Electronic Supplementary Material (ESI) for CrystEngComm

Supplementary Information

Molecular Crystals of 2-amino-1,3,4-thiadiazole with Inorganic Oxyacids – Crystal Engineering, Phase Transformations and NLO Properties

Irena Matulková[a,b], Jaroslav Cihelka[a], Michaela Pojarová[b], Karla Fejfarová[b], Michal Dušek[b], Ivana Císařová[a], Přemysl Vaněk[b], Jan Kroupa[b], Petr Němec[c], Naďa Tesařová[c] and Ivan Němec[a]

[a]*Faculty of Science, Department of Inorganic Chemistry, Charles University in Prague, Hlavova 8, 128 40 Prague 2, Czech Republic*
[b]*Institute of Physics ASCR, v.v.i., Na Slovance 2, 182 21 Prague 8, Czech Republic*
[c]*Department of Chemical Physics and Optics, Ke Karlovu 3, 121 16 Prague 2, Faculty of Mathematics and Physics, Charles University in Prague, Czech Republic*

* Corresponding author: Phone: +420 221 951 247; Fax: +420 221 951 253
E-mail address: matulkov@natur.cuni.cz

(**2-athdH_2PO_4**, **2-athd$_2HPO_3$** and **2-athd$_2ClO_4$**). All hydrogen atoms, except of H23 and H3, were placed into calculated positions (**2-athd$_2SeO_4H_2O$)**. The distance between H8 and O1 and H7 and O2 were fixed to 0.98 Å in the structure of **2-athdH_2PO_4.** The angle P-O-H was fixed with distance between P and H 2.30 Å (**2-athdH_2PO_4**). The bond lengths between hydrogen and nitrogen atoms were set to 0.87 Å (**2-athdH_2PO_4**, **2-athd$_2ClO_4$**, **2-athd$_2SeO_4H_2O$ -** H23 and H3 atoms and **2-athdClH_2O** – H3 atom). The isotropic temperature parameters of hydrogen atoms were calculated as 1.2 U_{eq} of the parent atom (**2-athdH_2PO_4**, **2-athd$_2ClO_4$**, **2-athdClH_2O** and **2-athd$_2SeO_4H_2O$**). The positions of hydrogen atoms of NH_2 group were refined in the initial stage but at the end their positions were fixed to ride with nitrogen atom (**2-athdH_2PO_4**). The distance between hydrogen atoms and nitrogen atoms was left unrestrained (**2-athdHSO_4** and **2-athdNO_3** – H3 atom) with exception of hydrogen atoms on N6 (**2-athd$_2ClO_4$**) and except of H3 (**2-athdClH_2O)**. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C-H in the range 0.93–0.98, N-H in the range 0.86–0.89 N-H to 0.86 O-H = 0.82 Å) and U_{iso}(H) (in the range 1.2–1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints (**2-athd$_2HPO_3$**). The hydrogen atoms, except H3 on N3, were constrained to ideal positions **2-athdNO_3**. Only the distance between O4 and H7 was fixed on 0.82 Å (**2-athdHSO_4**). The hydrogen atoms of water molecule could not be located from the difference Fourier map and therefore, were not modelled (**2-athd$_2SeO_4H_2O$)**. Because of the extinction the thermal parameters of oxygen atoms in selenate anion were restrained to be identical (**2-athd$_2SeO_4H_2O$)**.

TABLES

Table 1S. Experimental powder data for **2-athdNO$_3$**.

2 Theta (°)	d (Å)	Intensity (a.u.)	2 Theta (°)	d (Å)	Intensity (a.u.)
16.50	5.37	45	36.73	2.45	58
17.08	5.19	61	37.23	2.41	40
19.64	4.52	282	39.84	2.26	56
20.42	4.35	131	41.06	2.20	146
21.32	4.17	115	41.50	2.18	79
22.82	3.90	25	46.17	1.97	68
25.14	3.54	328	47.77	1.90	135
25.45	3.50	171	51.60	1.77	56
26.68	3.34	804	52.53	1.74	127
26.95	3.31	663	53.60	1.71	55
27.88	3.20	100000	54.84	1.67	93
28.96	3.08	479	55.39	1.66	29
33.14	2.70	47	56.16	1.64	48
33.65	2.66	92	57.52	1.60	2954
35.22	2.54	77	58.68	1.57	113

Table 2S. Experimental powder data for **2-athdClH$_2$O**.

2 Theta (°)	d (Å)	Intensity (a.u.)	2 Theta (°)	d (Å)	Intensity (a.u.)	2 Theta (°)	d (Å)	Intensity (a.u.)
11.77	7.51	2022	28.24	3.16	481	40.00	2.25	509
16.00	5.54	3981	28.79	3.10	2915	41.19	2.19	364
17.88	4.96	681	29.49	3.03	561	42.94	2.10	213
20.48	4.33	663	30.82	2.90	1638	43.76	2.07	243
20.77	4.27	2063	31.66	2.82	1797	45.87	1.98	246
20.98	4.23	910	32.29	2.77	559	47.26	1.92	304
21.28	4.17	377	32.83	2.73	1233	47.65	1.91	238
22.14	4.01	308	34.39	2.61	489	48.99	1.86	200
22.83	3.89	1003	35.47	2.53	894	49.23	1.85	350
23.17	3.84	385	35.82	2.51	1233	49.35	1.85	268
23.67	3.76	473	36.34	2.47	301	50.80	1.80	362
25.09	3.55	1507	36.82	2.44	771	52.54	1.74	224
25.28	3.52	658	37.40	2.40	416	55.08	1.67	220
25.82	3.45	319	37.65	2.39	577	55.44	1.66	484
26.29	3.39	3034	38.01	2.37	2125	55.58	1.65	286
26.59	3.35	316	38.12	2.36	1133	55.99	1.64	241
26.98	3.30	1158	38.41	2.34	431	57.43	1.60	360
27.17	3.28	2007	39.66	2.27	303	57.56	1.60	289
27.56	3.23	333	39.88	2.26	393			

Table 3S. Experimental powder data for **2-athd$_2$ClO$_4$**.

2 Theta (°)	d (Å)	Intensity (a.u.)	2 Theta (°)	d (Å)	Intensity (a.u.)
9.00	9.82	435	24.94	3.57	10060
15.66	5.65	361	26.88	3.31	885
16.75	5.29	339	27.69	3.22	953
17.87	4.96	5201	28.08	3.17	726
18.81	4.71	367	29.36	3.04	1362
19.05	4.66	472	29.69	3.01	1565
19.62	4.52	1636	36.02	2.49	708
19.81	4.48	657	39.65	2.27	364
23.12	3.84	497	47.37	1.92	342
24.65	3.61	2280	50.98	1.79	474

Table 4S. Experimental powder data for **2-athdClO$_4$**.

2 Theta (°)	d (Å)	Intensity (a.u.)	2 Theta (°)	d (Å)	Intensity (a.u.)
9.41	9.39	1253	28.24	3.16	492
15.33	5.78	999	28.50	3.13	392
17.70	5.01	572	29.81	3.00	394
18.64	4.76	912	30.37	2.94	901
18.88	4.70	2741	30.93	2.89	644
19.45	4.56	498	33.80	2.65	1396
20.05	4.42	701	34.54	2.60	385
20.20	4.39	854	36.05	2.49	526
21.66	4.10	4225	37.11	2.42	379
22.47	3.95	2558	37.78	2.38	373
22.83	3.89	1479	38.32	2.35	404
24.03	3.70	1846	39.59	2.27	421
24.28	3.66	2770	40.36	2.23	261
24.47	3.63	811	41.69	2.16	296
24.75	3.59	1593	45.47	1.99	411
25.43	3.50	2393	46.83	1.94	233
26.10	3.41	544	47.62	1.91	360
26.65	3.34	1340	50.98	1.79	288
27.19	3.28	1238	57.34	1.61	253
27.58	3.23	2802	59.94	1.54	238

Table 5S. Experimental powder data for **2-athd$_2$HPO$_3$**.

2 Theta (°)	d (Å)	Intensity (a.u.)	2 Theta (°)	d (Å)	Intensity (a.u.)
12.34	7.17	53	30.22	2.96	125
13.26	6.67	545	31.47	2.84	180
16.86	5.25	280	31.76	2.82	55
17.95	4.94	178	32.19	2.78	105
20.85	4.26	798	32.69	2.74	47
21.34	4.16	1878	34.05	2.63	406
21.89	4.06	243	35.78	2.51	251
22.50	3.95	293	37.61	2.39	105
22.92	3.88	800	38.66	2.33	83
24.04	3.70	257	41.80	2.16	253
24.78	3.59	38	43.98	2.06	330
25.52	3.49	916	44.82	0.02	195
25.73	3.46	305	48.90	1.86	90
26.65	3.34	100000	52.38	1.75	174
28.66	3.11	336	53.68	1.71	46
28.97	3.08	616	54.81	1.67	1776
29.88	2.99	79	55.95	1.64	119

Table 6S. Experimental powder data for **2-athdH$_2$PO$_4$**.

2 Theta (°)	d (Å)	Intensity (a.u.)	2 Theta (°)	d (Å)	Intensity (a.u.)
8.09	10.91	12173	35.07	2.56	1128
16.18	5.47	2198	36.45	2.46	1869
20.03	4.43	11382	36.54	2.46	1051
20.51	4.33	571	36.66	2.45	789
22.93	3.88	1287	38.41	2.34	1204
23.53	3.78	7064	38.52	2.34	629
24.42	3.64	14790	40.65	2.22	947
24.99	3.56	844	40.74	2.21	571
25.68	3.47	1211	41.86	2.16	754
27.03	3.30	2323	41.96	2.15	488
27.87	3.20	1151	42.30	2.13	513
28.69	3.11	727	42.88	2.11	520
30.47	2.93	1634	44.30	2.04	913
32.63	2.74	3224	44.47	2.04	1017
32.72	2.73	1554	46.80	1.94	603
34.14	2.62	635	49.27	1.85	491

Table 7S. Experimental powder data for **2-athd$_2$SeO$_4$H$_2$O**.

2 Theta (°)	d (Å)	Intensity (a.u.)	2 Theta (°)	d (Å)	Intensity (a.u.)	2 Theta (°)	d (Å)	Intensity (a.u.)
12.65	6.99	1361	31.98	2.80	1003	43.31	2.09	512
13.10	6.75	5085	32.78	2.73	589	45.85	1.98	331
17.10	5.18	1405	33.88	2.64	601	46.57	1.95	864
19.03	4.66	1237	34.06	2.63	1120	46.69	1.94	576
19.95	4.45	5710	34.16	2.62	636	47.78	1.90	465
20.34	4.36	7031	34.56	2.59	1717	48.09	1.89	732
21.30	4.17	3489	34.64	2.59	1172	48.22	1.89	502
22.28	3.99	3735	34.98	2.56	821	48.32	1.88	452
22.80	3.90	1950	35.08	2.56	502	50.55	1.80	615
23.05	3.85	1484	35.54	2.52	444	50.68	1.80	478
23.92	3.72	1882	35.86	2.50	365	51.21	1.78	819
25.46	3.50	1490	37.49	2.40	643	51.34	1.78	545
26.37	3.38	2840	37.92	2.37	317	51.71	1.77	392
26.91	3.31	1616	38.31	2.35	333	53.00	1.73	448
27.07	3.29	7072	40.01	2.25	461	53.72	1.70	378
27.15	3.28	3301	40.09	2.25	571	54.60	1.68	309
27.83	3.20	8872	40.40	2.23	1338	54.78	1.67	393
27.91	3.19	4246	40.49	2.23	1085	55.47	1.66	339
29.09	3.07	512	41.27	2.19	408	55.80	1.65	537
29.98	2.98	907	41.96	2.15	478	56.21	1.64	692
30.11	2.97	740	42.23	2.14	380	56.36	1.63	431
31.89	2.80	887	42.35	2.13	407			

Table 8S. Experimental powder data for **2-athdHSO$_4$**.

