

Supplementary materials

Semi-organic salts of aniline with inorganic acids: prospective materials for the second harmonic generation

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Table S1: Selected bond lengths [Å] and angles [°] for **an₂SO₄**

Bond/Angle	Value	Angle	Value
S1-O1	1.467(4)	O1-S1-O4	108.8(2)
S1-O2	1.452(3)	O2-S1-O3	109.9(2)
S1-O3	1.485(4)	O2-S1-O4	111.1(2)
S1-O4	1.463(2)	O3-S1-O4	108.7(2)
N1-C1	1.442(4)	N1-C1-C2	120.3(5)
N2-C7	1.451(4)	N1-C1-C6	119.0(5)
C1-C2	1.362(8)	C2-C1-C6	120.7(4)
C1-C6	1.391(8)	C1-C2-C3	118.6(5)
C2-C3	1.397(7)	C2-C3-C4	120.5(6)
C3-C4	1.37(1)	C3-C4-C5	119.8(5)
C4-C5	1.35(1)	C4-C5-C6	121.2(6)
C5-C6	1.365(7)	C1-C6-C5	119.2(5)
C7-C8	1.376(9)	N2-C7-C8	119.3(5)
C7-C12	1.359(8)	N2-C7-C12	119.2(5)
C8-C9	1.391(7)	C8-C7-C12	121.5(4)
C9-C10	1.38(1)	C7-C8-C9	118.9(5)
C10-C11	1.37(1)	C8-C9-C10	120.2(6)
C11-C12	1.389(7)	C9-C10-C11	119.7(5)
O1-S1-O2	110.4(2)	C10-C11-C12	120.7(6)
O1-S1-O3	107.9(2)	C7-C12-C11	119.1(6)

Hydrogen bonds				
D-H...A	d (D-H)	d (A...H)	d (D...A)	<(DHA)
N1-H1A...O1 ^a	0.87	1.92	2.747(6)	159
N1-H1B...O4 ^b	0.87	1.85	2.713(4)	173
N1-H1C...O3	0.87	1.84	2.696(6)	168
N2-H2A...O1	0.87	2.09	2.887(5)	153
N2-H2A...O3 ^c	0.87	2.42	2.921(5)	117
N2-H2B...O2 ^d	0.87	2.00	2.794(4)	150
N2-H2C...O3	0.87	2.60	2.946(5)	105
N2-H2C...O1 ^e	0.87	2.24	2.968(5)	141
N2-H2C...O4 ^e	0.87	2.40	3.152(7)	145

Note.

Equivalent positions: ^a $x, 1+y, z$; ^b $3/2-x, 1/2+y, -z$; ^c $3/2-x, -1/2+y, 1-z$; ^d $x, y, 1+z$; ^e $3/2-x, 1/2+y, 1-z$.

Abbreviations: A, acceptor; D, donor.

Table S2: Selected bond lengths [Å] and angles [°] for **an₂SeO₄**

Bond/Angle	Value	Angle	Value
Se1-O1	1.640(2)	O1-Se1-O4	108.7(1)
Se1-O2	1.627(1)	O2-Se1-O3	109.9(1)
Se1-O3	1.637(2)	O2-Se1-O4	112.07(7)
Se1-O4	1.637(1)	O3-Se1-O4	108.7(1)
N1-C1	1.445(2)	N1-C1-C2	119.9(3)
N2-C7	1.454(3)	N1-C1-C6	118.9(3)
C1-C2	1.384(4)	C2-C1-C6	121.2(2)
C1-C6	1.397(5)	C1-C2-C3	118.8(3)
C2-C3	1.389(4)	C2-C3-C4	120.5(3)
C3-C4	1.390(4)	C3-C4-C5	119.6(2)
C4-C5	1.375(4)	C4-C5-C6	121.3(3)
C5-C6	1.378(4)	C1-C6-C5	118.6(2)
C7-C8	1.383(5)	N2-C7-C8	119.5(3)
C7-C12	1.377(5)	N2-C7-C12	119.6(3)
C8-C9	1.383(3)	C8-C7-C12	121.0(2)
C9-C10	1.391(4)	C7-C8-C9	119.5(2)
C10-C11	1.394(5)	C8-C9-C10	119.4(3)
C11-C12	1.366(4)	C9-C10-C11	120.2(2)
O1-Se1-O2	109.0(1)	C10-C11-C12	119.7(3)
O1-Se1-O3	108.35(9)	C7-C12-C11	120.1(3)

Hydrogen bonds

D-H...A	d (D-H)	d (A...H)	d (D...A)	<(DHA)
N1-H1A...O1 ^a	0.87	1.88	2.723(3)	163
N1-H1B...O4 ^b	0.87	1.90	2.709(2)	154
N1-H1C...O3	0.87	1.93	2.696(3)	146
N2-H2A...O1	0.87	2.34	2.885(3)	121
N2-H2A...O3 ^c	0.87	2.24	2.918(3)	135
N2-H2B...O2 ^d	0.87	1.87	2.708(2)	160
N2-H2C...O3	0.87	2.18	2.931(3)	145
N2-H2C...O1 ^e	0.87	2.37	2.972(3)	126

Note.

