Journal of Solid State Chemistry **150,** 305–315 (2000)
doi:10.1006/jssc.1999.8595, available online at http://www.idealibrary.com on IDEAL®

The Crystal Structure, Vibrational Spectra, and Thermal Behavior of Piperazinium(2+) Selenate Monohydrate and *N,N′*-Dimethylpiperazinium(2+) Selenate Dihydrate

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Received August 13, 1999; in revised form November 29, 1999; accepted December 4, 1999

The crystal structure of piperazinium(2+) selenate monohydrate has been resolved; this substance crystallizes in the monoclinic space group $P2_1/n$, $a = 6.4586(8)$, $b = 11.8335(7)$, $c = 11.8065(7)$ Å, $\beta = 100.990(8)°$; $V = 885.80(13)$ Å^5, $Z = 4$, $R = 0.0446$ for 1556 observed reflections. A similar compound, *N,N′*-dimethylpiperazinium(2+) selenate dihydrate, crystallizes in a triclinic system with space group $P\bar{1}$ and lattice parameters $a = 6.7370(8)$, $b = 7.9845(9)$, $c = 12.3802(12)$ Å, $\alpha = 92.435(9)°$, $\beta = 100.219(9)°$, $\gamma = 114.699(10)°$; $V = 590.34(11)$ Å^3, $Z = 2$, $R = 0.0311$ for 2071 observed reflections. While, in the former structure, the cations of piperazinium(2+) in the chair conformation are arranged roughly plane-parallel above one another, in the second substance, the *N,N′*-dimethylpiperazinium (2+) ions lie approximately perpendicularly above one another. The FTIR and FT Raman spectra of both test substances have been measured and studied. The thermoanalytical properties were studied using TG, DTG, and DTA methods in the temperature range 293–533 K. DSC measurements were carried out in the temperature range 95–343 K. No phase transition was found in this temperature region for either of the compounds. © 2000 Academic Press

Key Words: **piperazinium(2+) selenate monohydrate; *N,N′*-dimethylpiperazinium(2+) selenate dihydrate; crystal structure; vibrational spectra; thermal behavior.**

INTRODUCTION

The compounds of selenic acid with piperazine and its derivatives have not yet been described in the literature. Of the compounds of sulfuric acid and piperazine, preparation of piperazinium(2+) sulfate monohydrate (1) and piperazinium(2+) hydrogen sulfate (2) have been described, but their crystal structures and thermal behavior have not been studied. This study deals with the preparation of the piperazinium(2+) selenate monohydrate ($\mathrm{PipzSeO_4.H_2O}$) and *N*,*N′*-dimethylpiperazinium(2+) selenate dihydrate ($\mathrm{DmpipzSeO_4.2H_2O}$) on the basis of study of their solubility diagrams, crystal structures, vibrational spectra, and thermoanalytical properties.

This work is part of our project dealing with the preparation and characterization of new compounds of the type of salts of inorganic acids with large organic bases. In these compounds, changes in the dynamic behavior of protons in hydrogen bonds can lead to the formation of interesting phases, i.e., ferroelectric compounds or fast proton conductors.

EXPERIMENTAL

The solubility study was carried out using the Schreinemakers method (3). Samples were tempered at 293 K and occasionally shaken. Establishment of equilibrium was studied by measuring the refractive index and took about 30 days.

The X-ray data collections were carried out on an Enraf–Nonius CAD4-MACH III four-circle diffractometer (Mo*Kα* radiation, graphite monochromator). The intensity was corrected for the Lorentz-polarization factor. The positions of the nonhydrogen atoms were determined using direct methods (SIR-92 (Ref. 4)), and the hydrogen atoms were localized on differential Fourier maps. The thermal parameters for the nonhydrogen atoms were refined anisotropically and, for the hydrogen atoms, isotropically. Refinement of the coordinates and the thermal parameters was carried out by the least squares method using the SHELX 97 program (5). The basic crystallographic data and the details of the measurement and refinement are summarized in Table 1. A list of the observed and calculated structural factors and the anisotropic displacement factors are available from the authors upon request.

IR spectra were measured on a Mattson Genesis FTIR spectrometer. Measurement was carried out at laboratory temperature by the diffuse reflectance method (DRIFTS)

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0022-4596/00 $35.00

TABLE 1
Basic Crystallographic Data, Data Collection, and Refinement Parameters of $PipzSeO_4.H_2O$ and $DmpipzSeO_4.2H_2O$

Empirical formula	$C_4H_{14}N_2O_5Se$	$C_6H_{20}N_2O_6Se$
Formula weight	249.13	295.20
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	monoclinic, $P2_1/n$	triclinic, $P\bar{1}$
Unit cell dimensions	$a = 6.4586(8)$ Å $\alpha = 90°$	$a = 6.7370(8)$ Å $\alpha = 92.435(9)°$
	$b = 11.8335(7)$ Å $\beta = 100.990(8)°$	$b = 7.9845(9)$ Å $\beta = 100.219(9)°$
	$c = 11.8065(7)$ Å $\gamma = 90°$	$c = 12.3802(12)$ Å $\gamma = 114.699(10)°$
Volume	885.80(13) $Å^3$	590.34(11) $Å^3$
Z, Calculated density	4, 1.868 g/cm^3	2, 1.661 g/cm^3
Absorption coefficient	4.23 mm^{-1}	3.19 mm^{-1}
$F(000)$	504	304
Crystal size	0.1 × 0.4 × 0.6 mm	0.5 × 0.6 × 1.0 mm
Theta range for data collection	2.46° to 24.98°	1.69° to 24.99°
Index ranges	$h(-7;7)$, $k(0;14)$, $l(-13;14)$	$h(-8;8)$, $k(-9;9)$, $l(-14;14)$
Reflections collected/unique	3021/1556 [R(int) = 0.0690]	2934/2071 [R(int) = 0.0248]
Completeness to $2\Theta = 24.98$	94.9%	99.7%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1556/0/166	2071/0/217
Goodness-of-fit on F^2	1.078	1.140
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0445$, $wR2 = 0.1115$	$R1 = 0.0311$, $wR2 = 0.0816$
R indices (all data)	$R1 = 0.0502$, $wR2 = 0.1159$	$R1 = 0.0326$, $wR2 = 0.0824$
Extinction coefficient	0.030(4)	0.184(9)
Largest diff. peak and hole	1.218 and − 2.161 e.$Å^{-3}$	1.023 and − 0.981 e.$Å^{-3}$
Number and Θ range of reflections for unit cell determination	25, 13.5° → 15°	25, 15° → 16°
Scan technique	Θ–2Θ	Θ–2Θ
Number of standard reflectoins	3	3
Standard reflections monitored in interval	60 min	60 min
Intensity variation	3%	decay 7%
Function minimized	$[\sum(w(F_0^2 - F_c^2))^2/\sum(w(F_0^2)^2]^{1/2}$	$[\sum(w(F_0^2 - F_c^2))^2/\sum(w(F_0^2)^2]^{1/2}$
Weighting scheme	$w = [\sigma^2(F_0^2) + 0.0825P^2 + 0.2115P]^{-1}$	$w = [\sigma^2(F_0^2) + 0.0636P^2 + 0.12P]^{-1}$
	$P = [F_0^2 + 2F_c^2]/3$	$P = [F_0^2 + 2F_c^2]/3$

(mixture of the sample with KBr in a ratio of approximately 1 : 20) in the 400–4000 cm^{-1} range (resolution 4 cm^{-1}, triangular apodization).