2 Theta (°)	d (Å)	Intensity (a.u.)	2 Theta (°)	d (Å)	Intensity (a.u.)	2 Theta (°)	d (Å)	Intensity (a.u.)
6.61	13.37	395	29.56	3.02	954	44.49	2.03	168
7.56	11.68	371	31.35	2.85	301	48.44	1.88	171
9.41	9.39	260	32.12	2.78	646	49.10	1.85	200
16.15	5.48	514	32.20	2.78	860	49.82	1.83	414
17.45	5.08	642	32.44	2.76	313	49.93	1.83	488
18.36	4.83	227	33.42	2.68	425	52.52	1.74	319
18.70	4.74	1612	34.28	2.61	2248	52.65	1.74	334
19.13	4.63	756	34.38	2.61	1207	52.83	1.73	294
20.31	4.37	565	35.33	2.54	352	54.12	1.69	771
21.79	4.07	3958	35.78	2.51	371	54.26	1.69	610
22.19	4.00	840	36.07	2.49	456	55.08	1.67	236
23.48	3.79	2698	37.60	2.39	313	55.12	1.66	274
24.40	3.64	377	38.06	2.36	612	55.54	1.65	200
25.33	3.51	895	39.41	2.28	511	56.43	1.63	208
26.89	3.31	1148	39.80	2.26	256	57.45	1.60	175
27.21	3.27	739	40.89	2.20	157	59.82	1.54	230
28.03	3.18	2328	44.12	2.05	385			

Table 9S: Selected bond lengths (Å) and angles (°) for **2-athdNO$_3$**.

Bond/Angle	Value (Å)/(°)	Angle		Value (°)
C2-S1	1.726(2)	N4-N3-H3		118.3
C2-N3	1.329(3)	N4-C5-S1		116.5(2)
C2-N6	1.316(3)	N6-C2-N3		125.4(2)
C5-S1	1.721(2)	N6-C2-S1		124.9(2)
C5-N4	1.296(3)	C2-N3-N4		117.5(2)
N3-N4	1.368(3)	C2-N3-H3		124.2
N3-H3	0.8356	C2-S1-C5		87.9(1)
N1-O1	1.239(3)	C5-N4-N3		108.4(2)
N1-O2	1.264(3)	O1-N1-O2		119.8(2)
N1-O3	1.250(3)	O1-N1-O3		121.0(2)
N3-C2-S1	109.7(2)	O3-N1-O2		119.3(2)
Hydrogen bonds				
D-H…A	d (D-H)	d (A…H)	d (D…A)	<(DHA)
N3-H3…O3[a]	0.84	1.94	2.762(3)	166
N6-H6A…O2[b]	0.86	2.04	2.880(3)	163
N6-H6B…O2[c]	0.86	2.02	2.871(3)	171
C5-H5…O1	0.83	2.36	3.289(3)	173

Note.
Equivalent positions: [a] 1-x, 1/2+y, 1/2-z; [b] -1+x, y, -1+z; [c] 1-x, -1/2+y, 1/2-z.
Abbreviations: A, acceptor; D, donor.

Table 10S: Selected bond lengths (Å) and angles (°) for **2-athdClH$_2$O**.

Bond	Value (Å)	Angle	Value (°)
C2-S1	1.727(3)	N4-C5-S1	116.5(3)
C2-N3	1.330(4)	N6-C2-N3	125.2(3)
C2-N6	1.316(4)	N6-C2-S1	124.9(2)
C5-S1	1.730(3)	N3-C2-S1	109.9(2)
C5-N4	1.294(5)	C2-N3-N4	117.4(3)
N3-N4	1.373(4)	C2-N3-H3	123.5
N3-H3	0.8166	N4-N3-H3	119.1
O1W-H1W	0.8274	C5-N4-N3	108.4(3)
O1W-H2W	0.7858	C2-S1-C5	87.7(2)

Hydrogen bonds

D-H…A	d (D-H)	d (A…H)	d (D…A)	<(DHA)
N3-H3…N4[a]	0.82	2.60	3.103(4)	122
N3-H3…O1W[b]	0.82	2.02	2.725(3)	144
N6-H6A…O1W[b]	0.86	2.26	2.944(4)	137
N6-H6A…Cl1	0.86	2.39	3.196(3)	155
O1W-H1W…Cl1[c]	0.83	2.29	3.099(3)	167
O1W-H2W…Cl1	0.79	2.42	3.200(2)	174

Note.
Equivalent positions: [a] 3-x, 1-y, 1-z; [b] 1+x, 3/2-y, 1/2+z; [c] 1-x, -1/2+y, 1/2-z.
Abbreviations: A, acceptor; D, donor.

Table 11S: Selected bond lengths (Å) and angles (°) for **2-athd$_2$ClO$_4$**.

Bond/Angle	Value (Å)/(°)	Angle	Value (°)
C2-S1	1.722(2)	N6-C2-N3	124.4(2)
C2-N3	1.332(3)	N6-C2-S1	125.8(2)
C2-N6	1.315(3)	C2-N3-N4	117.1(2)
C5-S1	1.738(2)	C2-N3-H3	122.7
C5-N4	1.281(3)	C2-S1-C5	87.9(1)
N3-N4	1.376(3)	C5-N4-N3	109.1(2)
N3-H3	0.8622	N23-C22-S21	113.5(2)
C22-S21	1.734(2)	N24-C25-S21	114.0(2)
C22-N23	1.316(3)	N26-C22-N23	123.8(2)
C22-N26	1.335(3)	N26-C22-S21	122.7(2)
C25-S21	1.727(2)	C22-N23-N24	111.8(2)
C25-N24	1.288(3)	C22-S21-C25	87.1(1)
N23-N24	1.381(3)	C25-N24-N23	113.5(2)
Cl1-O1	1.445(2)	O1-Cl1-O2	108.9(1)
Cl1-O2	1.452(2)	O1-Cl1-O3	110.13(9)
Cl1-O3	1.431(2)	O3-Cl1-O2	108.9(1)
Cl1-O4	1.425(2)	O4-Cl1-O1	108.9(1)
N3-C2-S1	109.8(2)	O4-Cl1-O2	109.9(1)
N4-N3-H3	120.2	O4-Cl1-O3	110.1(1)
N4-C5-S1	116.1(2)		

Hydrogen bonds				
D-H…A	d (D-H)	d (A…H)	d (D…A)	<(DHA)
N3-H3…N24[a]	0.86	1.93	2.759(3)	162
N6-H6A…N23[a]	0.86	2.06	2.880(3)	159
N6-H6B…O2	0.86	2.19	2.964(2)	149
N26-H26A…O1	0.89	2.07	2.937(2)	165
N26-H26B…O2[b]	0.91	2.15	3.052(2)	171

Note.
Equivalent positions: [a] 1+x, y, z; [b] 1/2+x, 1/2-y, 1/2+z; [c] 1-x, -1/2+y, 1/2-z.
Abbreviations: A, acceptor; D, donor.

Table 12S: Selected bond lengths (Å) and angles (°) for **2-athdClO$_4$**.

Bond/Angle	Value (Å)/(°)	Angle	Value (°)
C2-S1	1.721(1)	N4-C5-S1	116.0(1)
C2-N3	1.333(2)	N6-C2-N3	124.9(1)
C2-N6	1.319(2)	N6-C2-S1	125.09(9)
C5-S1	1.734(1)	C2-N3-N4	117.0(1)
C5-N4	1.287(2)	C2-N3-H3	126(1)
N3-N4	1.370(1)	C2-S1-C5	87.85(6)
N3-H3	0.84(2)	C5-N4-N3	109.2(1)
Cl1-O1	1.4460(9)	O1-Cl1-O2	108.19(6)
Cl1-O2	1.447(1)	O1-Cl1-O3	109.75(6)
Cl1-O3	1.4460(9)	O3-Cl1-O2	108.77(6)
Cl1-O4	1.428(1)	O4-Cl1-O1	109.90(6)
N3-C2-S1	109.97(8)	O4-Cl1-O2	110.45(7)
N4-N3-H3	117(1)	O4-Cl1-O3	109.76(6)
Hydrogen bonds			
D-H…A	d (D-H)	d (A…H)	d (D…A)	<(DHA)
N3-H3…O1	0.84(2)	2.26(2)	2.945(1)	139(2)
N3-H3…O3[a]	0.84(2)	2.58(2)	3.062(1)	117(2)
N3-H3…O3[b]	0.84(2)	2.39(2)	3.0225(2)	133(2)
N6-H6A…O3[a]	0.88	2.55	3.090(1)	120
N6-H6A…O1[c]	0.88	2.27	2.992(2)	139
N6-H6A…O3[b]	0.88	2.39	3.085(1)	136
N6-H6A…O2[d]	0.88	2.04	2.881(2)	159
C5-H5…O4[e]	0.95	2.53	3.294(2)	138

Note.
Equivalent positions: [a] 1+x, y, z; [b] 1-x, 1-y, 1-z; [c] 2-x, 1-y, 1-z; [d] 1+x, y, -1+z; [e] x, 1/2-y, -1/2+z.
Abbreviations: A, acceptor; D, donor.

Table 13S: Selected bond lengths (Å) and angles (°) for **2-athd$_2$HPO$_3$**.

Bond/Angle	Value (Å)/(°)	Angle	Value (°)
C2-S1	1.736(4)	N6-C2-N3	124.5(3)
C2-N3	1.323(5)	N6-C2-S1	125.8(3)
C2-N6	1.306(5)	C2-N3-N4	117.3(3)
C5-S1	1.745(4)	C2-N3-H3	121.1
C5-N4	1.275(6)	C2-S1-C5	87.6(2)
N3-N4	1.382(4)	C5-N4-N3	109.3(3)
P1-O1	1.508(3)	O1-P1-O2	113.5(2)
P1-O2	1.505(3)	O1-P1-O3	112.9(2)
P1-O3	1.565(3)	O3-P1-O2	110.9(2)
P1-H1	1.106	O1-P1-H1	112.2
N3-C2-S1	109.7(3)	O2-P1-H1	98.5
N4-N3-H3	121.6	O3-P1-H1	107.9
N4-C5-S1	116.1(3)		

Hydrogen bonds				
D-H…A	d (D-H)	d (A…H)	d (D…A)	<(DHA)
N3-H3…O2[a]	0.86	1.81	2.654(4)	167
N6-H6A…O2[b]	0.86	1.90	2.752(4)	170
N6-H6B…O1[a]	0.86	1.98	2.820(4)	164
C5-H5…O1[c]	0.93	2.44	3.254(4)	146

Note.
Equivalent positions: [a] -1/2+x, 1/2-y, z; [b] 1/2+x, 1/2-y, z; [c] -1/2+x, 1/2-y, 1+z.
Abbreviations: A, acceptor; D, donor.

Table 14S: Selected bond lengths (Å) and angles (°) for **2-athdH_2PO_4**.