Equivalent positions: ^a $x, 1+y, z$; ^b $3/2-x, 1/2+y, -z$; ^c $3/2-x, -1/2+y, 1-z$; ^d $x, y, 1+z$; ^e $3/2-x, 1/2+y, 1-z$.

Abbreviations: A, acceptor; D, donor.

Table S3: Selected bond lengths [Å] and angles [°] for **an₂SeO₄·2H₂O**

Bond/Angle	Value	Angle	Value	
Se1-O1	1.634(4)	O1-Se1-O1 ^a	109.4(2)	
Se1-O2	1.633(3)	O1-Se1-O2 ^a	108.8(2)	
Se1-O1 ^a	1.634(4)	O2-Se1-O1 ^a	108.8(2)	
Se1-O2 ^a	1.633(3)	O2-Se1-O2 ^a	109.6(2)	
N1-C1	1.478(7)	O1 ^a -Se1-O2 ^a	110.2(2)	
C1-C2	1.355(8)	N1-C1-C2	119.1(5)	
C1-C6	1.376(7)	N1-C1-C6	119.0(5)	
C2-C3	1.38(1)	C1-C2-C3	119.6(6)	
C3-C4	1.372(9)	C1-C6-C5	118.5(5)	
C4-C5	1.369(9)	C2-C1-C6	121.9(6)	
C5-C6	1.37(1)	C2-C3-C4	119.0(6)	
O3W-H1W	0.74(7)	C3-C4-C5	121.2(7)	
O3W-H2W	0.90(7)	C4-C5-C6	119.8(6)	
O1-Se1-O2	110.2(2)	H1W-O3W-H2W	107(6)	
Hydrogen bonds				
D-H...A	d (D-H)	d (A...H)	d (D...A)	<(DHA)
O3W-H1W...O1 ^b	0.74(7)	2.14(6)	2.863(6)	167(8)
O3W-H2W...O2 ^c	0.90(7)	1.94(7)	2.791(6)	157(5)
N1-H1A...O3W ^d	0.87	1.95	2.824(6)	176
N1-H1B...O2 ^d	0.87	1.91	2.758(6)	165
N1-H1C...O1	0.87	2.01	2.818(6)	154

Note.

Equivalent positions: ^a -x, y, 1/2-z; ^b x, -1+y, z; ^c 1/2+x, -1/2+y, z; ^d 1/2+x, 1/2+y, z

Abbreviations: A, acceptor; D, donor.

Table S4: FTIR and Raman spectra of an_2SeO_4

FTIR (cm^{-1})	Raman (cm^{-1})	Assignment	FTIR (cm^{-1})	Raman (cm^{-1})	Assignment
	3454 wb	ν (N-H...O)	1122 m		Ph (9b), ν CN
	3413 wb	ν (N-H...O)	1091 sh		Ph (5), ρ NH_3^+
3354 mb		ν (N-H...O)	1066 vw	1065 vw	Ph (17a)
	3200 vw	ν (N-H...O)	1040 vw		Ph (15)
	3071 s	ν CH	1027 vw	1031 m	Ph (18a)
	2980 w	?	1005 vw	1006 vs	Ph (12), ρ NH_3^+
	2927 w	?		993 sh	Ph (12), ρ NH_3^+
2733 mb		ν (N-H...O)	898 s	890 w	ν_3 SeO_4^{2-}
2604 mb	2625 w	ν (N-H...O)	857 sb	858 m	ν_3 SeO_4^{2-}
2098 wb		ν (N-H...O)		843 m	ν_3 SeO_4^{2-}
1802 vw		?	832 sb		?
1676 m		δ NH_3^+		822 s	ν_1 SeO_4^{2-}
1642 m		δ NH_3^+	793 m	794 s	Ph (11), ρ NH_3^+ , γ (N-H...O)
1633 sh		δ NH_3^+	749 s		Ph (11), ν CN
1619 m		δ NH_3^+	741 m		Ph (11), ν CN
1607 s	1605 m	Ph (8b), δ NH_3^+	736 s		Ph (11), γ (X-H...O)
1588 s		Ph (8a), δ NH_3^+	723 sh		Ph (4)
1573 sh		δ NH_3^+	689 m		Ph (4)
1531 s		δ NH_3^+	655 mb		?
1498 s	1500 vw	Ph (19a), δ_s NH_3^+	619 w	619 w	Ph (6b)
1462 m		Ph (19b)	615 w		Ph (6b), γ (X-H...O)
1367 sh		Ph (3), δ CCN	535 w		Ph (6a)
1345 w		Ph (14)	522 sh	523 w	Ph (6a)
1341 w		Ph (14)	494 m		δ CCC
1327 w		Ph (14), δ CCN	478 m		Ph (16b), ρ NH_3^+
1290 w		Ph (3), δ CCN	476 sh		Ph (16b), ρ NH_3^+
1244 wb		?	455 w		Ph (16a)
1224 w		Ph (9b), δ CCN	426 mb	418 w	Ph (16a), ν_4 SeO_4^{2-}
1213 w		Ph (9a)		391 w	?
1199 w	1205 m	Ph (9a)		359 m	ν_2 SeO_4^{2-}
1191 w		Ph (9a)		323 w	External mode
1173 sh	1176 m	Ph (9a)		134 sh	External mode
1163 w		?		116 vs	External mode
1153 m		Ph (9b), ρ NH_3^+			