Raman spectra were recorded on a Bruker Equinox 55/S FTIR spectrometer with a FRA 106/S Raman module (2 cm^{-1} resolution, Blackman–Harris 4-Term apodization, 1064 nm NdYAG laser excitation, 300 mW power at the sample) in the 50–3600 cm^{-1} region.

DSC measurements were carried out on a Perkin–Elmer DSC 7 power-compensated apparatus in the 95–343 K temperature region (helium atmosphere). A heating rate of 10 K/min was selected to measure approximately 10 mg of finely ground sample placed in an aluminum capsule.

Thermoanalytical properties were studied using TG, DTG, and DTA recordings. The measurements were carried out on a Derivatograph OD-102 instrument from MOM Budapest. A static atmosphere (air) was used in a 293–533 K temperature range and at a heat rate of 10 K/min.

Determination of Se(VI) (6) was carried out by potentiometric titration of Br_2, released by the sample with KBr in HCl medium, by hydrazinium(2 +) sulfate. Organic elemental analysis was carried out on a Perkin–Elmer CHN Analyzer 2400 instrument.

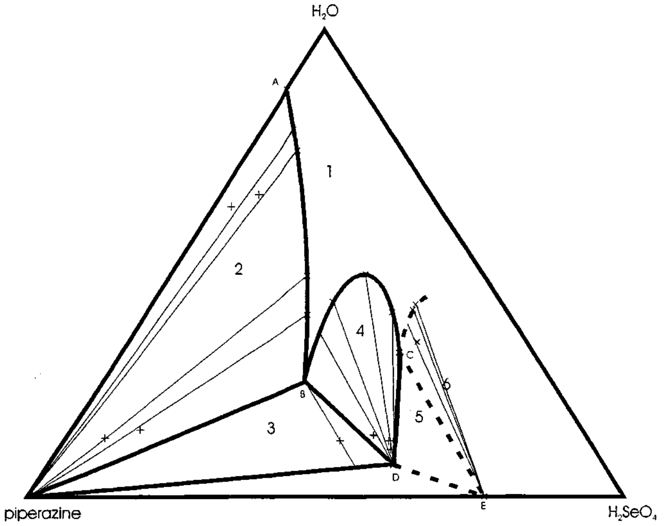

FIG. 1. Solubility diagram in the piperazine–H_2SeO_4–H_2O system at 293 K.

TABLE 2

Fractional Atomic Coordinates (for Non-H Atoms×10^4, for H Atoms×10^3) and Equivalent or Isotropic Displacement Factors (×10^3) with Standard Deviations in Brackets—PipzSeO$_4$.H$_2$O, $U_{eq}=1/3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j$

	x	y	z	U_{eq} (Å^2)
Se	1317(1)	1430(1)	7339(1)	3(1)
O(1)	2670(5)	2480(3)	7985(2)	0(1)
O(2)	340(4)	1790(2)	5992(2)	8(1)
O(3)	2874(5)	346(3)	7273(2)	41(1)
O(4)	− 563(5)	1093(3)	8003(3)	4(1)
N(12)	3115(6)	− 574(3)	5132(3)	1(1)
C(10)	3060(7)	394(4)	4316(3)	2(1)
C(11)	5160(8)	− 1195(4)	5281(4)	4(1)
N(22)	5366(6)	894(3)	0821(3)	2(1)
C(20)	6658(7)	792(4)	9902(4)	5(1)
C(21)	3234(7)	409(4)	10463(3)	4(1)
O(5)	1439(9)	2124(5)	2166(4)	1(1)
H(10A)	306(7)	9(4)	364(4)	5(11)
H(10B)	189(7)	77(4)	429(3)	0(10)
H(11A)	532(8)	− 158(4)	461(5)	7(15)
H(11B)	512(7)	− 189(4)	583(4)	1(12)
H(12A)	289(8)	− 39(5)	588(4)	7(13)
H(12B)	221(7)	− 94(4)	488(4)	7(13)
H(20A)	612(9)	128(4)	942(5)	7(14)
H(20B)	821(9)	120(4)	1031(5)	1(14)
H(21A)	250(7)	42(4)	1103(4)	9(11)
H(21B)	252(8)	92(5)	981(5)	0(14)
H(22A)	534(9)	188(6)	1093(5)	9(17)
H(22B)	588(6)	69(3)	1136(4)	4(10)
H(5A)	210(9)	264(6)	243(5)	4(19)
H(5B)	65(10)	214(6)	234(5)	0(20)

RESULTS AND DISCUSSION

Solubility Study

The solubility diagram in the H_2SeO_4–piperazine–H_2O system at 293 K is depicted in Fig. 1. In the figure we see the crystallization field of the initial piperazine (field 2), the crystallization field of piperazinium(2+) selenate monohydrate (field 4), and the incomplete crystallization field of piperazinium(2+) hydrogen selenate (field 6). Fields 3 and 5 correspond to equilibrium between the two solid phases and a solution with compositions corresponding to points B and C. Point B corresponds to a composition of 40.66% piperazine, 34.34% H_2SeO_4, and 25.00% H_2O, and point C corresponds to a composition of 21.71% piperazine, 47.72% H_2SeO_4, and 30.57% H_2O. The empty area in the diagram around the point depicting H_2SeO_4 was not studied experimentally. In this region, supersaturated viscous solutions are formed that do not allow phase separation. Piperazinium(2+) selenate monohydrate is congruently soluble. For further study, this substance was prepared by neutralization of an aqueous solution of piperazine by selenic acid solution. The solution was concentrated on a vacuum evaporator; the crystals obtained were collected under vacuum and recrystallized from water. The composition corresponded to the calculated values (found 31.75% Se, 11.05% N, 19.45% C, and 6.83% H_2O; calculated 31.70% Se, 11.24% N, 19.27% C, and 7.23% H_2O). It was not possible to isolate the expected piperazinium(2+) hydrogen selenate.