Bond/Angle	Value (Å)/(°)	Angle	Value (°)
C2-S1	1.735(4)	N6-C2-N3	125.1(4)
C2-N3	1.340(6)	N6-C2-S1	125.1(3)
C2-N6	1.310(5)	C2-N3-N4	116.2(3)
C5-S1	1.745(4)	C2-N3-H3	124.4
C5-N4	1.267(6)	C2-S1-C5	87.6(2)
N3-N4	1.377(5)	C5-N4-N3	110.3(3)
P1-O1	1.549(3)	O1-P1-O2	104.0(2)
P1-O2	1.571(3)	O1-P1-O3	109.7(2)
P1-O3	1.522(3)	O3-P1-O2	109.0(2)
P1-O4	1.508(3)	O3-P1-O4	111.9(2)
O1-H7	0.9723	O4-P1-O1	109.0(2)
O2-H8	0.9916	O4-P1-O2	112.9(2)
N3-C2-S1	109.8(3)	P1-O1-H7	123.3
N4-N3-H3	119.4	P1-O2-H8	115.5
N4-C5-S1	116.1(3)		

Hydrogen bonds				
D-H…A	d (D-H)	d (A…H)	d (D…A)	<(DHA)
N3-H3…O3[a]	0.88	1.86	2.687(5)	157
N6-H6A…O4[b]	0.86	1.91	2.763(4)	176
N6-H6B…O1	0.89	2.13	2.934(4)	149
O1-H7…O3[c]	0.97	1.52	2.489(4)	174
O2-H8…O4[d]	0.99	1.56	2.534(4)	167
C5-H5…O3[e]	0.93	2.49	3.399(5)	167

Note.
Equivalent positions: [a] 1+x, y, -1+z; [b] 1+x, 2-y, -1/2+z; [c] 1+x, y, z; [d] x, 2-y, 1/2+z; [e] 1/2+x, 3/2-y, -1/2+z.
Abbreviations: A, acceptor; D, donor.

Table 15S: Selected bond lengths (Å) and angles (°) for **2-athd$_2$SeO$_4$H$_2$O**.

Bond/Angle	Value (Å)/(°)	Angle	Value (°)
C2-S1	1.734(5)	C2-N3-N4	116.2(4)
C2-N3	1.335(6)	C2-N3-H3	125.4
C2-N6	1.299(7)	C2-S1-C5	87.4(2)
C5-S1	1.737(5)	C5-N4-N3	109.8(4)
C5-N4	1.280(7)	S1-C5-H5	121.8
N3-N4	1.375(6)	N23-C22-S21	111.0(4)
Se1-O1	1.633(4)	N24-N23-H23	115.4
Se1-O2	1.656(4)	N24-C25-S21	116.5(4)
Se1-O3	1.650(4)	N24-C25-H25	121.7
Se1-O4	1.652(4)	N26-C22-N23	123.2(4)
C22-S21	1.720(5)	N26-C22-S21	125.7(4)
C22-N23	1.370(7)	C22-N23-N24	113.8(4)
C22-N26	1.317(7)	C22-N23-H23	130.2
C25-S21	1.730(5)	C22-S21-C25	88.0(3)
C25-N24	1.279(8)	C25-N24-N23	110.6(4)
N23-N24	1.393(6)	S21-C25-H25	121.7
N3-C2-S1	110.3(3)	O1-Se1-O2	109.8(2)
N4-N3-H3	118.3	O1-Se1-O3	110.5(2)
N4-C5-S1	116.3(4)	O3-Se1-O2	109.0(2)
N4-C5-H5	121.8	O3-Se1-O4	106.8(2)
N6-C2-N3	125.1(5)	O4-Se1-O1	110.3(2)
N6-C2-S1	124.6(4)	O4-Se1-O2	110.4(2)

Hydrogen bonds				
D-H…A	d (D-H)	d (A…H)	d (D…A)	<(DHA)
N3-H3…O3[a]	0.85	1.85	2.701(5)	175
N6-H6A…O4[a]	0.86	2.01	2.794(6)	152
N6-H6B…O1[b]	0.86	2.52	2.873(6)	106
N6-H6B…O5[c]	0.86	2.07	2.870(6)	154
N23-H23…O4[c]	1.00	1.71	2.676(6)	163
N26-H26A…O1[d]	0.86	1.91	2.734(6)	161
N26-H26B…O2	0.86	2.09	2.841(6)	146
N26-H26B…N24[e]	0.86	2.55	3.006(6)	114
C25-H25…O1[f]	0.93	2.32	3.126(6)	145
C25-H25…O5[g]	0.93	2.57	3.193(7)	125

Note.
Equivalent positions: [a] 1+x, 1-y, 1/+z; [b] x, 1-y, 1/2+z; [c] x, 1-y, -1/2+z; [d] x, 2-y, 1/2+z; [e] -1+x, 2-y, -1/2+z; [f] 1+x, y, 1+z; [g] 1+x, y, z.
Abbreviations: A, acceptor; D, donor.

Table 16S: Selected bond lengths (Å) and angles (°) for **2-athdHSO$_4$**.

Bond/Angle	Value (Å)/(°)	Angle	Value (°)
C2-S1	1.731(2)	N6-C2-N3	125.8(2)
C2-N3	1.323(3)	N6-C2-S1	124.4(2)
C2-N6	1.310(3)	C2-N3-N4	117.0(2)
C5-S1	1.732(3)	C2-N3-H3	124(2)
C5-N4	1.278(3)	C2-S1-C5	87.7(1)
N3-N4	1.374(3)	C5-N4-N3	109.3(2)
S2-O1	1.445(2)	S1-C5-H5	119(2)
S2-O2	1.450(2)	O1-S2-O2	114.3(1)
S2-O3	1.459(2)	O1-S2-O3	112.91(9)
S2-O4	1.565(2)	O3-S2-O2	110.75(9)
O4-H7	0.80(2)	O3-S2-O4	107.4(1)
N3-C2-S1	109.8(2)	O4-S2-O1	103.2(1)
N4-N3-H3	119(2)	O4-S2-O2	107.6(1)
N4-C5-S1	116.2(2)	S2-O4-H7	111(3)
N4-C5-H5	125(2)		

Hydrogen bonds				
D-H…A	d (D-H)	d (A…H)	d (D…A)	<(DHA)
N3-H3…O2[a]	0.81(3)	1.95(3)	2.736(3)	165(3)
N6-H6A…O3	0.82(3)	2.08(3)	2.892(3)	172(3)
N6-H6B…O1[b]	0.81(3)	2.07(3)	2.871(3)	174(3)
O4-H7…O3[c]	0.80(3)	1.84(3)	2.620(2)	164(4)

Note.
Equivalent positions: [a] 1/2+x, 1/2-y, 1-z; [b] -x, 1/2+y, 3/2-z; [c] -1/2+x, 1/2-y, 1-z.
Abbreviations: A, acceptor; D, donor.

Table 17S: Comparison of geometric parameters (distances from the thiadiazole ring plane; angles between the plane of thiadiazole ring and the plane of NH_2 group).

	Distance of fitted atoms of the plane of NH_2 groups (Å)			C-N bond (Å)	inter-planar angles (°)	Distance of H3 - atom from the ring
	N - atom	HXA - atom	HXB - atom			
2-athd*	-0.0045	-0.0647	-0.0047	1.3456(13)	4.84(1)	
2-athdNO_3	0.0063	0.0109	0.0056	1.3163(3)	0.34(0)	0.0034
2-athd$_2ClO_4$	0.0049	-0.0017	0.0110	1.315	0.49(0)	-0.0027
	0.0191	-0.1049	-0.0968	1.335	15.15(1)	
2-athdClO_4	-0.0146	-0.0166	-0.0180	1.3191(15)	0.36(2)	-0.0029
2-athd$_2HPO_3$	0.0058	0.0524	0.0884	1.3045(3)	8.65(1)	-0.0273
2-athdH_2PO_4	0.0259	0.2151	0.0873	1.30987(11)	17.24(0)	-0.023
2-athdClH_2O	-0.0083	-0.0315	0.0043	1.31639(12)	1.55(0)	-0.0027
2-athdHSO_4	0.0198	-0.0539	0.0417	1.3105(5)	5.29(1)	-0.0157
2-athd$_2SeO_4H_2O$	-0.0080	-0.0036	-0.0140	1.2992(6)	0.42(1)	0.0544
	0.0178	0.0173	0.0264	1.3172(6)	0.65(2)	-0.1465

Note.
Symbols: N-atom (N6 or N26), HXA-atom (H6A of H26A), HXB-atom (H6B or H26B); H-atom (H3 or H23). The asterisk indicate the 2-amino-1,3,4-thiadiazole from the Crystal Structural Database (database code CSD – NIYD0001).

Table 18S: Average experimental and calculated bond lengths for 2-amino-1,3,4-thiadiazole and its cation

2-athd	Average X-ray data	Geometry optimisation	**2-athd(1+)**	Average X-ray data	Geometry optimisation
	bond (Å)	B3LYP/6-311+G (d,p) bond (Å)		bond (Å)	B3LYP/6-311+G (d,p) bond (Å)
C22-S21	1.734(2)	1.760	C2-S1	1.728	1.739
C22-N23	1.316(3)	1.310	C2-N3	1.335	1.339
C22-N26	1.335(3)	1.362	C2-N6	1.312	1.320
C25-S21	1.727(2)	1.751	C5-S1	1.735	1.757
C25-N24	1.288(3)	1.292	C5-N4	1.282	1.283
N23-N24	1.381(3)	1.375	N3-N4	1.376	1.366

Table 19S: Average experimental and calculated angles for 2-amino-1,3,4-thiadiazole and its cation

2-athd	Average X-ray data	Geometry optimisation	**2-athd(1+)**	Average X-ray data	Geometry optimisation
	angle (°)	B3LYP/6-311+G (d,p) angle (°)		angle (°)	B3LYP/6-311+G (d,p) angle (°)
N23-C22-S21	113.5(2)	113.7	N3-C2-S1	110.0	109.3
N24-C25-S21	114.0(2)	114.3	N4-C5-S1	116.3	115.6
N26-C22-N23	123.8(2)	123.8	N6-C2-N3	124.8	125.4
N26-C22-S21	122.7(2)	122.4	N6-C2-S1	125.1	125.3
C22-N23-N24	111.8(2)	112.6	C2-N3-N4	116.6	117.8
C22-S21-C25	87.1(1)	85.9	C2-S1-C5	87.7	87.7
C25-N24-N23	113.5(2)	113.6	C5-N4-N3	109.4	109.4

Table 20Sa: Comparison of geometric parameters (distances from the thiadiazole ring plane of N6) in the temperature X-ray measured single crystal of **2-athdClO$_4$**.

Temperature (K)	**2-athdClO$_4$**		
	Distance of N6 atom from the ring	C-N bond (Å)	inter-planar angles (°)
110	0.0128(17)	1.3174(14)	2.66(7)
130	0.0119(19)	1.3175(15)	1.76(8)
150	0.0159(20)	1.3179(16)	2.12(8)
170	0.0144(21)	1.3163(17)	2.07(9)
190	0.0123(19)	1.3174(15)	0.37(6)
210	0.0126(22)	1.3156(17)	0.40(7)
230	0.0143(22)	1.3147(17)	0.46(7)
250	0.0122(23)	1.3148(18)	0.37(7)
270	0.0126(23)	1.3142(17)	0.44(7)
290	0.0130(25)	1.3130(19)	0.40(8)

Table 20Sb: Comparison of geometric parameters (distances from the thiadiazole ring plane of N3) in the temperature X-ray measured single crystal of **2-athdHSO$_4$**.