Note: Abbreviations and symbols: vs, very strong; s, strong; m, medium; w, weak; b, broad; sh, shoulder; ν , stretching; δ , deformation or in-plane bending; γ , π , out-of-plane bending; ρ , rocking; ω , wagging; τ , torsion; s, symmetric; as, antisymmetric; atom X = O, N.

Table S5: FTIR and Raman spectra of **an₂SeO₄·2H₂O**

FTIR (cm ⁻¹)	Raman (cm ⁻¹)	Assignment	FTIR (cm ⁻¹)	Raman (cm ⁻¹)	Assignment
	3208 vw	v (X-H...O)	1152 w	1158 m	Ph (9b), ρ NH ₃ ⁺
	3067 s	v CH	1125 m		Ph (9b), v CN
3059 w	3059 s	v CH		1104 w	Ph (5), ρ NH ₃ ⁺
3049 w	3050 sh	v CH	1090 w	1087 w	Ph (5), ρ NH ₃ ⁺
	3014 vw	v CH	1066 w		Ph (17a)
	2984 w	?	1027 w	1026 m	Ph (18a)
2854 mb		v (X-H...O)	1004 w	1003 vs	Ph (12), ρ NH ₃ ⁺
2729 m		v (X-H...O)		969 w	Ph (10b), ρ NH ₃ ⁺
	2613 w	v (X-H...O)	899 s		v ₃ SeO ₄ ²⁻
2593 mb	2581 w	v (X-H...O)		881 m	v ₃ SeO ₄ ²⁻ , Ph (10b)
2361 w		v (X-H...O)	867 s		v ₃ SeO ₄ ²⁻
2097 mb		v (X-H...O)	840 sh		?
1694 w		v ₃ + v ₁ SeO ₄ ²⁻	832 s	834 vs	v ₁ SeO ₄ ²⁻
1678 w		δ NH ₃ ⁺	792 sh	797 m	Ph (11), ρ NH ₃ ⁺ , γ (X-H...O)
1648 w		δ NH ₃ ⁺ , δ H ₂ O	748 s		Ph (11), v CN
1631 sh	1629 m	δ NH ₃ ⁺	740 s	741 w	Ph (11), v CN
1617 sh		δ NH ₃ ⁺	736 s		Ph (11), γ (X-H...O)
1608 m	1609 m	Ph (8b), δ NH ₃ ⁺	722 sh		Ph (4)
1586 m		Ph (8a), δ NH ₃ ⁺	688 s	689 w	Ph (4)
1570 m		δ NH ₃ ⁺	620 m	617 m	Ph (6b)
1529 m		δ NH ₃ ⁺	615 sh		Ph (6b), γ (X-H...O)
1498 s	1500 w	Ph (19a), δ _s NH ₃ ⁺	535 m	534 w	Ph (6a)
1462 w	1462 w	Ph (19b)		525 w	Ph (6a)
	1380 vw	Ph (3), δ CCN	494 m		?
1341 w	1341 vw	?	479 m		Ph (16b), ρ NH ₃ ⁺
1327 w		Ph (14), δ CCN	455 mb	457 m	?
1292 w		Ph (3), δ CCN	423 mb	423 m	Ph (16a), v ₄ SeO ₄ ²⁻
1225 w	1224 m	Ph (9b), δ CCN	417 sh		Ph (16a), v ₄ SeO ₄ ²⁻
1214 w	1212 m	Ph (9a)		403 m	?
1198 w		Ph (9a)		335 mb	v ₂ SeO ₄ ²⁻
1189 w	1180 m	Ph (9a)		273 w	External mode
	1173 m	Ph (9a)		165 m	External mode

