w 1040 w 1007 w	1062 (23) 1022 (11) 1008 (24)
ν O–H...O, ν N–H...O	2745 s		ρ NH ₃ ⁺	950 w 901 m	
?		2709 (7)	?	840 sh	
ν O–H...O, ν N–H...O	2676 s 2608 s 2544 s 2491 s		ν_1 SeO ₃ ²⁻ ν_3 SeO ₃ ²⁻	814 s 743 vs 724 sh	812 (100) 747 (18) 722 (12)
	2153 m	2150 (3)	?	640 m 629 m 572 w	
?	2068 sh		τ NH ₃ ⁺	523 m 514 m	
δ_{as} NH ₃ ⁺ , δ H ₂ O	1635 m	1655 (3)	ν_2 SeO ₃ ²⁻	442 m 418 m	447 (5)
δ_{as} NH ₃ ⁺	1616 m		ν_4 SeO ₃ ²⁻		394 (19)
δ_s NH ₃ ⁺	1559 m	1565 (1)			381 (11)
	1546 m				353 (19)
sciss CH ₂	1478 w 1464 w 1456 w	1474 (17) 1466 (17) 1457 (14) 1444 (11)	External modes		248 (4) 170 (11) 137 (12) 121 (14)

Note. Abbreviation: s, strong; vs, very strong; m, medium; w, weak; b, broad; sh, shoulder; ν , stretching; δ , deformation or in-plane bending; ω , wagging; sciss, scissoring; ρ , rocking; t, torsional; s, symmetric; as, antisymmetric.

Deformation vibrations of the whole cations were observed below 1350 cm⁻¹ in the spectra.

Bands of the symmetric and antisymmetric deformation vibrations of the NH₃⁺ groups in the 1650–1490 cm⁻¹ region indicate the presence of the cation of the doubly protonated base in the crystal structure. As the chain length increases, the symmetric deformation vibration of the NH₃⁺ group is shifted to higher wavenumbers and, simultaneously, splitting of the bands of the antisymmetric deformation vibrations disappears (see Tables 9–11). Manifestations of the rocking vibrations of the NH₃⁺ group were observed in the 1200–900 cm⁻¹ wavenumber region.

Vibration of the selenite anion were observed below 850 cm⁻¹. The positions of the vibrational bands clearly demonstrate the presence of SeO₃²⁻ ions in the structures. In agreement with correlation analysis results (see Tables 7 and 8) the vibrational manifestation of SeO₃²⁻ anion is almost identical for *propse* and *butse* (though no splitting of vibrational bands related to different Z number was observed) and differ for *ense*. Lower factor group symmetry in *ense* (*D*₂ compared to *C*_{2h} in *propse*

and *butse*) results in much intense splitting of ν_3 vibration (almost symmetric doublet in IR spectrum). The shift of ν_1 vibration to lower wavenumbers is also significant. However, expected level of factor group splitting has not been observed in any spectra of the compound studied. This fact could be explained by small inter-ion interaction in the unit cells and also in terms of the fact that all the measurements were carried out on polycrystalline samples at room temperature.

Manifestation of external modes were found in the Raman spectra of all the compounds in the region below 250 cm⁻¹.

3.6. Thermal behavior

Ethylene diammonium selenite is stable in the air up to a temperature of about 390 K. Then the compound decomposes. 1,3-Propylene diammonium selenite dihydrate and 1,4-butylene diammonium selenite dihydrate are stable in the air up to a temperature of only about 325 and 310 K, respectively. Then they lose molecules of water of crystallization and simultaneously decompose.

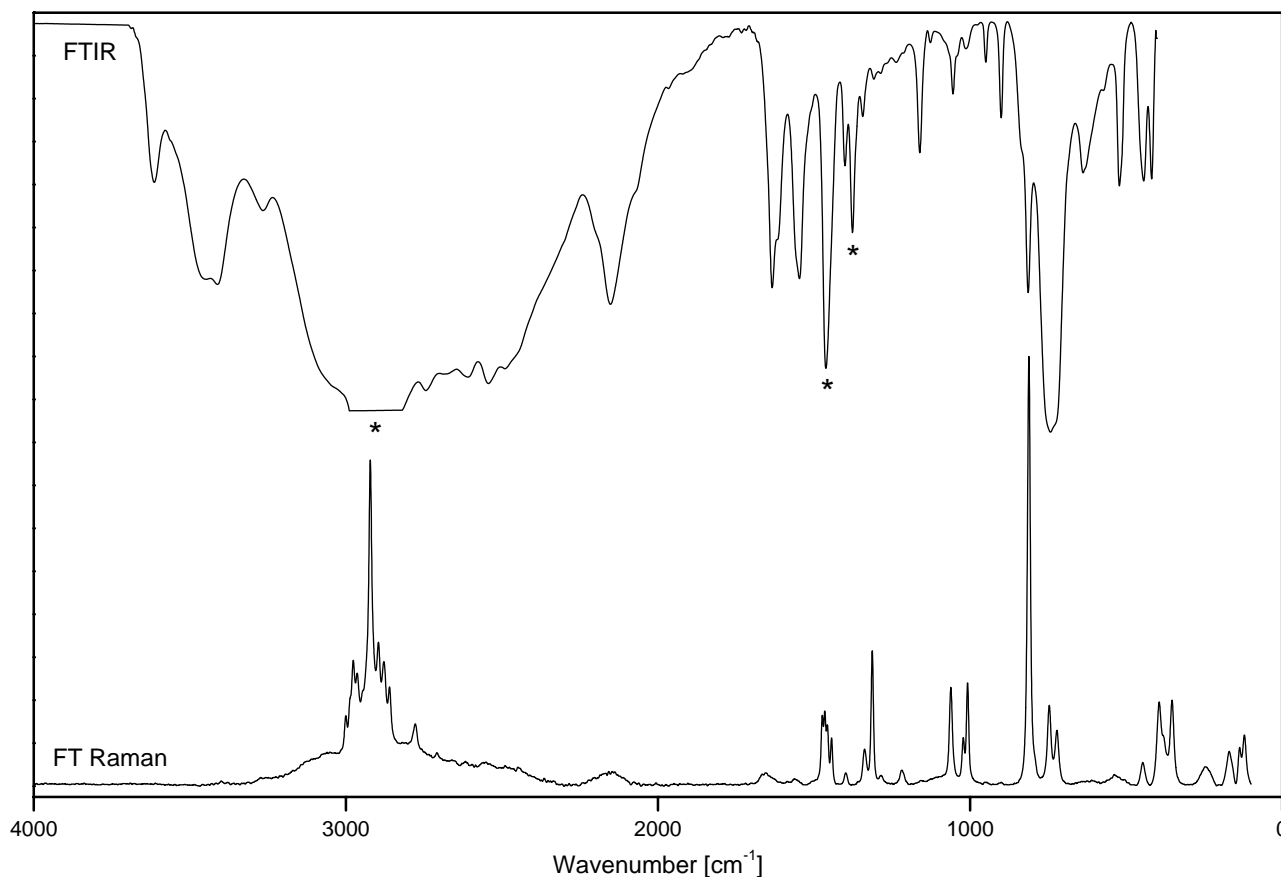


Fig. 9. FTIR (nujol mull) and FT Raman spectra of *butse*. Nujol bands are indicated by asterisk.

The anhydrous compounds cannot be obtained by continuous heating.

The DSC measurements of each of the title compounds did not exhibit any effect on the curve that would indicate a phase transition.

Acknowledgments

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