Temperature (K)	**2-athdHSO$_4$**		
	Distance of N3 atom from the ring	C-N bond (Å)	inter-planar angles (°)
110	-0.0166(13)	1.3175(13)	3.95(1)
130	-0.0174(13)	1.3155(16)	5.31(1)
150	-0.0139(13)	1.3172(15)	4.57(1)
170	-0.0156(11)	1.3169(15)	5.03(0)
190	-0.0125(11)	1.3158(16)	5.77(0)
210	-0.0154(11)	1.3158(17)	6.88(0)
230	-0.0115(11)	1.3164(14)	6.99(0)
250	-0.0126(12)	1.3163(16)	6.94(1)
270	-0.0094(11)	1.3161(17)	7.04(0)
290	-0.0118(11)	1.3166(16)	7.12(0)

Table 20Sc: Comparison of geometric parameters (distances from the thiadiazole ring plane of N6 or N26) in the temperature X-ray measured single crystal of **2-athd$_2$ClO$_4$**.

Temperature (K)	**2-athd$_2$ClO$_4$**					
	Distance of N6 atom from the ring	Distance of N26 atom from the ring	C2-N6 bond (Å)	C22-N26 bond (Å)	inter-planar angles (°)	inter-planar angles (°)
150	-0.0061(9)	-0.0100(9)	1.315(3)	1.339(2)	0.52(3)	10.00(2)
283	-0.0010(0)	-0.0079(0)	1.320(5)	1.336(4)	0.82(0)	0.47(0)
315	0.1317	-0.1127	1.310(7)	1.328(7)	5.860	0.97

Figures

Figure 1S: Atom numbering of **2-athdNO$_3$**. The dashed lines indicate hydrogen bonds.

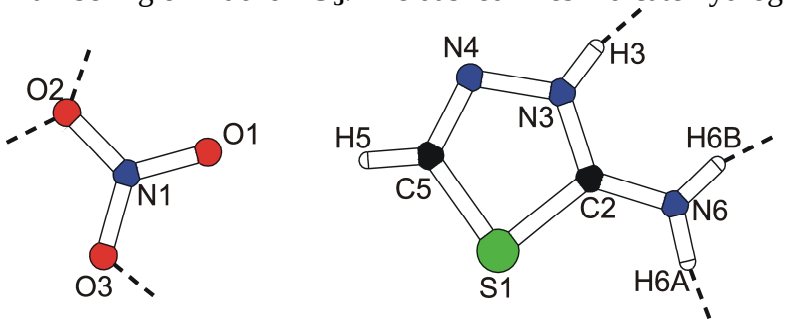

Figure 2S: Atom numbering of **2-athdClH$_2$O**. The dashed lines indicate hydrogen bonds.

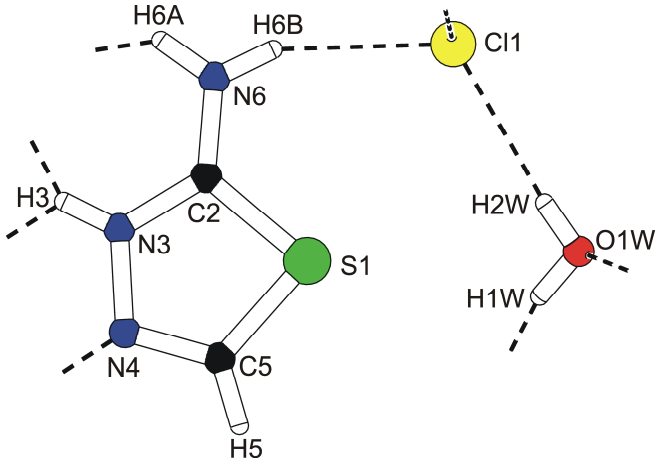

Figure 3S: Atom numbering of **2-athd$_2$ClO$_4$**. The dashed lines indicate hydrogen bonds.

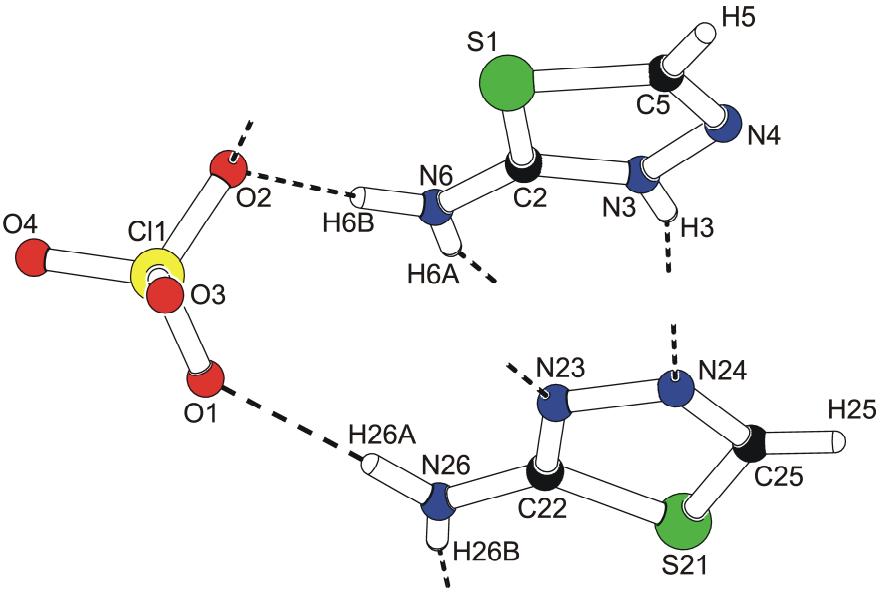

Figure 4S: Atom numbering of **2-athdClO$_4$**. The dashed lines indicate hydrogen bonds.

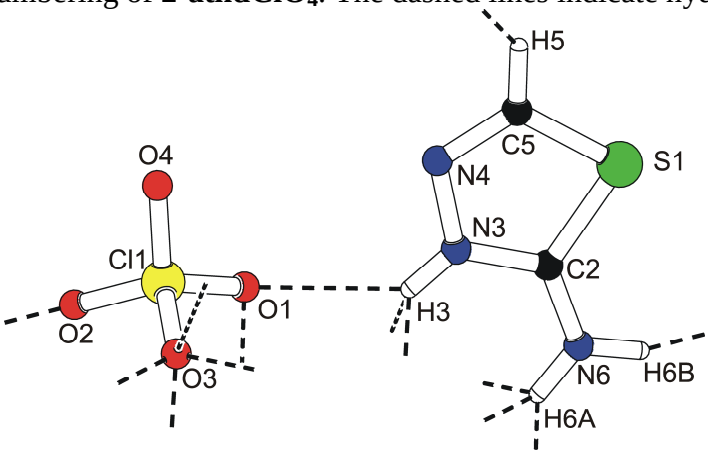

Figure 5S: Atom numbering of **2-athd$_2$HPO$_3$**. The dashed lines indicate hydrogen bonds.

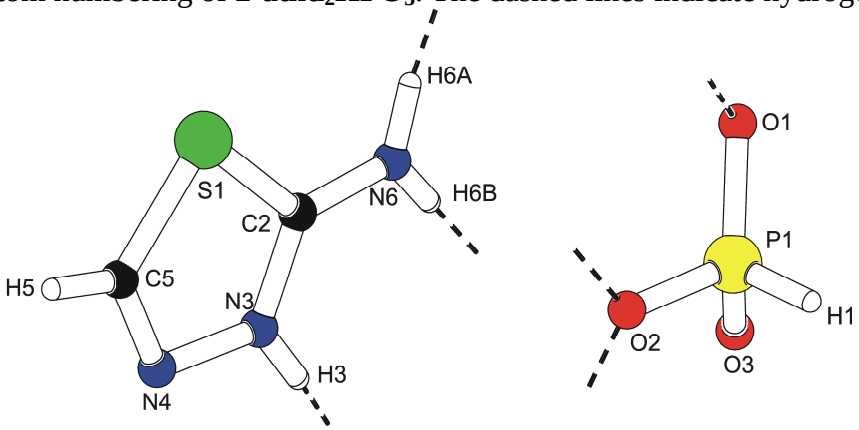

Figure 6S: Atom numbering of **2-athdH$_2$PO$_4$**. The dashed lines indicate hydrogen bonds.

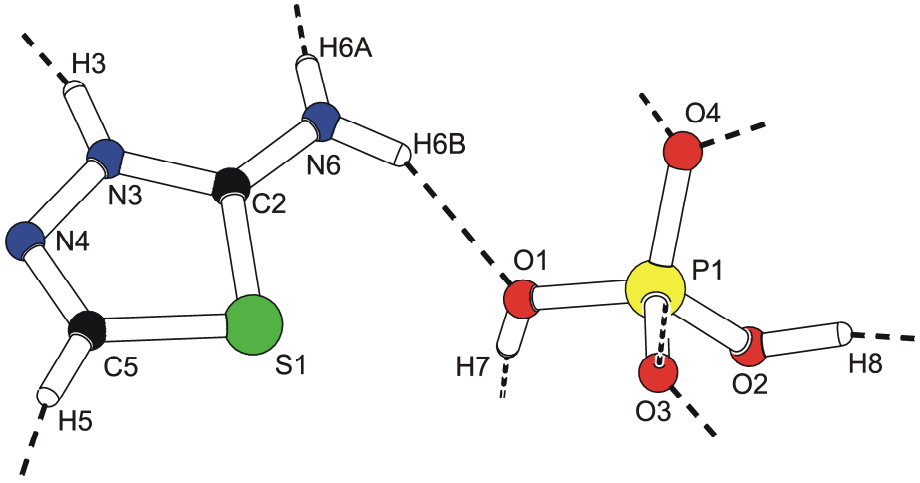

Figure 7S: Atom numbering of **2-athd$_2$SeO$_4$H$_2$O**. The dashed lines indicate hydrogen bonds.

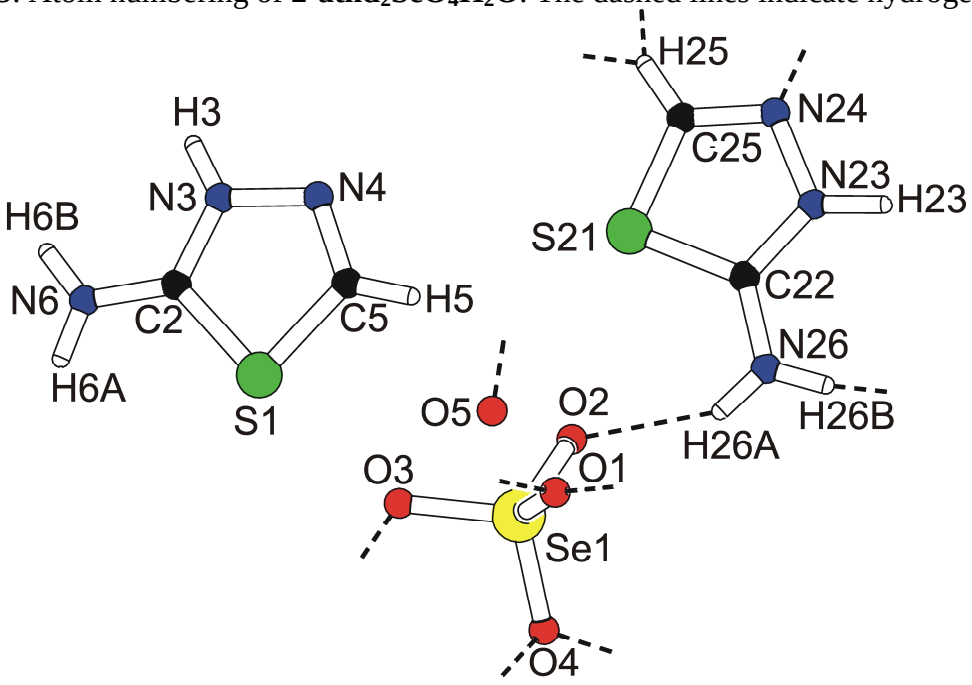

Figure 8S: Atom numbering of **2-athdHSO$_4$**. The dashed lines indicate hydrogen bonds.