TABLE 3

Bond Lengths (Å) and Selected Angles (°)—PipzSeO$_4$.H$_2$O

Se–O(1)	1.624(3)	H(12A)–N(12)–H(12B)	105(5)
Se–O(2)	1.651(2)	N(12)–C(11)–C(10)^{vi}	109.6(4)
Se–O(3)	1.641(3)	N(12)–C(11)–H(11A)	112(3)
Se–O(4)	1.616(3)	N(12)–C(11)–H(11B)	109(3)
N(12)–C(11)	1.492(6)	C(10)^{vi}–C(11)–H(11A)	112(3)
N(12)–C(10)	1.493(6)	C(10)^{vi}–C(11)–H(11B)	114(3)
C(11)–C(10)^{vi}	1.496(6)	H(11A)–C(11)–H(11B)	99(4)
C(10)–H(10A)	0.87(5)	N(12)–C(10)–C(11)^{vi}	111.0(3)
C(10)–H(10B)	0.87(5)	N(12)–C(10)–H(10A)	106(3)
C(11)–H(11A)	0.93(5)	N(12)–C(10)–H(10B)	109(3)
C(11)–H(11B)	1.05(5)	C(11)^{vi}–C(10)–H(10A)	115(3)
N(22)–C(20)	1.495(5)	C(11)^{vi}–C(10)–H(10B)	107(3)
N(22)–C(21)	1.477(6)	H(10A)–C(10)–H(10B)	109(4)
C(20)–C(21)^{iii}	1.490(6)	C(21)–N(22)–C(20)	112.3(3)
C(20)–H(20A)	0.84(5)	C(20)–N(22)–H(22A)	100(3)
C(20)–H(20B)	1.13(6)	C(20)–N(22)–H(22B)	113(3)
C(21)–H(21A)	0.89(4)	C(21)–N(22)–H(22A)	113(3)
C(21)–H(21B)	1.01(6)	C(21)–N(22)–H(22B)	113(3)
		H(22A)–N(22)–H(22B)	105(4)
		N(22)–C(21)–C(20)^{iii}	111.1(4)
		N(22)–C(21)–H(21A)	112(3)
O(1)–Se–O(2)	109.12(15)	N(22)–C(21)–H(21B)	104(3)
O(1)–Se–O(3)	109.92(16)	C(20)^{iii}–C(21)–H(21A)	107(3)
O(3)–Se–O(2)	106.36(14)	C(20)^{iii}–C(21)–H(21B)	113(3)
O(4)–Se–O(1)	110.33(16)	H(21A)–C(21)–H(21B)	109(4)
O(4)–Se–O(2)	110.27(15)	C(21)^{iii}–C(20)–N(22)	110.5(4)
O(4)–Se–O(3)	110.75(18)	C(21)^{iii}–C(20)–H(20A)	120(3)
C(11)–N(12)–C(10)	111.5(3)	C(21)^{iii}–C(20)–H(20B)	116(3)
C(10)–N(12)–H(12A)	115(3)	N(22)–C(20)–H(20A)	103(4)
C(10)–N(12)–H(12B)	106(4)	N(22)–C(20)–H(20B)	103(3)
C(11)–N(12)–H(12A)	107(3)	H(20A)–C(20)–H(20B)	102(4)
C(11)–N(12)–H(12B)	111(4)	H(5A)–O(5)–H(5B)	106(8)

Hydrogen bonds

Donor-H	Donor...Acceptor	H...Acceptor	Donor-H...Acceptor
N(12)–H(12A)	N12...O3	H12A...O3	N12–H12A...O3
0.95(5)	2.784(4)	1.86(5)	164(5)
N(12)–H(12B)	N12...O2^{i}	H12B...O2^{i}	N12–H12B...O2^{i}
0.74(5)	2.771(5)	2.03(5)	172(5)
N(22)–H(22A)	N22...O2^{ii}	H22A...O2^{ii}	N22–H22A...O2^{ii}
1.17(7)	2.748(5)	1.57(7)	176(5)
N(22)–H(22B)	N22...O3^{iii}	H22B...O3^{iii}	N22–H22B...O3^{iii}
0.70(4)	2.745(5)	2.07(4)	163(4)
O(5)–H(5A)	O5...O4^{iv}	H5A...O4^{iv}	O5–H5A....O4^{iv}
0.77(7)	2.906(8)	2.15(7)	168(6)
O(5)–H(5B)	O5...O1^{v}	H5B...O1^{v}	O5–H5B....O1^{v}
0.58(6)	2.825(6)	2.25(6)	171(9)

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

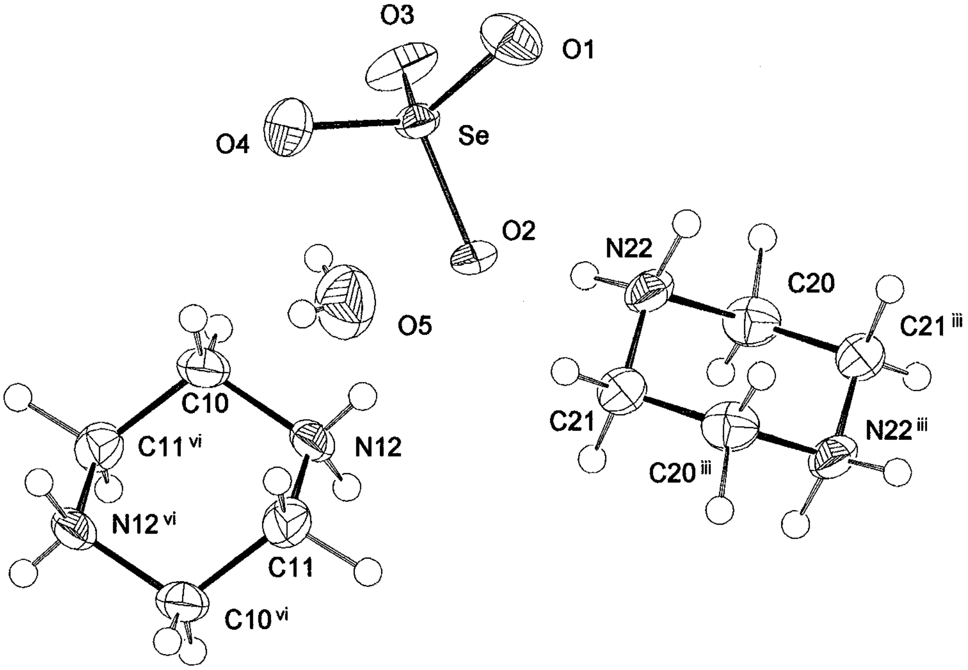

FIG. 2. Atom numbering of $PipzSeO_4.H_2O$.

In the same way, *N*,*N*′-dimethylpiperazinium(2+) selenate dihydrate was prepared without studying the corresponding solubility diagram. The composition of the substance corresponded to the calculated values (found 26.32% Se, 9.35% N, 24.71% C, and 13.08% H_2O; calculated 26.75% Se, 9.49% N, 24.40% C, and 12.21% H_2O).