Table S6: FTIR and Raman spectra of **an₂SO₄**

FTIR (cm ⁻¹)			FT Raman (cm ⁻¹)			Assignment	FTIR (cm ⁻¹)			FT Raman (cm ⁻¹)			Assignment		
298 K	200 K	100 K	298 K	190 K	100 K		298 K	200 K	100 K	298 K	190 K	100 K			
3433 mb	3388 mb	3356 mb				v (N-H...O)				1173 m	1173 m	1174 m	Ph (9a)		
	3239 mb	3214 m				v (N-H...O)				1160 w	1160 w	1161 w	Ph (9b), ρ NH ₃ ⁺		
	3146 mb	3123 m				v (N-H...O)					1149 s		Ph (9b), ρ NH ₃ ⁺		
	3068 w	3070 w	3071 m	3071 m	3071 m	v CH, v (N-H...O)	1137 s	1139 sb	1136 s	1124 w	1122 w	1125 w	v ₃ SO ₄ ²⁻ , Ph (9b), v CN		
3060 w	3060 w	3061 w	3061 m	3061 m	3058 m	v CH, v (N-H...O)				1105 sh	1106 vw		Ph (5), ρ NH ₃ ⁺		
3050 m	3048 w	3046 w	3051 w	3050 w	3048 w	v CH, v (N-H...O)				1095 s			v ₃ SO ₄ ²⁻ , Ph (5), ρ NH ₃ ⁺		
			3025 w	3028 w	3028 w	v CH, v (N-H...O)	1089 s	1088 sb	1081 s		1089 w	1089 w	v ₃ SO ₄ ²⁻ , Ph (19b)		
			3017 w	3016 w	3015 w	v CH, v (N-H...O)	1069 s	1070 s	1071 s			1066 w	Ph (15)		
			2985 w	2986 w	2987 w	v (N-H...O)	1056 s		1057 s				Ph (17a), v ₃ SO ₄ ²⁻		
2894 sb						v (N-H...O), v (O-H...O)	1026 s	1025 s	1022 s	1027 m	1027 m	1027 m	Ph (18a), γ (O-H...O)		
2593 sb	2597 sb	2598 sb				v (O-H...O)	1003 w	1003 w	1003 w	1004 vs	1004 vs	1004 vs	Ph (12), ρ NH ₃ ⁺		
		2394 m				v (O-H...O)		981 w	982 w		979 s	982 s	v ₁ SO ₄ ²⁻ , Ph (10b), ρ NH ₃ ⁺		
	2125 w	2125 w				v (O-H...O)		976 w	977 w	976 s			v ₁ SO ₄ ²⁻ , Ph (10b), ρ NH ₃ ⁺		
2092 mb	2080 mb	2083 mb				?	973 sh	972 w	973 w				Ph (5)		
1947 w	1945 w	1947 w				?			968 w				Ph (17a)		
1873 w	1874 w	1874 w				?		906 m	907 m				?		
1746 w	1747 w	1747 w				?	905 m		904 sh				Ph (10b)		
	1688 w	1698 w				δ NH ₃ ⁺	843 w	842 w	844 w				Ph (1), γ (O-H...O)		
	1643 sh	1645 sh				δ NH ₃ ⁺					820 w	821 w	Ph (10a)		
	1627 m	1630 m	1629 w	1627 w	1628 w	δ NH ₃ ⁺				816 w	814 w	814 w	Ph (10a)		
	1617 m	1620 m				δ NH ₃ ⁺	803 w		801 vw	800 m	800 m	800 m	Ph (11), ρ NH ₃ ⁺		
		1615 sh				δ NH ₃ ⁺		746 s	747 s				Ph (11), v CN		
1608 s	1609 m	1609 m	1608 m	1609 m	1610 m	Ph (8b)	743 s	740 s	740 s		741 vw		Ph (11), v CN		
	1600 m	1602 m				Ph (8b), δ NH ₃ ⁺		736 s	736 s				Ph (11)		
1589 s	1589 m	1591 m		1600 sh	1598 w	Ph (8a), δ NH ₃ ⁺			721 w				Ph (4)		
1574 s	1575 sh	1566 s				δ NH ₃ ⁺	690 s		690 s				Ph (4)		
1555 s	1558 s	1559 sh				δ NH ₃ ⁺		688 s	688 s				Ph (4)		
	1533 m	1530 m				?	641 m	644 m	646 m	644 w	644 vw		Ph (6b)		
	1515 sh	1515 sh				?			618 sh	618 w	616 w	619 w	v ₄ SO ₄ ²⁻ , Ph (6b)		
1500 s	1499 s	1498 s	1500 vw	1500 vw		Ph (19a)	615 m	615 m	614 m				v ₄ SO ₄ ²⁻		
1462 m	1462 m	1462 m	1462 vw	1462 vw	1460 vw	Ph (19b)	607 m	605 m	604 m	607 sh	609 vw	610 vw	v ₄ SO ₄ ²⁻		
1405 vw						?	533 m	534 m	535 w	533 w	534 w	534 w	Ph (6a)		
1390 vw						Ph (3), δ CCN	528 w	527 w	526 w	515 vw	525 vw	524 vw	Ph (6a)		
1341 m	1340 m	1339 w				?	490 s	491 s	491 s		493 vw		v ₂ SO ₄ ²⁻		
1329 w	1329 w	1329 w				Ph (14), δ CCN	478 s	479 s	479 s	453 w	454 w	456 w	v ₂ SO ₄ ²⁻ , Ph (16b), ρ NH ₃ ⁺		
	1321 w	1322 w				Ph (14), δ CCN			466 w				Ph (16b), ρ NH ₃ ⁺		
1294 m	1293 m	1294 m				Ph (3), δ CCN		454 w	453 w				?		
		1229 w	1225 m	1227 m	1229 m	Ph (9b), δ CCN	445 m	445 m	446 m	443 w	445 w	445 w	?		
1216 w	1217 w	1217 w	1215 m	1217 m	1217 m	?	419 m	420 m	420 m				Ph (16a)		
		1209 w	1206 vw		1204 vw	Ph (9a)			402 m				External mode		
1191 w	1197 w	1197 vw		1189 sh		?						186 sh	External mode		
			1181 m	1180 m	1180 m	Ph (9a)						174 m	177 m	181 m	External mode