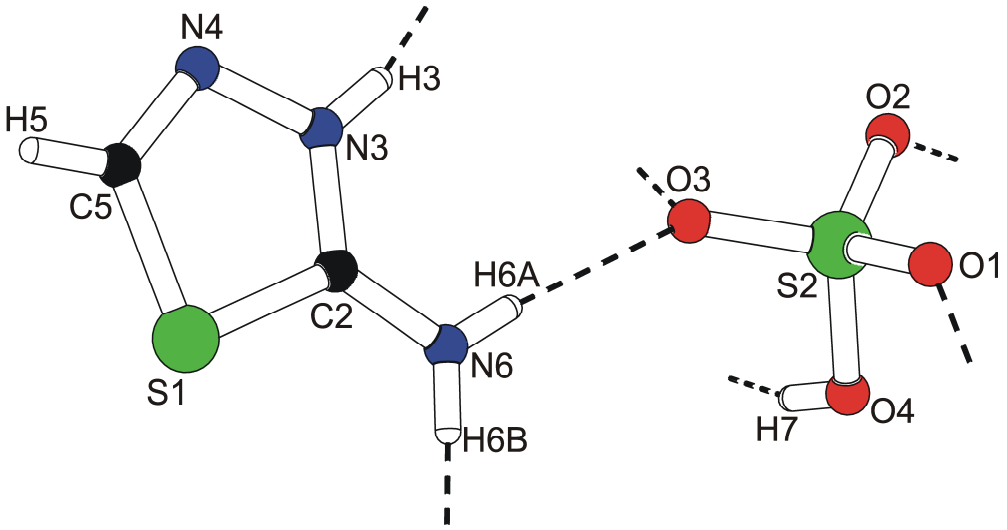

Figure 9S: The molecules of water and Cl^- ions interaction in the structure of **2-athdClH$_2$O**. The dashed lines indicate hydrogen bonds.

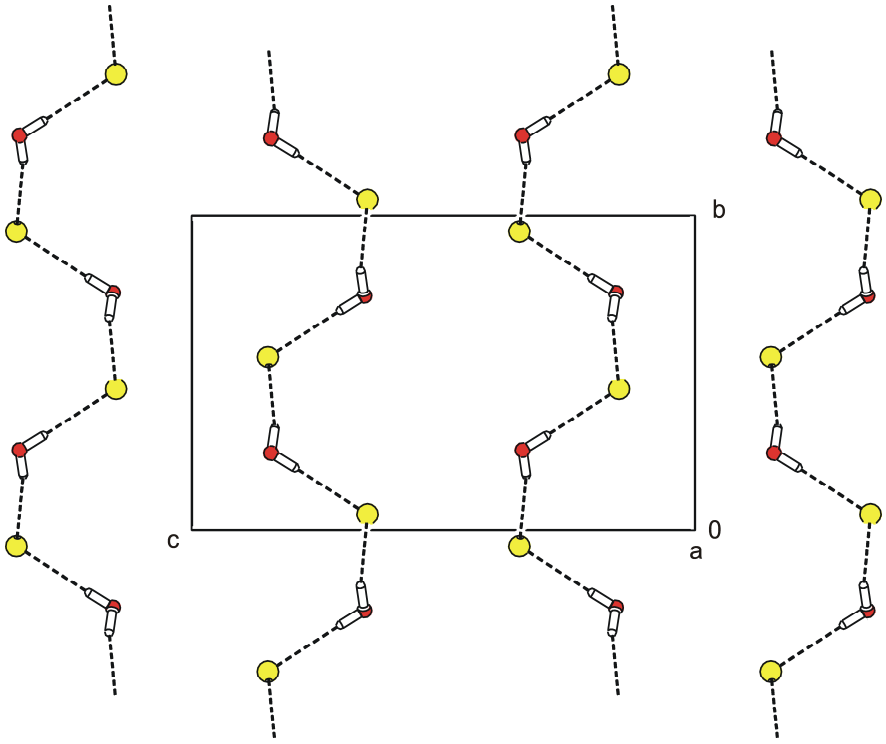

Figure 10S: Packing scheme of **2-athdClH$_2$O**. The dashed lines indicate hydrogen bonds.

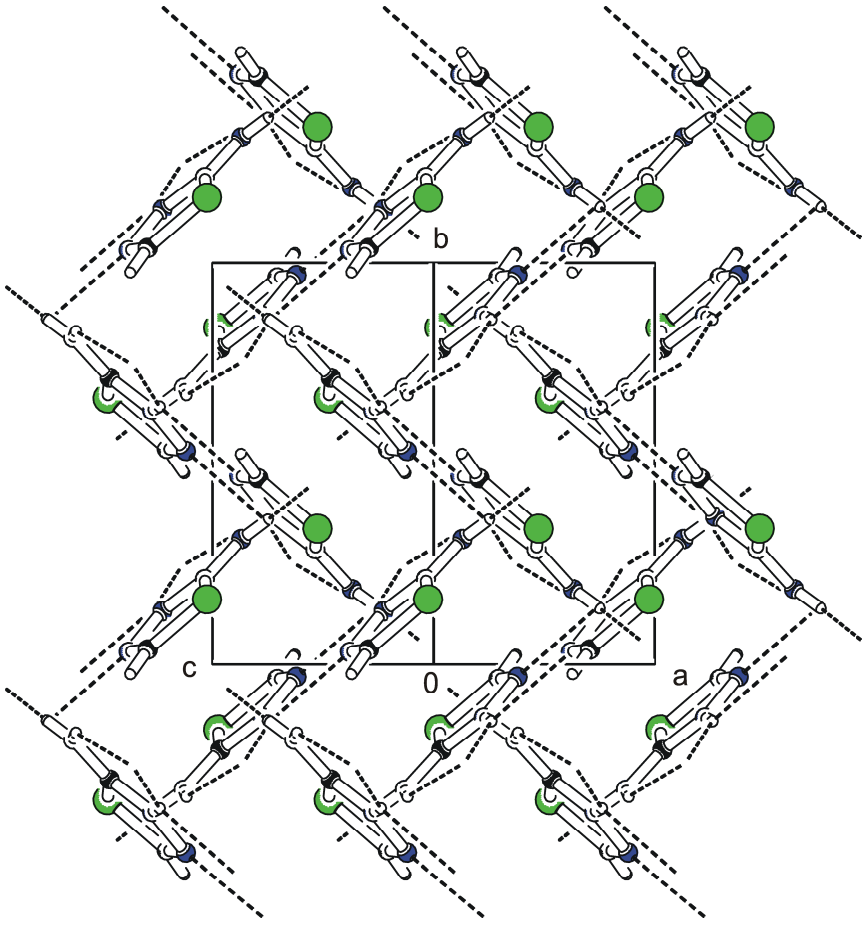

Figure 11S: Packing scheme of **2-athdHPO$_3$** (view along the [100] direction). The dashed lines indicate hydrogen bonds.

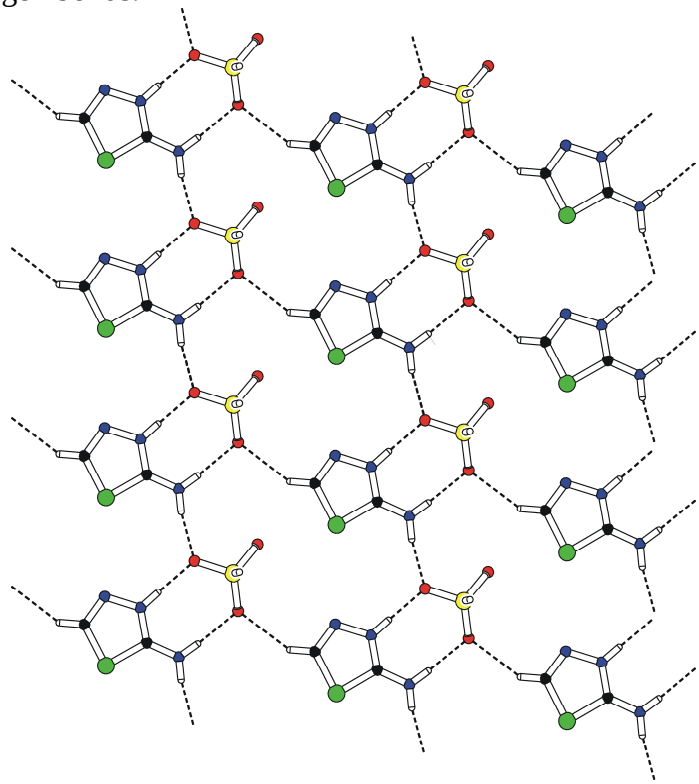

Figure 12S: The anionic layers in the structure **2-athdH$_2$PO$_4$** (view along the [010] direction). The dashed lines indicate hydrogen bonds.

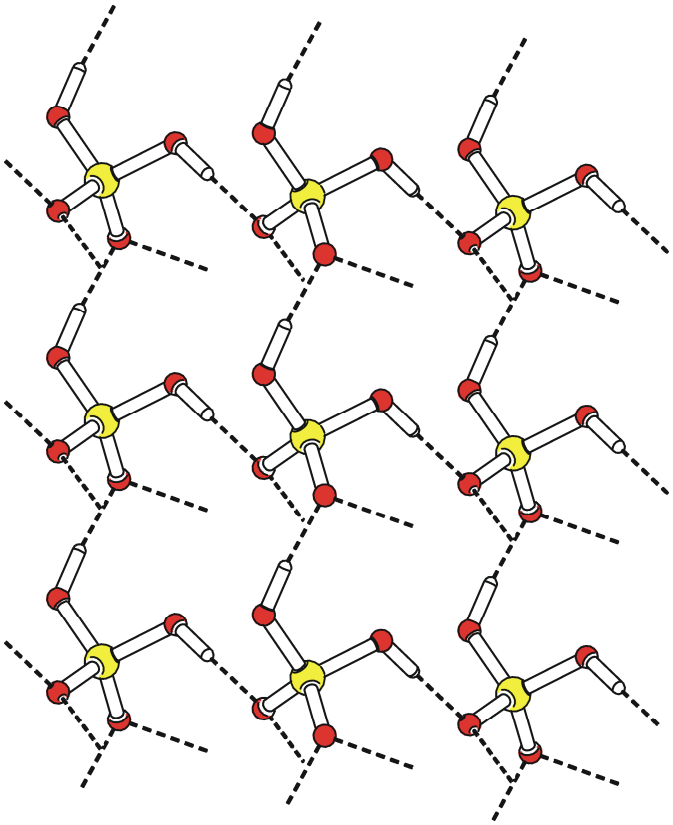

Figure 13S: DSC curves of **2-athd$_2$SeO$_4$H$_2$O**.