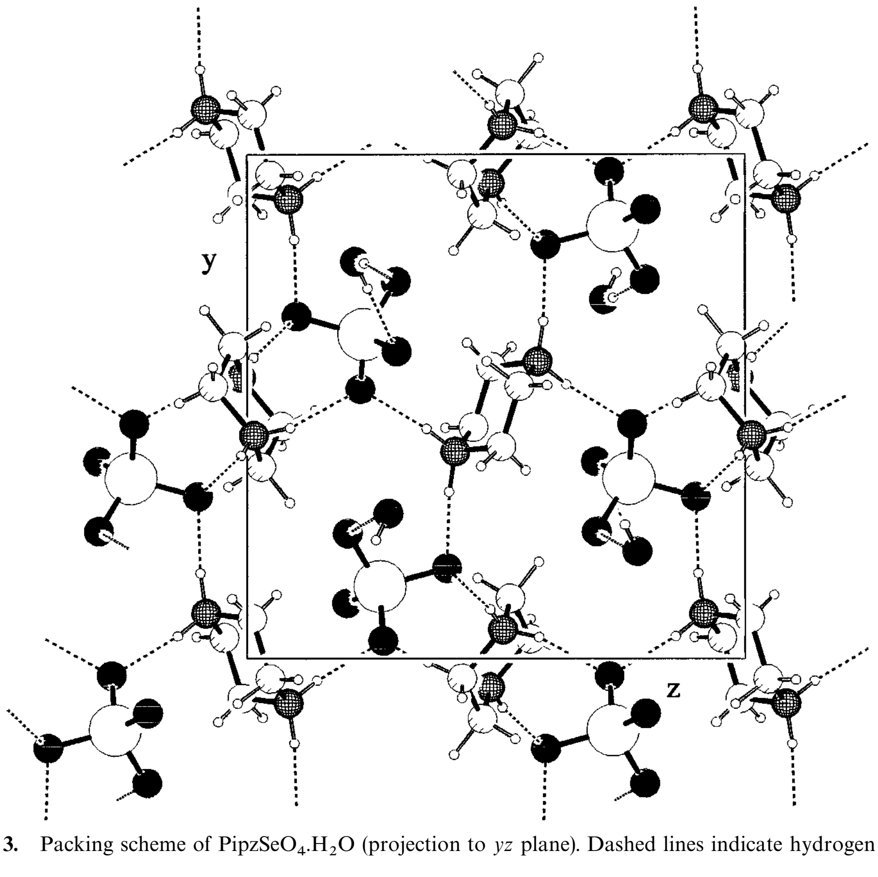

FIG. 3. Packing scheme of $PipzSeO_4.H_2O$ (projection to *yz* plane). Dashed lines indicate hydrogen bonds.

TABLE 4
Fractional Atomic Coordinates (for non-H atoms×10^4, for H atoms×10^3) and Equivalent or Isotropic Displacement Factors (×10^3) with Standard Deviations in Brackets—DmpipzSeO$_4$.2H$_2$O, $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$

	x	y	z	U_{eq} (Å^2)
Se	10745(1)	1417(1)	− 2466(1)	27(1)
O(1)	12094(5)	3438(3)	− 2827(2)	68(1)
O(2)	12416(5)	734(4)	− 1714(2)	63(1)
O(3)	8866(3)	1502(3)	− 1798(2)	39(1)
O(4)	9353(3)	− 85(3)	− 3588(2)	44(1)
N(10)	9047(4)	5182(3)	− 1168(2)	31(1)
C(10)	11413(5)	3846(4)	− 668(2)	37(1)
C(11)	12349(5)	4508(4)	321(3)	36(1)
C(14)	8138(7)	4529(5)	− 2163(3)	45(1)
N(20)	5053(4)	1078(3)	4097(2)	29(1)
C(20)	5445(5)	− 614(4)	4007(2)	32(1)
C(21)	4216(5)	1970(4)	4735(2)	32(1)
C(24)	6153(6)	2403(5)	3340(3)	51(1)
O(30)	8340(5)	3495(4)	5193(3)	56(1)
O(31)	13169(5)	1527(4)	580(2)	62(1)
H(10)	906(6)	− 627(5)	− 136(3)	42(9)
H(20)	385(6)	83(4)	395(3)	34(9)
H(10A)	1220(6)	− 374(4)	− 120(3)	40(8)
H(10B)	1129(5)	− 271(5)	− 50(3)	36(8)
H(11A)	1380(6)	− 357(5)	70(3)	36(9)
H(11B)	1244(6)	− 546(5)	18(3)	39(9)
H(14A)	660(8)	− 525(6)	− 235(4)	57(11)
H(14B)	866(7)	− 469(5)	− 274(4)	55(11)
H(14C)	836(6)	− 347(5)	− 208(3)	37(9)
H(20A)	500(5)	− 114(4)	330(3)	39(8)
H(20B)	705(6)	− 23(5)	424(3)	46(9)
H(21A)	454(6)	− 297(5)	470(3)	40(8)
H(21B)	263(6)	− 241(4)	452(3)	37(8)
H(24A)	575(6)	164(5)	261(3)	54(12)
H(24B)	768(8)	288(6)	356(3)	57(11)
H(24C)	584(7)	335(6)	342(4)	60(12)
H(30A)	885(6)	− 254(5)	548(3)	34(9)
H(30B)	834(7)	− 340(6)	447(4)	59(12)
H(31A)	1298(9)	108(7)	− 9(5)	83(15)
H(31B)	1257(8)	75(7)	86(4)	69(15)