Figure S1 (Supporting Information): Atom numbering of isomorphous crystals of an_2SO_4 and an_2SeO_4 . Dashed lines indicate hydrogen bonds.

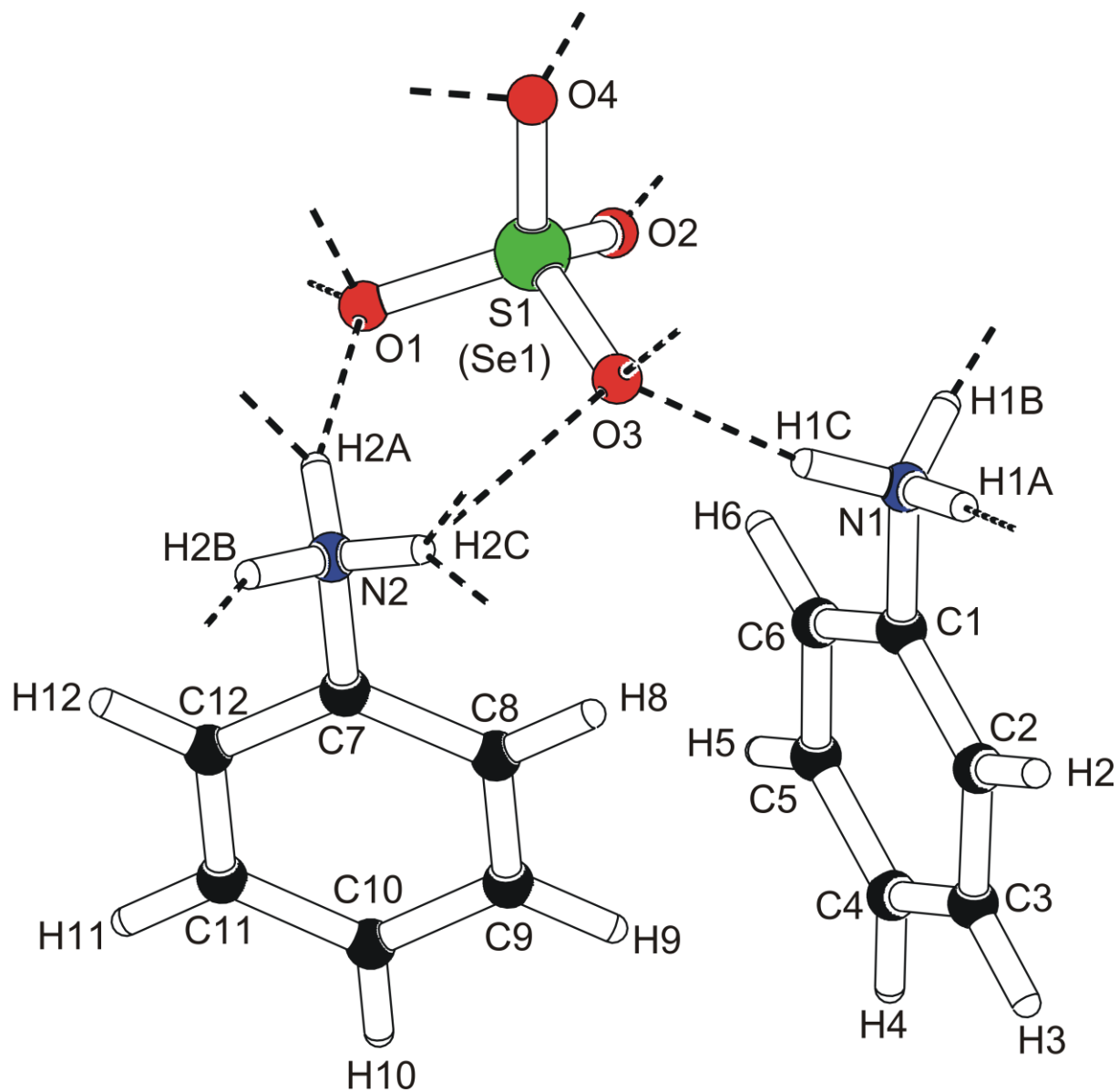


Figure S2 (Supporting Information): Atom numbering of $\text{an}_2\text{SeO}_4 \cdot 2\text{H}_2\text{O}$. The dashed lines indicate the hydrogen bonds.

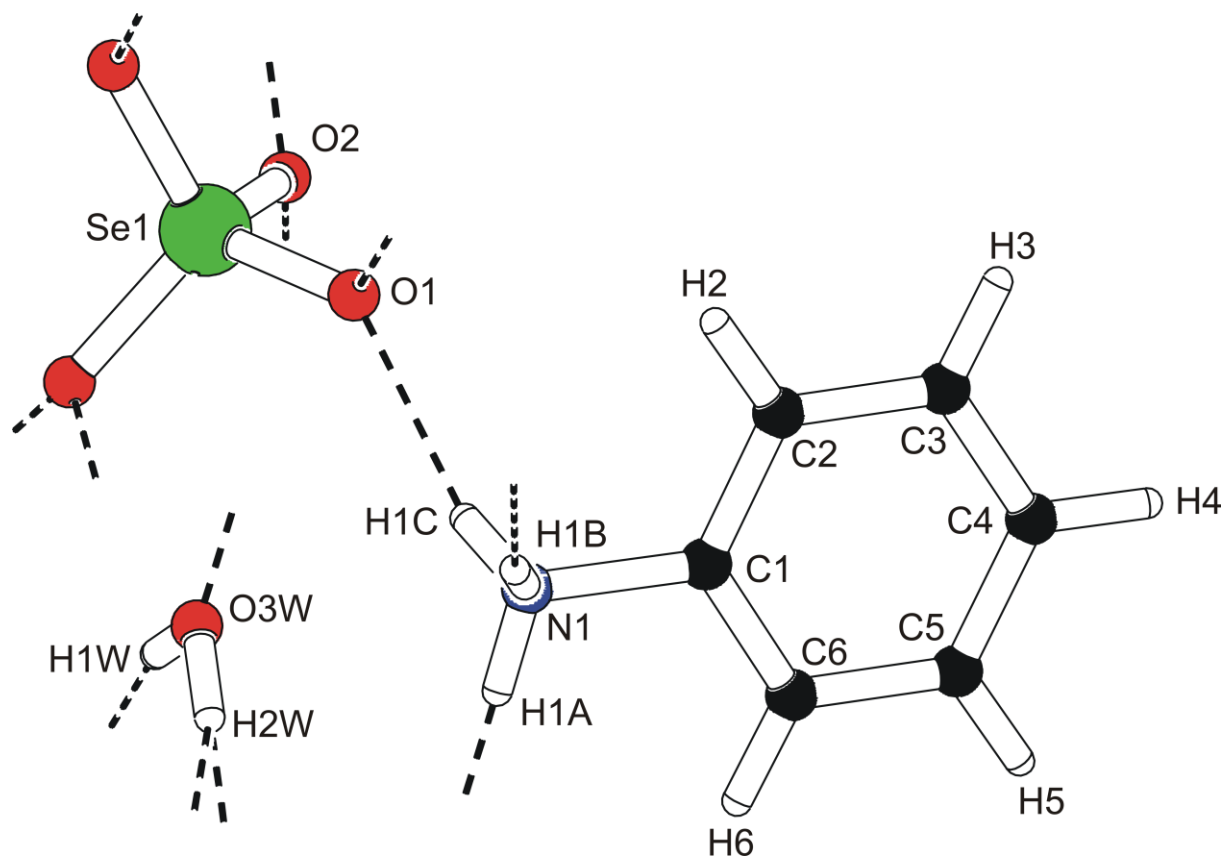


Figure S3 (Supporting Information): FTIR (nujol mull) and FT Raman spectra of **an₂SeO₄**.
Nujol bands are indicated by asterisks.