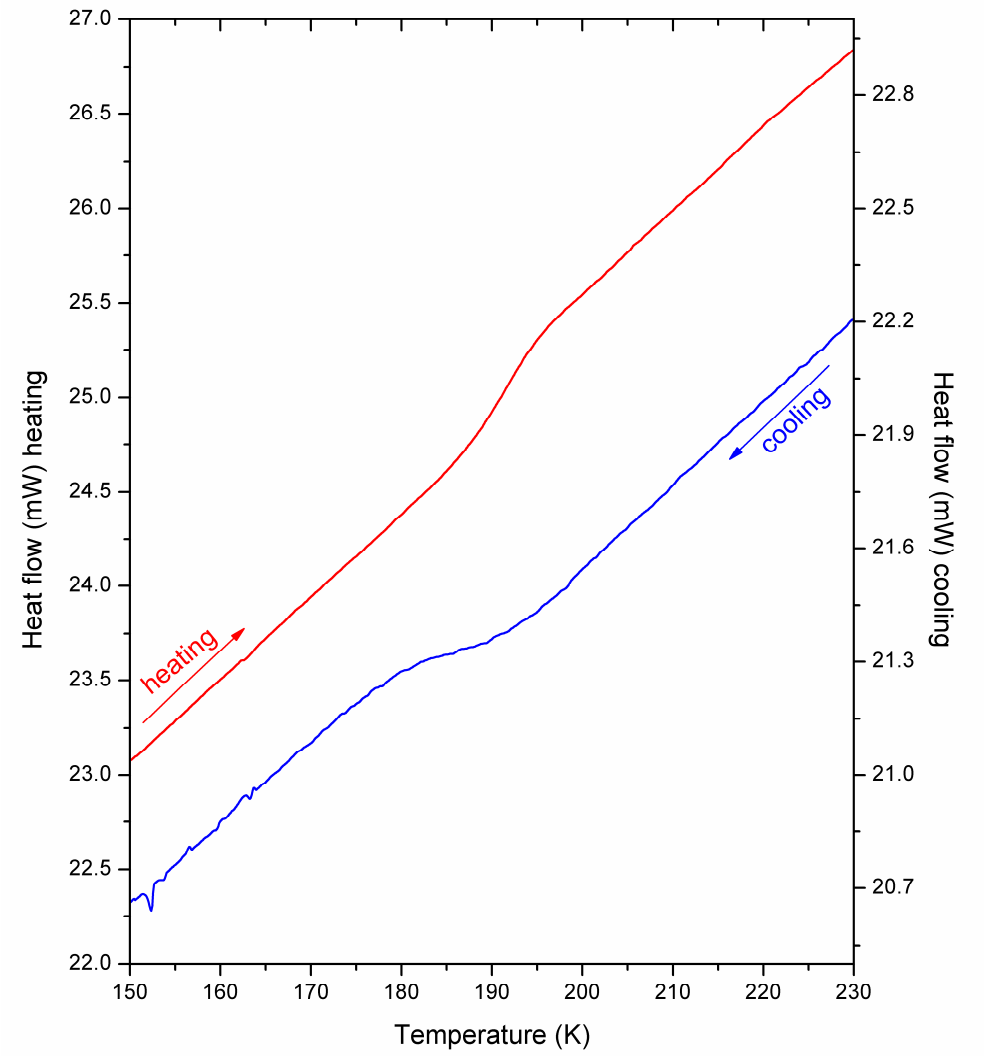

Figure 14S: DSC curves of **2-athdHSO$_4$**.

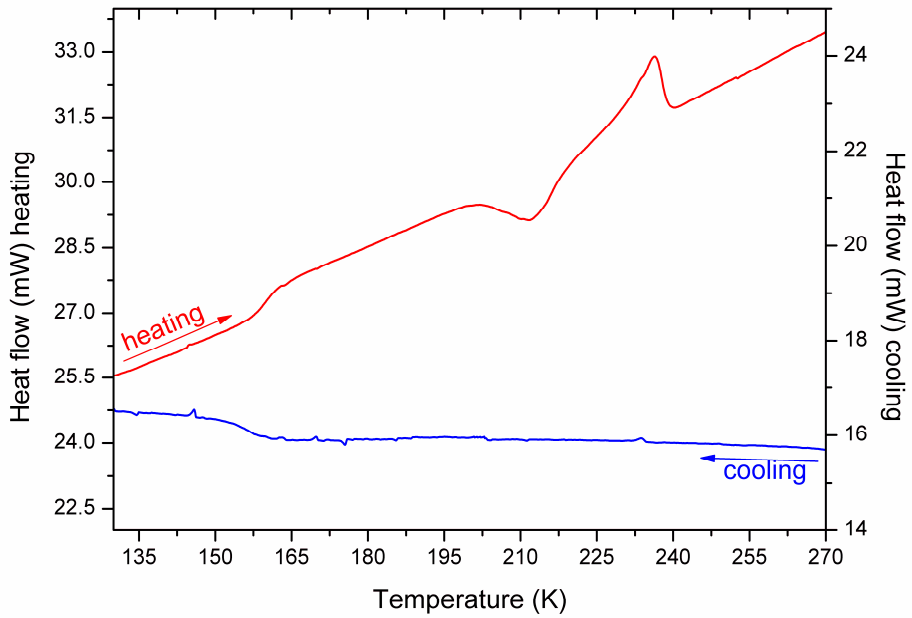

Figure 15S: DSC curves of **2-athdClO$_4$**.

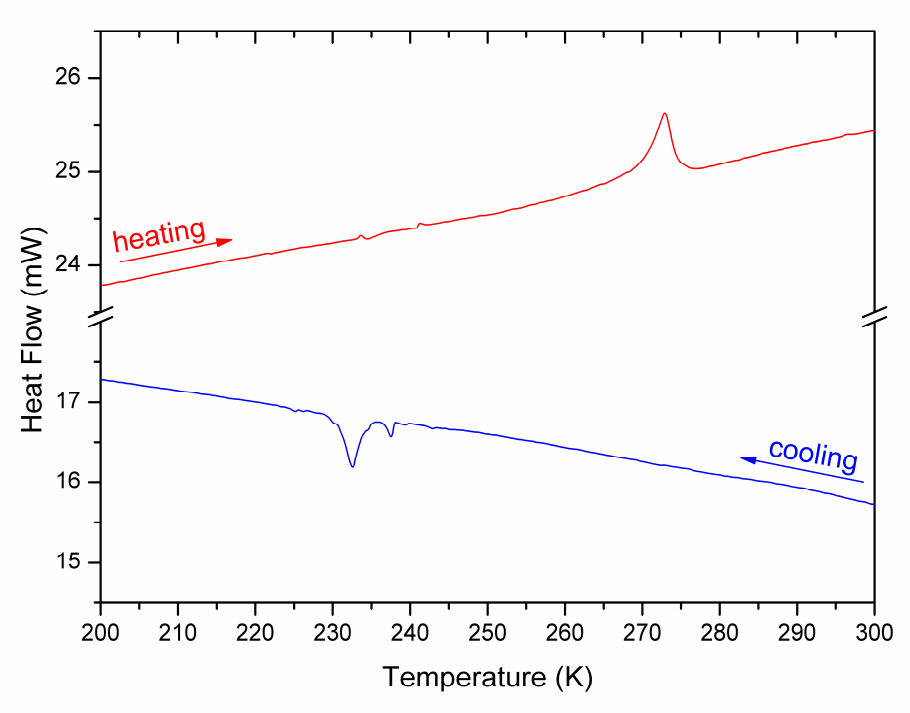

Figure 16S: DSC curves of **2-athd$_2$ClO$_4$**.

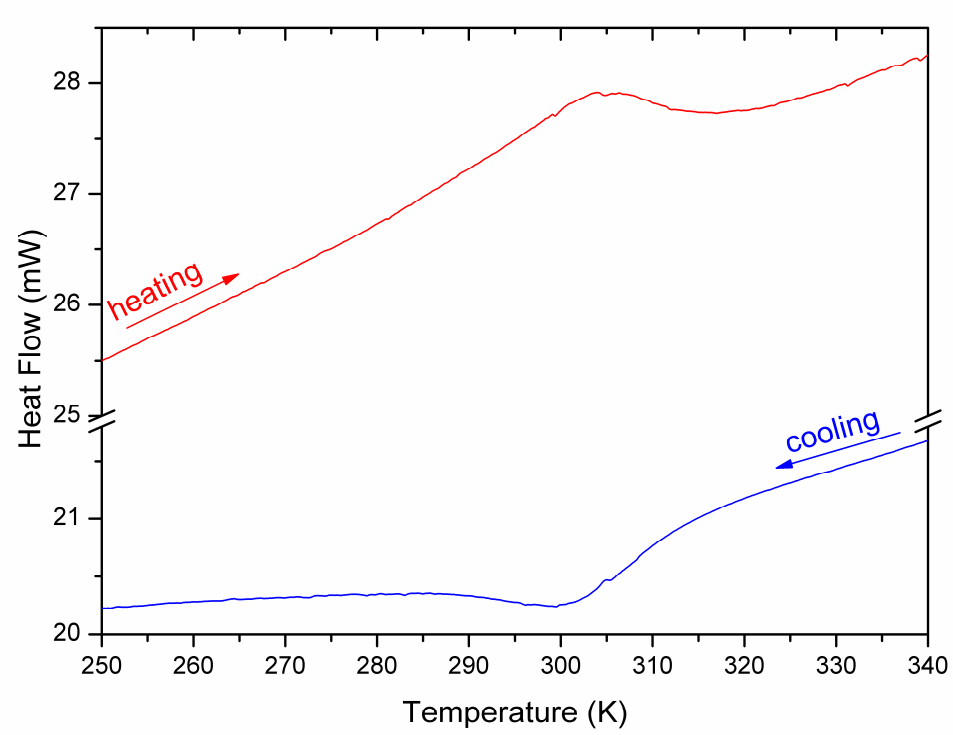

Figure 17S: Temperature dependence of the interplanar angle of cation (thiadiazole ring *vs*. amino group plain) in the crystal structure of **2-athdHSO$_4$** (a) and in the crystal structure of **2-athdClO$_4$** (b).

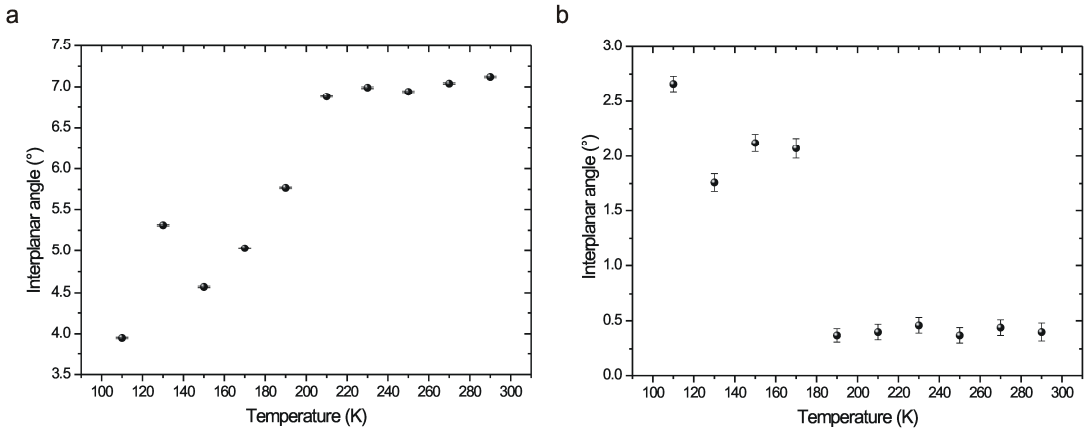

Figure 18S: FT Raman spectra of **2-athd$_2$SeO$_4$H$_2$O** at different temperatures.