TABLE 5
Bond Lengths (Å) and Selected Angles (°)—DmpipzSeO$_4$.2H$_2$O

Se–O(1)	1.615(2)	N(10)–C(14)–H(14C)	114(3)
Se–O(2)	1.617(2)	H(14A)–C(14)–H(14B)	106(4)
Se–O(3)	1.651(2)	H(14A)–C(14)–H(14C)	108(4)
Se–O(4)	1.644(2)	H(14B)–C(14)–H(14C)	108(3)
N(10)–C(10)	1.495(4)	N(10)–C(10)–C(11)	111.3(2)
N(10)–C(11)^{i}	1.490(4)	N(10)–C(10)–H(10A)	107(2)
C(10)–C(11)	1.496(4)	N(10)–C(10)–H(10B)	103(2)
N(10)–C(14)	1.489(4)	C(11)–C(10)–H(10A)	111(2)
C(14)–H(14A)	0.93(5)	C(11)–C(10)–H(10B)	114(2)
C(14)–H(14B)	0.88(4)	H(10A)–C(10)–H(10B)	111(3)
C(14)–H(14C)	0.80(4)	N(10)^{i}–C(11)–C(10)	111.1(2)
C(10)–H(10A)	0.90(3)	N(10)^{i}–C(11)–H(11A)	104(2)
C(10)–H(10B)	0.97(3)	N(10)^{i}–C(11)–H(11B)	108(2)
C(11)–H(11A)	0.97(4)	C(10)–C(11)–H(11A)	111(2)
C(11)–H(11B)	0.80(4)	C(10)–C(11)–H(11B)	113(2)
N(20)–C(20)	1.485(3)	H(11A)–C(11)–H(11B)	109(3)
N(20)–C(21)^{ii}	1.486(3)	C(20)–N(20)–C(21)^{ii}	110.3(2)
C(20)–C(21)	1.507(4)	C(20)–N(20)–C(24)	111.7(3)
N(20)–C(24)	1.491(4)	C(21)^{ii}–N(20)–C(24)	111.7(2)
C(24)–H(24A)	0.99(4)	N(20)–C(24)–H(24A)	106(2)
C(24)–H(24B)	0.92(5)	N(20)–C(24)–H(24B)	111(2)
C(24)–H(24C)	0.87(4)	N(20)–C(24)–H(24C)	108(3)
C(20)–H(20A)	0.89(4)	H(24A)–C(24)–H(24B)	106(3)
C(20)–H(20B)	0.98(4)	H(24A)–C(24)–H(24C)	122(4)
C(21)–H(21A)	0.91(4)	H(24B)–C(24)–H(24C)	105(4)
C(21)–H(21B)	0.96(4)	N(20)–C(20)–C(21)	110.5(2)
		N(20)–C(20)–H(20A)	110(2)
		N(20)–C(20)–H(20B)	108(2)
O(1)–Se(1)–O(2)	111.5(2)	C(21)–C(20)–H(20A)	110(2)
O(1)–Se(1)–O(4)	108.8(1)	C(21)–C(20)–H(20B)	110(2)
O(2)–Se(1)–O(4)	109.7(1)	H(20A)–C(20)–H(20B)	109(3)
O(1)–Se(1)–O(3)	109.1(1)	N(20)^{ii}–C(21)–C(20)	110.0(2)
O(2)–Se(1)–O(3)	110.9(1)	N(20)^{ii}–C(21)–H(21A)	108(2)
O(4)–Se(1)–O(3)	106.7(1)	N(20)^{ii}–C(21)–H(21B)	108(2)
C(14)–N(10)–C(11)^{i}	112.0(3)	C(20)–C(21)–H(21A)	110(2)
C(14)–N(10)–C(10)	111.0(2)	C(20)–C(21)–H(21B)	113(2)
C(11)^{i}–N(10)–C(10)	110.1(2)	H(21A)–C(21)–H(21B)	108(3)
N(10)–C(14)–H(14A)	108(3)	H(30A)–O(30)–H(30B)	106(4)
N(10)–C(14)–H(14B)	112(3)	H(31A)–O(31)–H(31B)	106(5)

Hydrogen bonds

Donor-H	Donor...Acceptor	H...Acceptor	Donor-H...Acceptor
N(10)–H(10)	N(10)...O(3)	H(10)...O(3)^{iii}	N(10)–H(10)...O(3)^{iii}
0.89(4)	2.675(3)	1.78(4)	175(4)
N(20)–H(20)	N(20)...O4^{iv}	H(20)...O4^{iv}	N(20)–H(20)...O4^{iv}
0.73(4)	2.676(3)	1.94(4)	178(4)
O(30)–H(30A)	O(30)...O(4)^{v}	H(30A)...O(4)^{v}	O(30)–H(30A)...O(4)^{v}
0.73(4)	2.809(4)	2.10(4)	162(4)
O(30)–H(30B)	O(30)...O(1)^{vi}	H(30B)...O(1)^{vi}	O(30)–H(30B)...O(1)^{vi}
0.90(5)	2.896(4)	2.01(5)	172(4)
O(31)–H(31A)	O(31)...O(2)	H(31A)...O(2)	O(31)–H(31A)...O(2)
0.86(6)	2.791(4)	1.96(6)	162(5)
O(31)–H(31B)	O(31)...O(3)^{vi}	H(31B)...O(3)^{vi}	O(31)–H(31B)...O(3)^{vi}
0.72(5)	2.877(4)	2.16(5)	174(5)

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

The deuterated compounds $(CH_2)_4(ND_2^+)_2.SeO_4^{2-}.D_2O$ and $(CH_2)_4(ND^+CH_3)_2.SeO_4^{2-}.2D_2O$ were prepared by repeated recrystallization of natural PipzSeO$_4$.H$_2$O and DmpipzSeO$_4$.2H$_2$O, respectively, from D$_2$O (99%) in a dessicator over KOH.

Crystal Structure of Piperazinium (2+) Selenate Monohydrate

The fractional coordinates of atoms are given in Table 2, and selected bond lengths and angles are given in Table 3. The atom numbering can be seen in Fig. 2 and the packing

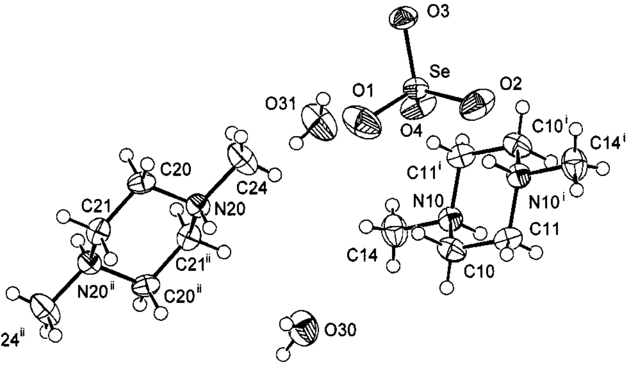

FIG. 4. Atom numbering of DmpipzSeO_4.2H_2O.

scheme is depicted in Fig. 3 (PLATON software (7)). The crystal structure of piperazinium(2+) selenate monohydrate consists of piperazinium cations, selenate anions, and water molecules interconnected by hydrogen bonds of the N–H...O and O–H...O type with lengths of 2.75 to 2.91 Å (see Table 3). The piperazinium(2+) cations adopt a chair conformation and are arranged in the structure roughly plane parallel above one another. The slightly deformed tetrahedral SeO_4^{2-} ions exhibit an Se–O bonding distance in the range from 1.616 to 1.651 Å (see Table 3). Different bond length Se–O are due to different hydrogen acceptor behavior: longer bonds are due to the fact that the O-atoms act twice as H-acceptor since in the shorter bonds oxygen acts just once as H-acceptor (8).

Crystal Structure of N,N′-Dimethylpiperazinium(2+) Selenate Dihydrate

The fractional coordinates of the atoms are given in Table 4 and selected bond lengths and angles are given in Table 5. The atom numbering can be seen in Fig. 4 and the packing scheme is depicted in Fig. 5. The asymmetric unit contains the *N,N′*-dimethylpiperazinium(2+) cation in the chair conformation, the selenate anion, and two water molecules. These structural units are interconnected by a system of hydrogen bonds of the N–H...O and O–H...O type with lengths of 2.68 to 2.90 Å (see Table 5). The selenate ions are somewhat deformed in the crystal structure—bonding angles in the range 106.7 to 111.5° and Se–O bonding distances of 1.615 to 1.651 Å (see Table 5).