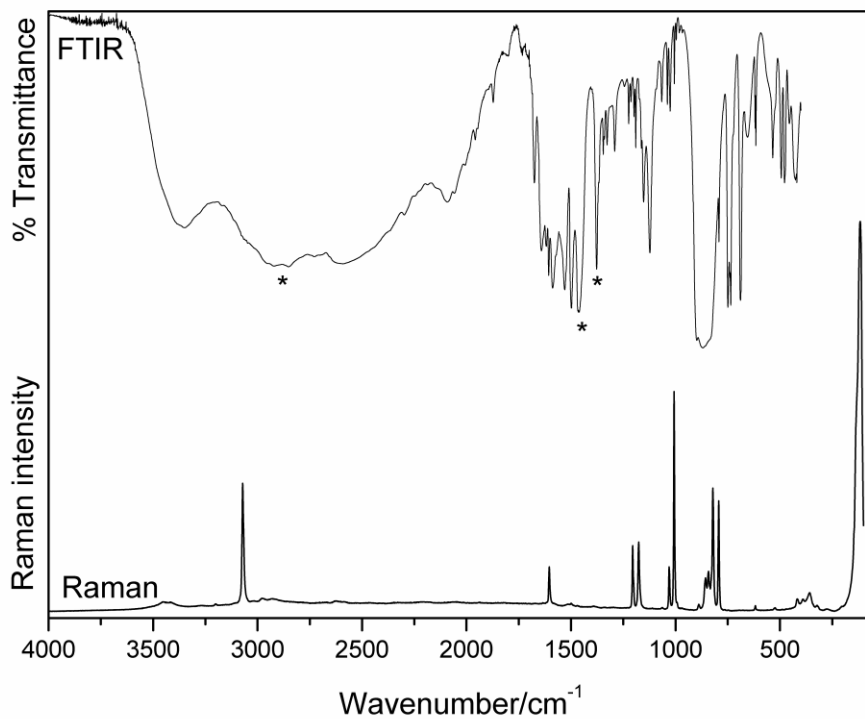


Figure S4 (Supporting Information): FTIR (nujol mull) and FT Raman spectra of $\text{an}_2\text{SeO}_4 \cdot 2\text{H}_2\text{O}$. Nujol bands are indicated by asterisks.

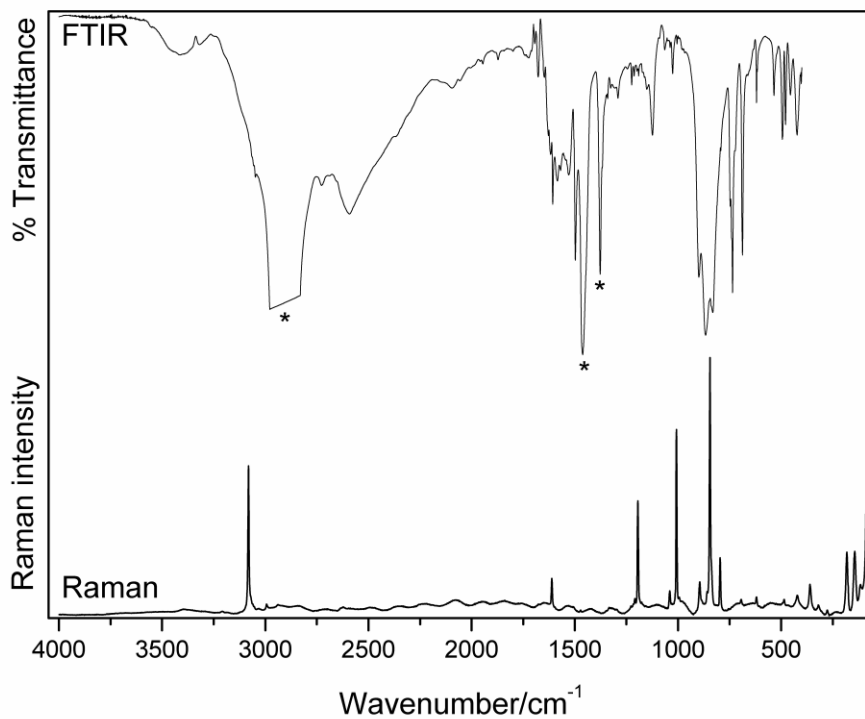


Figure S5 (Supporting Information): Correlation diagram of XO_4^{2-} internal modes ($X = \text{Se}, \text{S}$) in an_2SeO_4 and an_2SO_4 crystals.

Free ion modes	Degrees of freedom	Free ion XO_4^{2-} T_d	„Site“ symmetry C_1	Factor group C_2	Vibrational modes
ν_1	4	A_1		A (IR, Ra)	$2\nu_1, 4\nu_2, 6\nu_3, 6\nu_4$
ν_2	4	E		B (IR, Ra)	$2\nu_1, 4\nu_2, 6\nu_3, 6\nu_4$
ν_3	4	F_2			
ν_4	4	F_2			

Figure S6 (Supporting Information): Correlation diagram of the SeO_4^{2-} internal modes in $\text{an}_2\text{SeO}_4\cdot 2\text{H}_2\text{O}$ crystals.