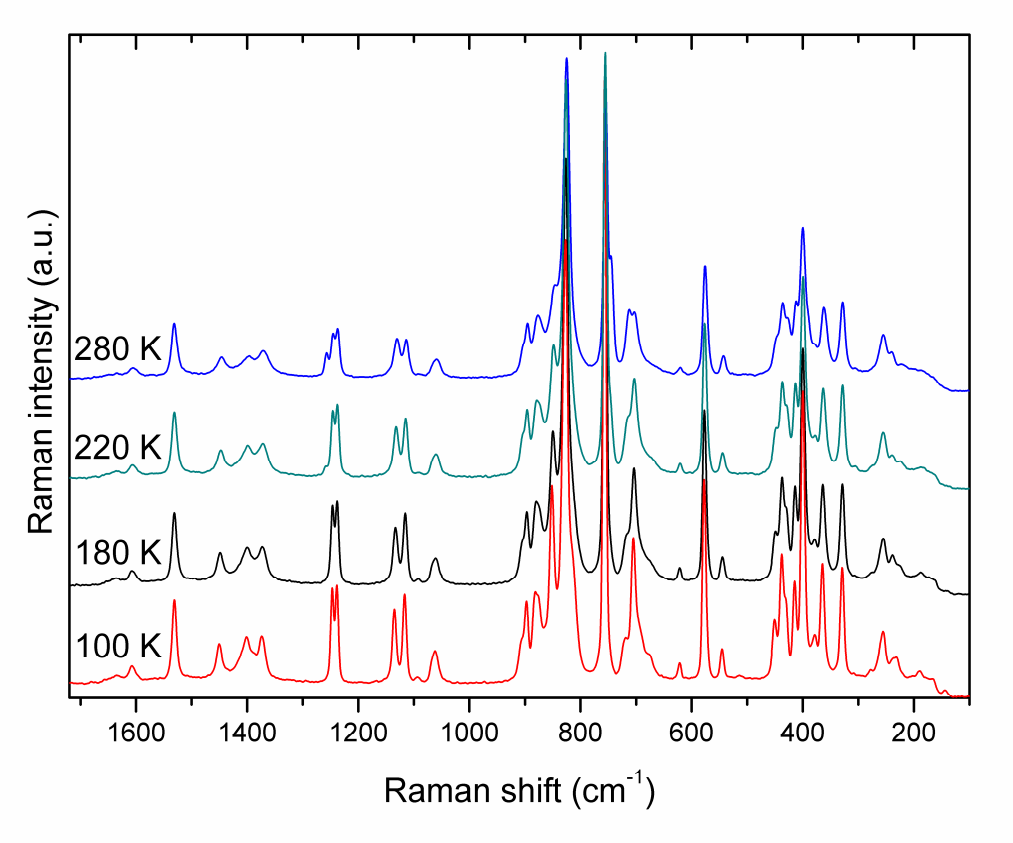

Figure 19S: FTIR spectra of **2-athd$_2$SeO$_4$H$_2$O** at different temperatures.

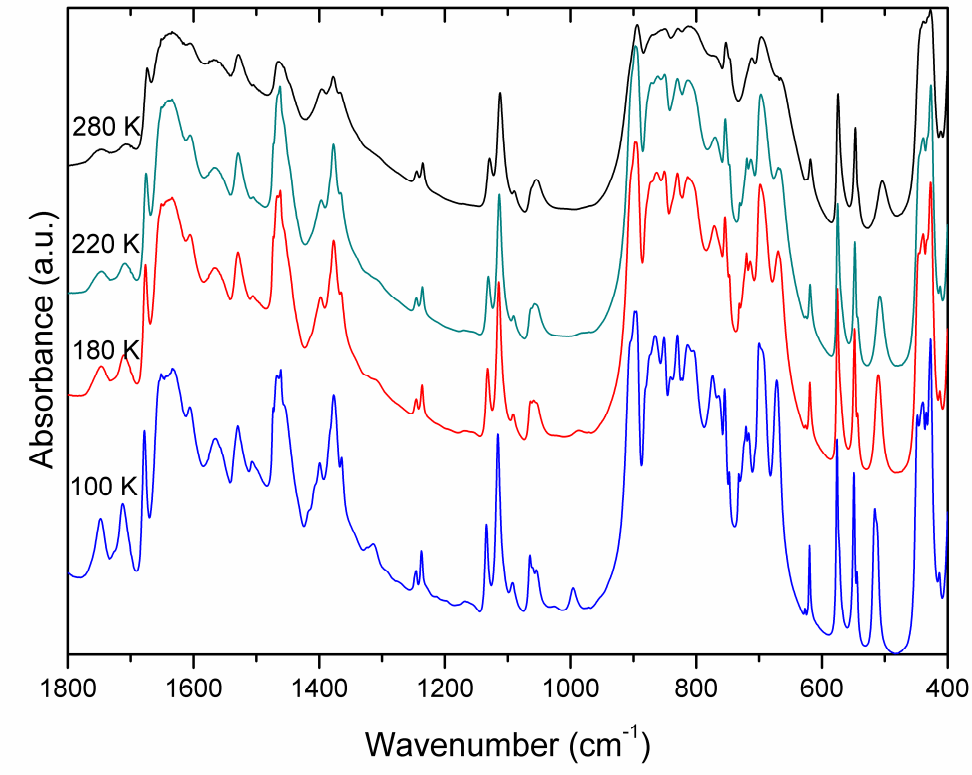

Figure 20S: FT Raman spectra of **2-athdHSO$_4$** at different temperatures.

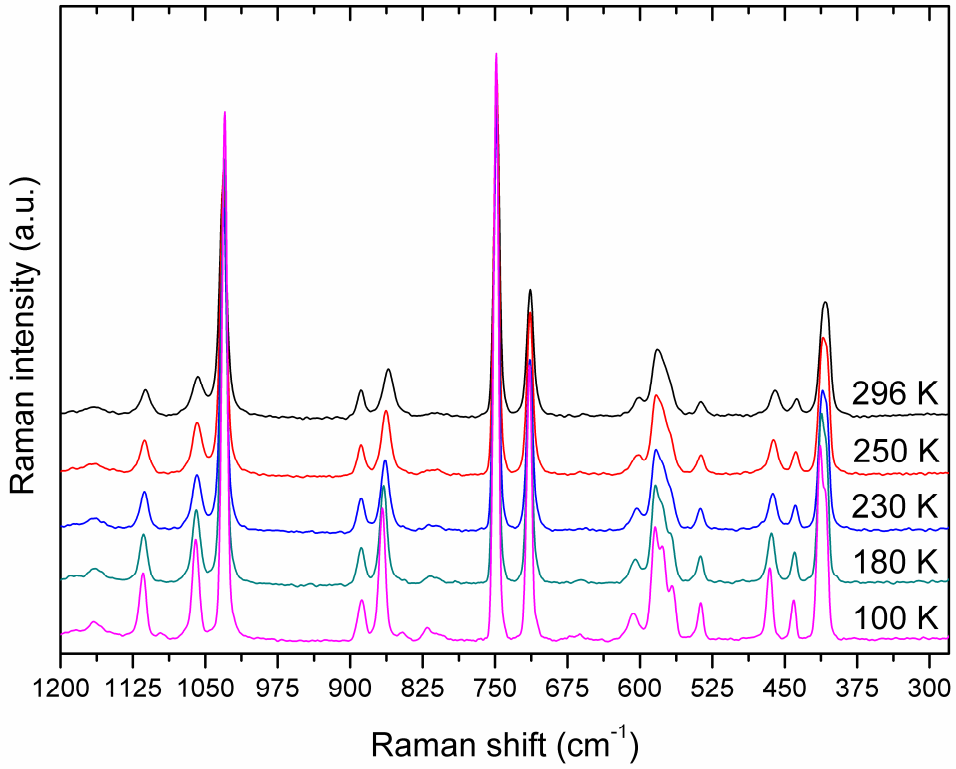

Figure 21S: FTIR spectra of **2-athdHSO$_4$** at different temperatures.

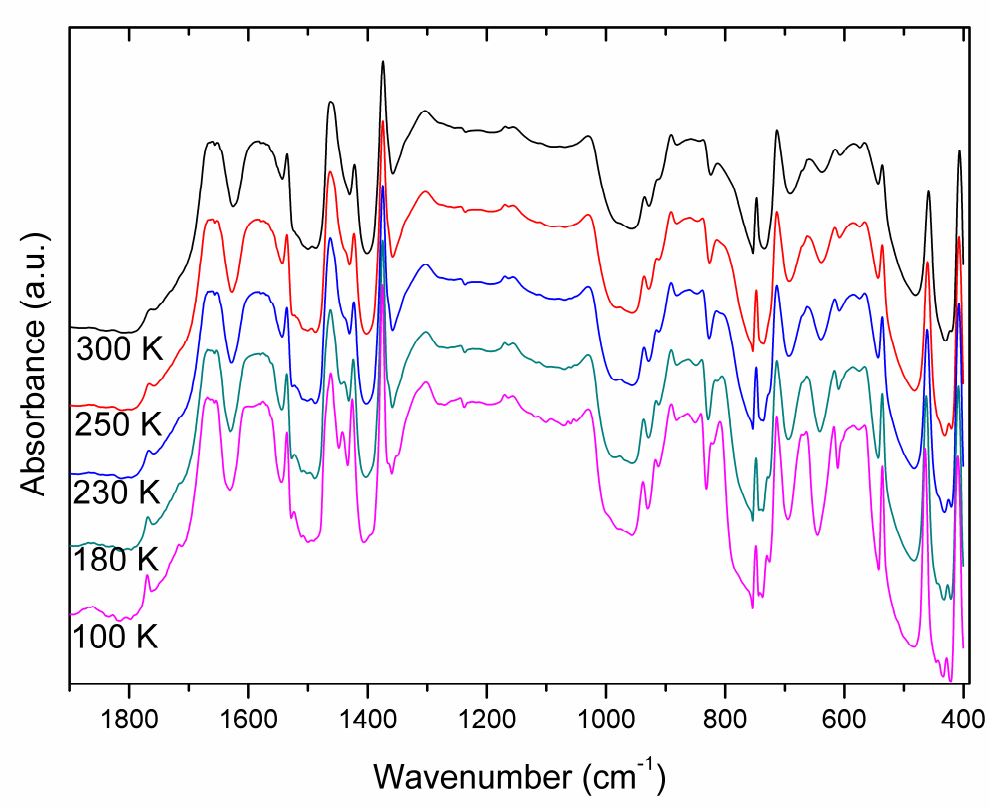

Figure 22S: FT Raman spectra of **2-athdClO$_4$** at different temperatures.