Vibrational Spectra

Detailed interpretation of the vibrational spectra is based on an earlier study of piperazine (9–11), *N,N′*-dimethylpiperazine (12–14) and selenate anion (15) and is also consistent with the results obtained for similar compounds with selenious acid (16). The IR spectra of the deuterates were measured in order to confirm this interpretation. Standard correlation methods (17) were used for more detailed study of the expected vibrational features of the SeO_4^{2-} groups. The results obtained are presented in Tables 6 and 8. The vibrational spectra of piperazinium(2+) selenate monohydrate are depicted in Fig. 6. The wavenumbers of the observed bands are given in Table 7. The spectra of

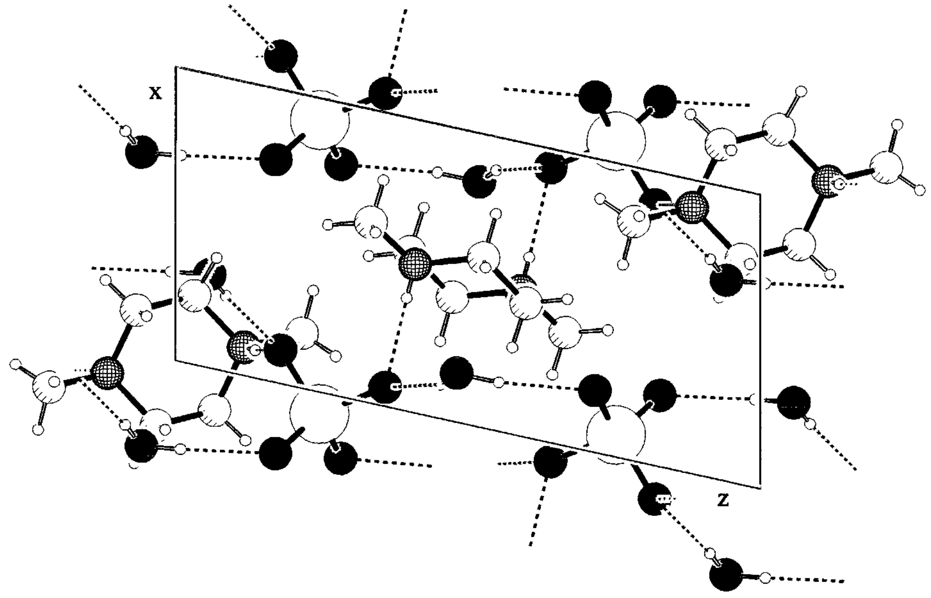

FIG. 5. Packing scheme of DmpipzSeO_4.2H_2O (projection to *xz* plane). Dashed lines indicate hydrogen bonds.

TABLE 6
Correlation Analysis of SeO_4^{2-} Internal Modes in $PipzSeO_4.H_2O$ Crystal

Free ion modes	Degrees of freedom	Free ion symmetry T_d	Site symmetry C_1	Factor group symmetry C_{2h}	Vibration modes	Activity IR	Activity Raman
ν_1	4	$\mathbf{A}_1$	**A**	$\mathbf{A}_g$	$\nu_1, 2\nu_2, 3\nu_3, 3\nu_4$		$\alpha_{xx}, \alpha_{yy}, \alpha_{zz}, \alpha_{xy}$
ν_2	4	**E**		$\mathbf{A}_u$	$\nu_1, 2\nu_2, 3\nu_3, 3\nu_4$	z	
ν_3	4	$\mathbf{F}_2$		$\mathbf{B}_g$	$\nu_1, 2\nu_2, 3\nu_3, 3\nu_4$		α_{xz}, α_{yz}
ν_4	4	$\mathbf{F}_2$		$\mathbf{B}_u$	$\nu_1, 2\nu_2, 3\nu_3, 3\nu_4$	x, y	

N,*N*′-dimethylpiperazinium(2+) selenate dihydrate are depicted in Fig. 7, and the wavenumbers of the maxima are given in Table 9.

Broad, medium- to strong-intensity bands in the IR spectra in the 3600–3200 cm^{-1} region are characteristic of the stretching vibrations of the O–H groups of water mol-

TABLE 7
FTIR and FT Raman Spectra $PipzSeO_4.H_2O$

Assignment	IR	Raman (peak intensity)	Assignment	IR	Raman (peak intensity)
ν O–H...O	3445m		δ N–C–H, δ C–C–H	1214w	1214(3)
	3380m			1197sh	
	3250s				1168(3)
ν CH_2	3013s	3017(22)	ω CH_2, ρ NH_2	1087s	
		3004(17)		1061m	1062(10)
		2974(31)			1046(19)
ν N–H...O		2928(7)	γ N–H...O	1010m	
		2891(4)		975m	
	2818s	2820(5)		952m	
	2756s	2765(5)	ν_3 SeO_4^{2-}	908s	916(3)
	2620s	2660(3)		883s	889(19)
	2585m	2580(2)		870sh	862(21)
	2500m	2490(3)	ν_1 SeO_4^{2-}	840m	
	2415m		ν_1 SeO_4^{2-}, νCN, δCNC, δNCH	822m	828(100)
?	2360m		ν_1 SeO_4^{2-}		816(30)
	2300m			808m	804(18)
	2190m		γ O–H...O	741w	
	2080w			661w	
	2005w		δCNH, δCCH, δNCC	582m	
	1900w			572m	
	1798w		?	529m	
	1745w			504w	
δ NH_2, δ H_2O	1655m	1657(1)	δNCC, δCCH, δCNC	462w	468(12)
δ NH_2	1611m	1613(2)			457(7)
	1560m				448(9)
sciss CH_2	1461s	1478(6)	ν_4 SeO_4^{2-}	428m	427(9)
		1452(9)		418w	416(16)
	1440s	1436(6)		411w	
twi CH_2		1415(6)			389(11)
	1389m		ν_2 SeO_4^{2-}		354(15)
	1381m				334(14)
δCNH, δNCH, δCCH	1330m		external modes		170(3)
	1317m	1317(14)			123(7)
?	1267w				85(20)

Note. Abbreviations used in Tables 7 and 9: s, strong; m, medium; w, weak; b, broad; sh, shoulder; ν, stretching; δ, deformation or in-plane bending; γ, out-of-plane bending; ω, wagging; ρ, rocking; sciss, scissoring; twi, twisting; τ, torsional; $_s$, symmetric; $_{as}$, asymmetric.