Free ion modes	Degrees of freedom	Free ion SeO_4^{2-} T_d	Site symmetry		Factor group C_{2h}	Vibrational modes	
			C_2				
ν_1	4	A_1	—	A	—	A_g (Ra)	$\nu_1, 2\nu_2, 3\nu_3, 3\nu_4$
ν_2	4	E	—	A	—	A_u (IR)	$\nu_1, 2\nu_2, 3\nu_3, 3\nu_4$
ν_3	4	F_2	\diagdown	A B	\diagup	B_g (Ra)	$\nu_1, 2\nu_2, 3\nu_3, 3\nu_4$
ν_4	4	F_2	\diagdown	A B	\diagup	B_u (IR)	$\nu_1, 2\nu_2, 3\nu_3, 3\nu_4$

Figure S7 (Supporting Information): FTIR (nujol mull) spectra of **an₂SO₄** at the temperature 298 and 100 K. Nujol bands are indicated by asterisks.

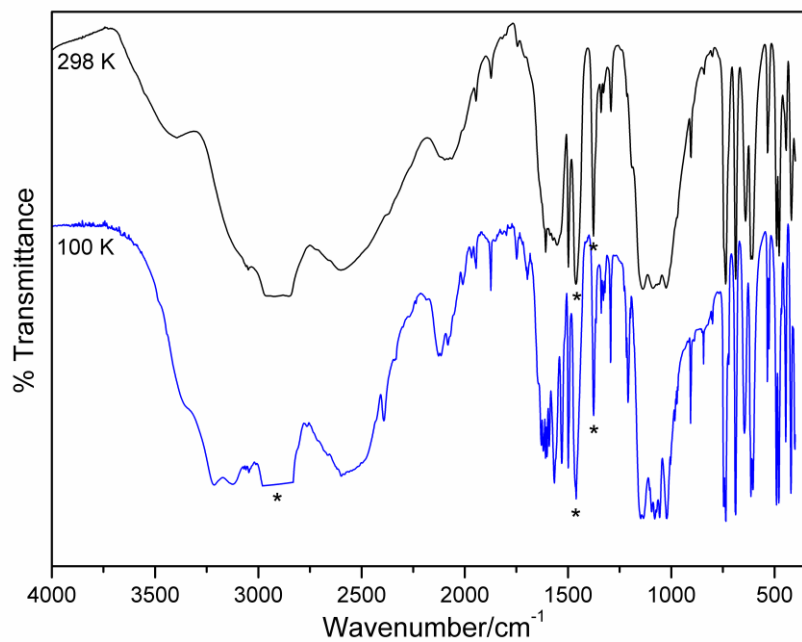


Figure S8 (Supporting Information): FT Raman spectra of **an₂SO₄** at the temperature 298 and 100 K.

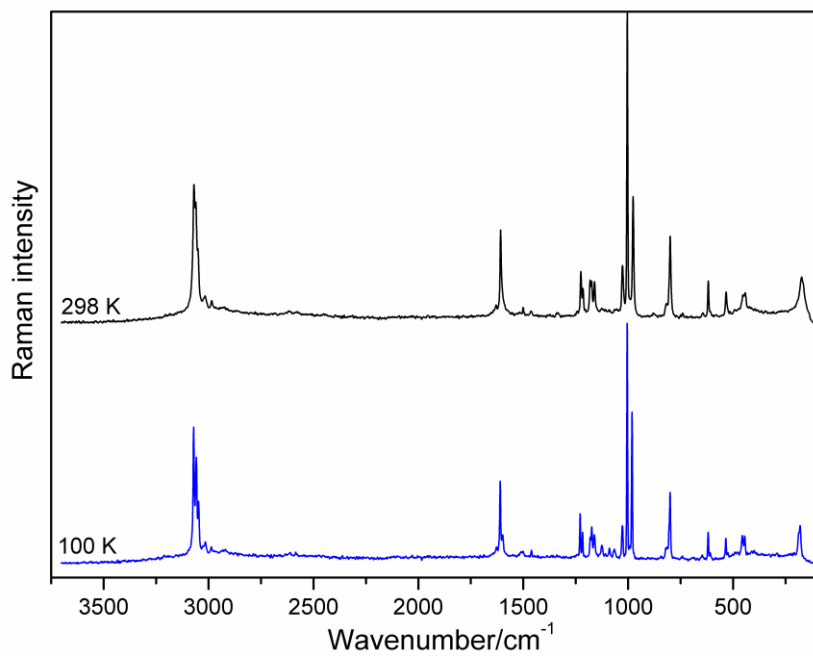


Figure S9 (Supporting Information): FT Raman spectra of **an₂SO₄** at different temperatures (region of deformation modes of amino group).