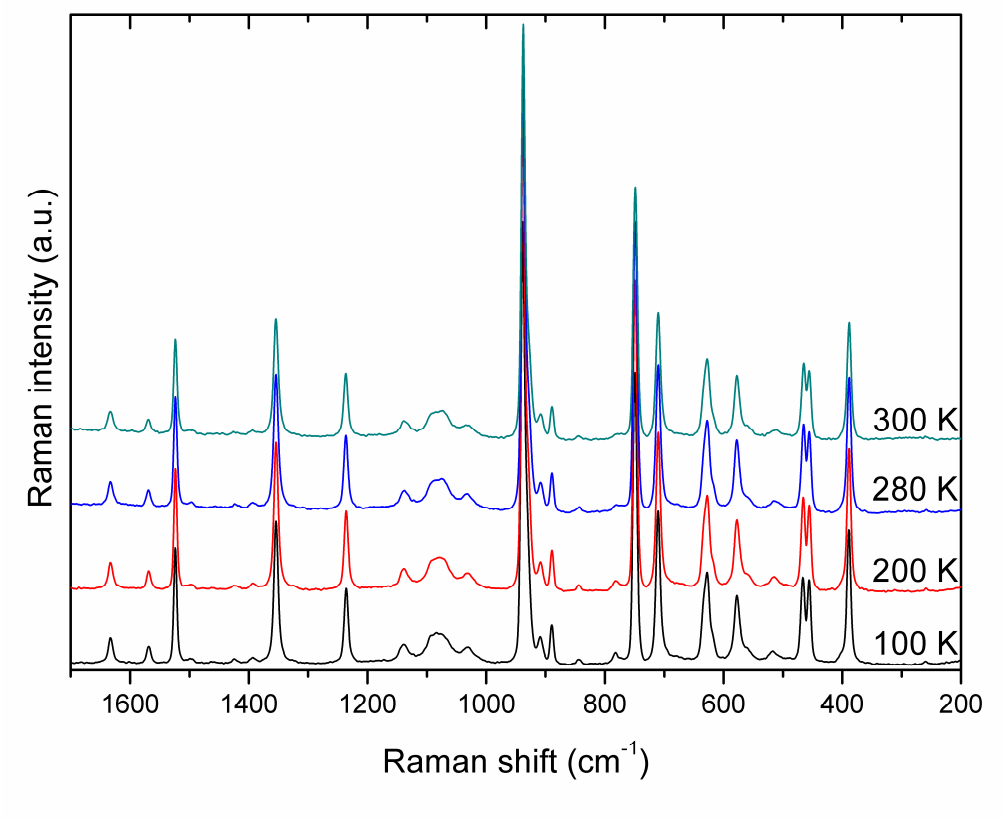

Figure 23S: FTIR spectra of **2-athdClO$_4$** at different temperatures.

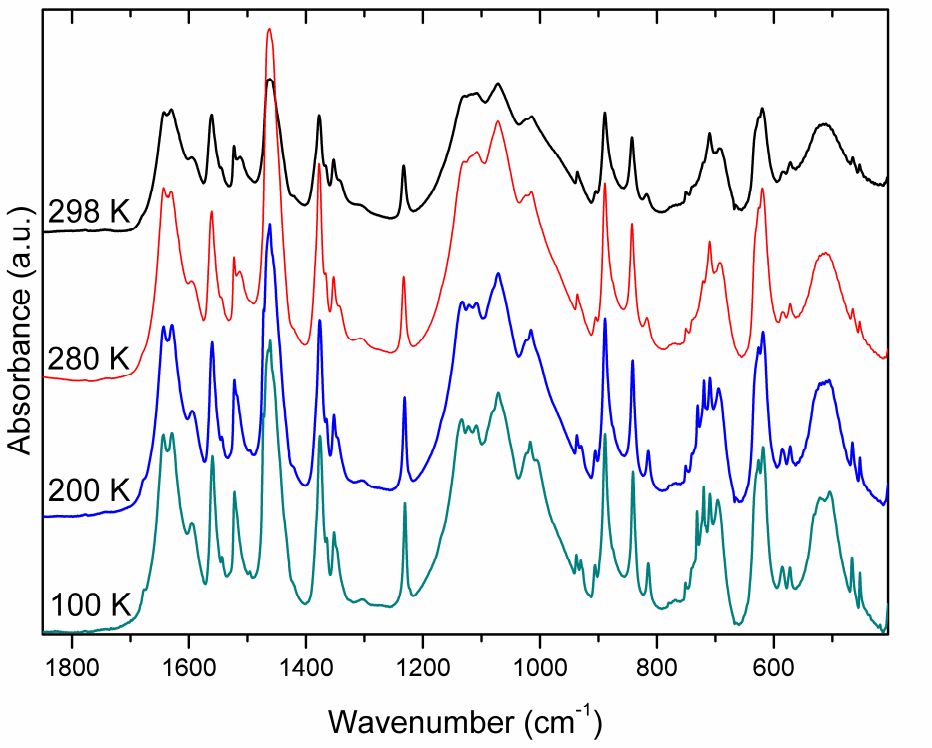

Figure 24S: FT Raman spectra of **2-athd$_2$ClO$_4$** at different temperatures.

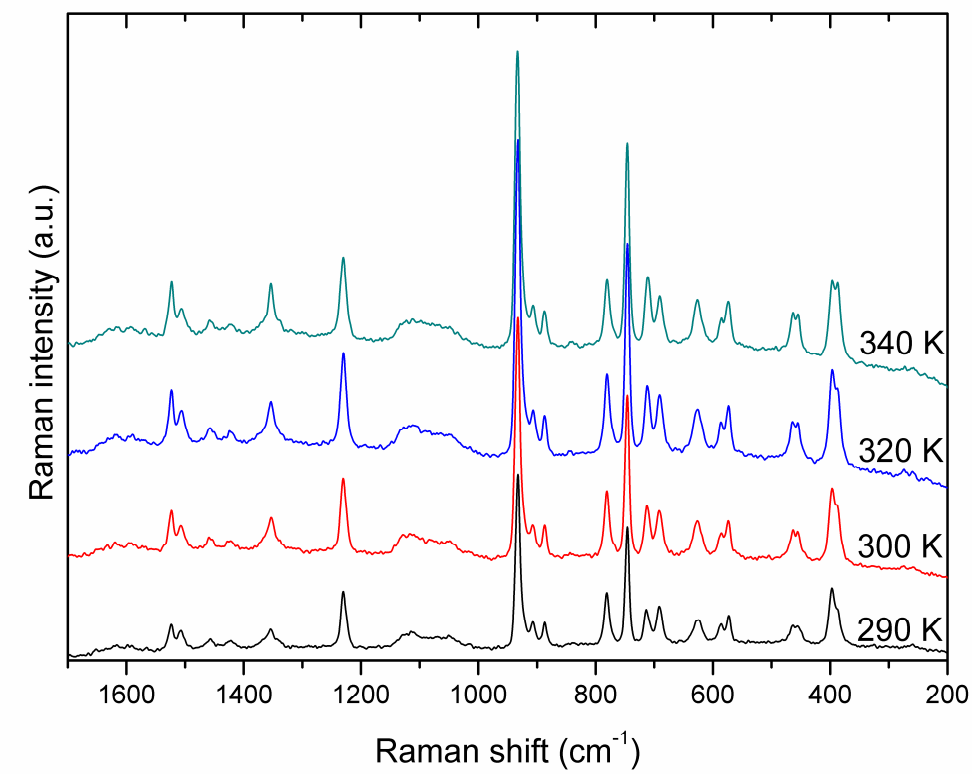

Figure 25S: FTIR spectra of **2-athd$_2$ClO$_4$** at different temperatures.

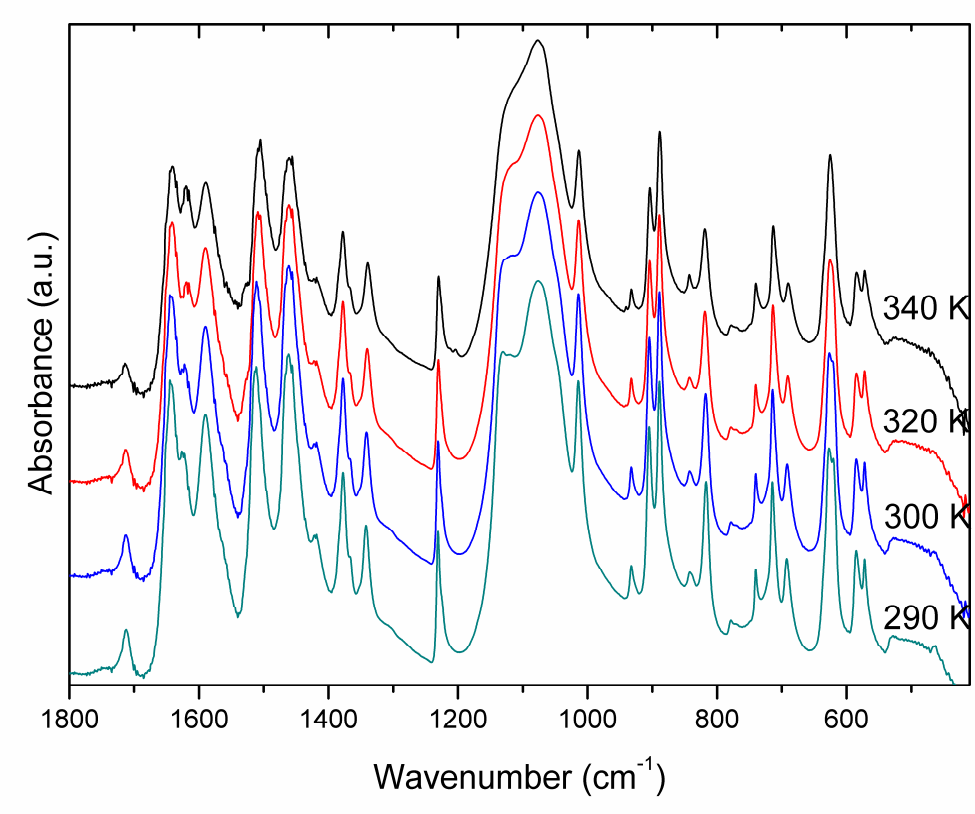

Figure 26S: Temperature dependence of the donor...acceptor (N3...O1) distance of the N-H...O hydrogen bond in **2-athdHSO$_4$**. Dashed line represents ideal linear dependence.

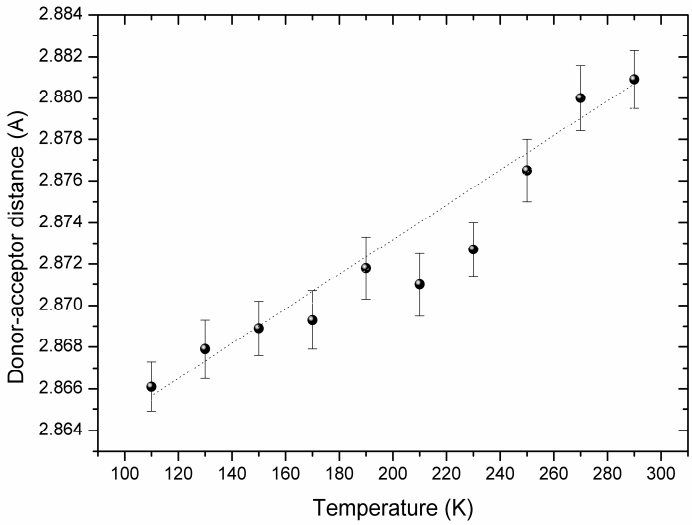

Figure 27S: Temperature dependence of the donor...acceptor (N6...O3^b) distance of the N-H...O hydrogen bond in **2-athdClO$_4$**. Dashed line represents ideal linear dependence.