TABLE 8
Correlation Analysis of SeO_4^{2-} Internal Modes in $DmpipzSeO_4.2H_2O$ Crystal

Free ion modes	Degrees of freedom	Free ion symmetry T_d	Site symmetry C_1	Factor group symmetry C_i	Vibration modes	Activity	
						IR	Raman
ν_1	2	A_1		A_g	ν_1, $2\nu_2$, $3\nu_3$, $3\nu_4$		all α
ν_2	2	E	A				
ν_3	2	F_2		A_u	ν_1, $2\nu_2$, $3\nu_3$, $3\nu_4$	x, y, z	
ν_4	2	F_2					

ecules connected by weak hydrogen bonds in crystals. It is apparent from the crystal structures that these hydrogen bonds are of the O–H...O type with lengths of 2.79–2.91 Å. The position of the band at 3250 cm^{-1} in the spectrum of $PipzSeO_4.H_2O$ is rather surprising because, on the basis of the correlation curves (18) between the wavenumber of the ν O–H vibration and the length of the hydrogen bond, the band corresponding to these H-bonds could be expected to be located at 3400–3500 cm^{-1}. The stretching vibrations of the N–H groups which participate in cation–anion hydrogen bonds (N–H...O type with lengths of 2.68–2.79 Å) appear in the IR spectra as very broad, medium- to strong-intensity bands in the 2850–2000 cm^{-1} region. The position of the center of this band ($\sim$ 2400 cm^{-1}) in the spectrum of $DmpipzSeO_4.2H_2O$ fully corresponds to the conclusions in the study of the dependence of the wavenumber of the ν N–H vibration on the length of the hydrogen bond N–H...O (19). In $PipzSeO_4.H_2O$, in contrast to expecta-

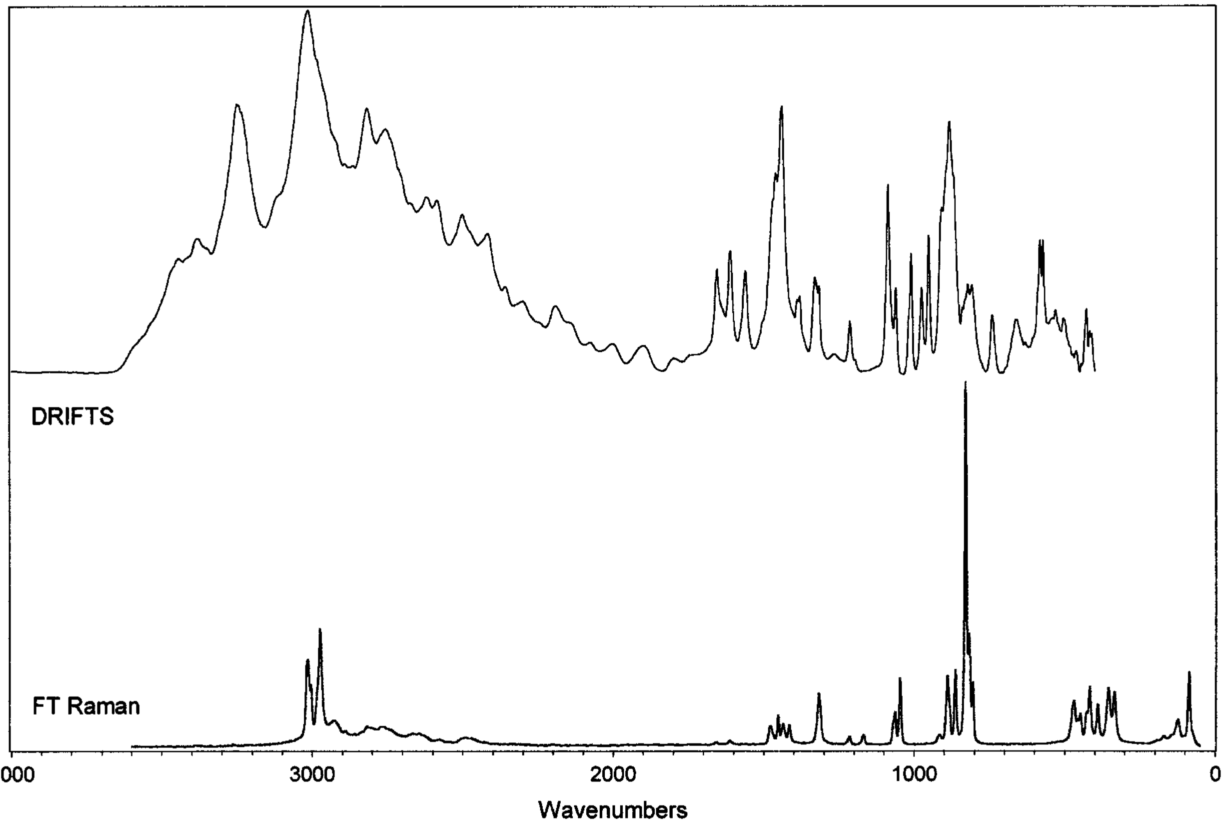

FIG. 6. FTIR (DRIFTS) and FT Raman spectra of $PipzSeO_4.H_2O$.

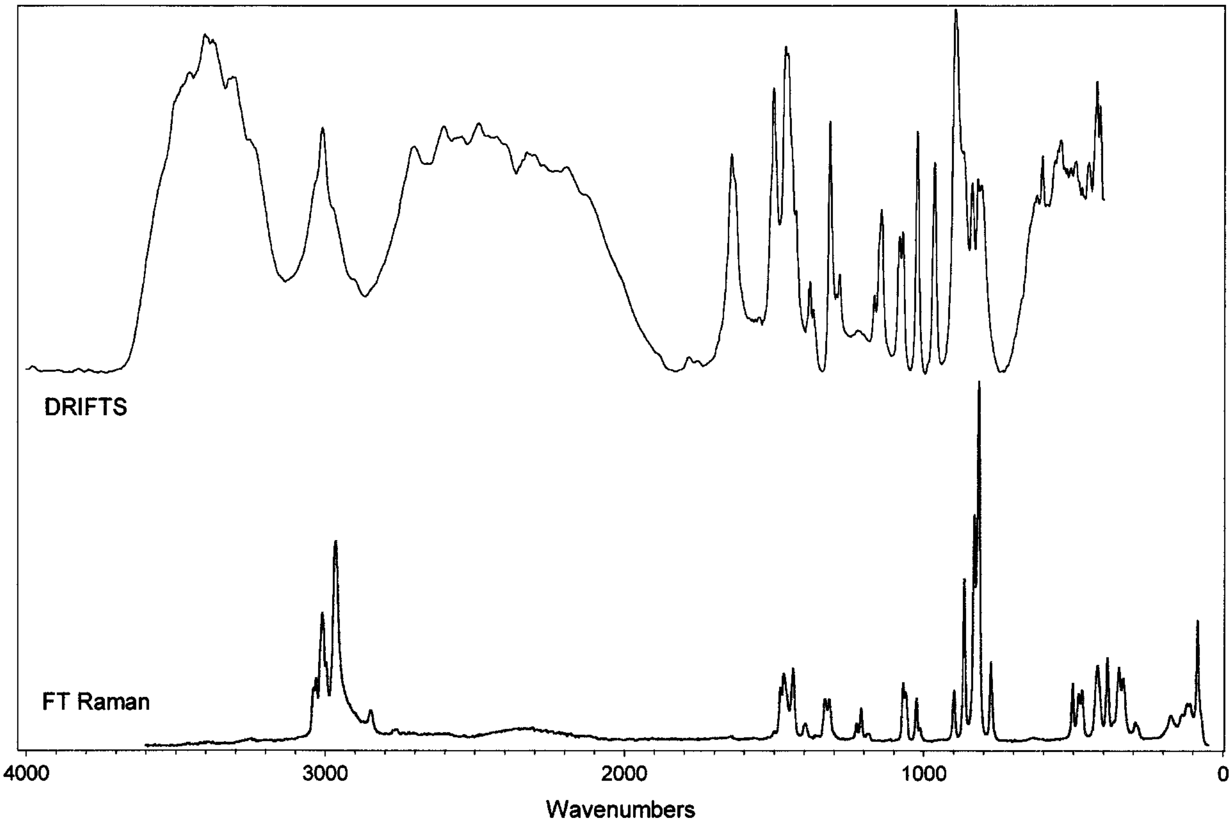

FIG. 7. FTIR (DRIFTS) and FT Raman spectra of $DmpipzSeO_4.2H_2O$.

tions, the position of the band maximum is shifted by about 300 cm^{-1} to higher wavenumbers (~ 2800 cm^{-1}). The presence of subbands of the ν O–H...O and ν N–H...O vibrations is probably a result of interactions with overtones and combination bands. The two weak bands at 741 and 661 cm^{-1} in the IR spectra of $PipzSeO_4.2H_2O$ can be assigned to manifestations of out-of-plane O–H...O bending vibrations. In the case of $DmpipzSeO_4.2H_2O$, these bands are apparently overlapped by the stretching vibrations of the selenate anion. The bands in the 1080–950 cm^{-1} region can be assigned to similar γ N–H...O vibrations. Corresponding shifts of all the bands of the stretching and out-of-plane bending vibrations occur in the spectra of the deuterated compounds.

Manifestations of the deformation vibrations δ H_2O are visible in the 1660–1640 cm^{-1} region, where they overlap with the bands of the deformation vibrations of the NH^+ and NH_2^+ groups. The bands of these types of vibrations are sensitive to deuteration, as expected.

A number of bands visible in the 3040–2970 cm^{-1} interval (especially in the Raman spectra) are characteristic for the stretching vibrations of the CH_2 and CH_3 groups. Manifestations of deformation vibrations of these groups are localized in the 1480–1370 cm^{-1} region.

The bands of the deformation vibrations of the piperazine or dimethylpiperazine skeleton can be observed below about 1330 cm^{-1}. In this region the bands of the stretching vibrations of ν C–N can also be readily differentiated as can the vibration bands of the selenate anion. Similar to the vibration bands of the CH_2 and CH_3 groups, all of these bands have low sensitivity to exchange of the acidic hydrogens for deuterium atoms, and any changes observed (especially in their shape and intensity) are primarily a consequence of superposition with the vibration bands that are sensitive to this partial deuteration.

For the internal vibrations of the selenate anion in the spectra of $PipzSeO_4.H_2O$, the observed factor group splitting is comparable to the conclusions of correlation analysis (see Table 6). Conditions in the region of the ν_1 vibration is further complicated by overlapping with the mixed vibration ν CN, δCNC, δNCH. In contrast to expectations, the spectra of $DmpipzSeO_4.2H_2O$ (see Table 8) exhibited a smaller splitting of the bands of the degenerate vibrations. The splitting of the band of the totally symmetric ν_1 vibration is also surprising.

Manifestations of external modes were also found in the Raman spectra of both compounds in the region under 200 cm^{-1}.

TABLE 9
FTIR and FT Raman Spectra of $DmpipzSeO_4.2H_2O$

Assignment	IR	Raman (peak intensity)	Assignment	IR	Raman (peak intensity)
ν O–H...O	3460s		δ C–C–H, δ N–C–H		1209(9)
	3400s				1185(2)
	3380s		ν C–N, δ C–C–H	1166w	
	3310s			1142m	
	3250m		γ N–H...O, ν CC, ν CN,	1082m	
ν C–H	3040sh	3040(14)	δ NCH	1070m	1069(16)
		3031(17)			1061(14)
	3010s	3011(34)	δN–C–H, δC–C–H, νC–N	1021m	1024(12)
		2998(21)			1012(4)
	2975sh	2966(53)	δ N–C–H, δ C–C–H	964m	
?	2905sh	2848(8)	ν_3 SeO_4^{2-}	895s	899(14)
ν N–H...O	2705m	2765(3)		868m	865(46)
	2605s		ν_1 SeO_4^{2-}	838m	832(63)
	2545m			819m	815(100)
	2490s		ν C–N	807m	776(23)
	2430m		?	623m	
	2330m	2330(3)		605m	
	2195m			553m	
	2130sh		δ C–N–C, δ N–C–C		502(16)
?	1785w			493m	482(13)
	1758w			470m	471(14)
δ NH, δ H_2O	1642m	1641(1)	δ C–N–C	449m	
δ NH	1550w		ν_4 SeO_4^{2-}	421s	419(20)
	1502s	1500(3)		412s	
δ_{as} CH_3, δ CH_2		1479(15)	δ C–N–C, δ N–C–C		387(23)
	1463s	1469(18)	ν_2 SeO_4^{2-}		348(20)
	1456s				333(17)
	1428m	1437(20)	δ C–N–C, δ N–C–C		293(5)
δ_s CH_3, twi CH_2	1381w	1396(5)	τ CH_3		174(7)
	1370w		external modes		138(8)
δ N–C–H, δ C–C–H		1331(12)			120(11)
	1315s	1316(12)			110(11)
	1282w				85(35)
?	1222wb	1224(5)			

Note. See Table 7 for definitions of abbreviations.

Thermal Behavior

At a temperature of 303 K, piperazinium(2+) selenate monohydrate loses water of crystallization, up to a temperature of 533 K no thermal effect is observed and above this temperature it decomposes. *N*,*N*′-dimethylpiperazinium (2+) selenate dihydrate is thermally stable to heating to a temperature of 358 K, at which 0.5 of a water molecule is lost. The loss of the remaining 1.5 water molecules occurs at 408 K and the substance completely decomposes at 448 K, accompanied by a huge exo-effect with a maximum at 483 K.

Study of both the compounds by the DSC method was carried out in the temperature interval 95–343 K; no effect that would correspond to a phase transition was observed. As the point groups of both the test compounds do not correspond to any of the 10 polar crystallographic classes and a phase transition to a polar group has not been found, these two compounds cannot exhibit ferroelectric properties in the temperature interval 95–343 K. Similarly, no phase transition was found that would lead at elevated temperature to the formation of a phase with high proton conductivity. The possibility of increased proton conductivity of the test substances at laboratory temperature will be the subject of a future physical study.

ACKNOWLEDGMENTS

This study was carried out with financial assistance from the Grant Agency of the Czech Republic, Grant 203/98/1198, and the Grant Agency of Charles University of Prague, Grant 13/1998/B CH.

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