

Supplementary material

Supramolecular nature of multicomponent crystals formed from 2,2'-thiodiacetic acid with 2,6-diaminopurine or N9-(2-Hydroxyethyl)adenine

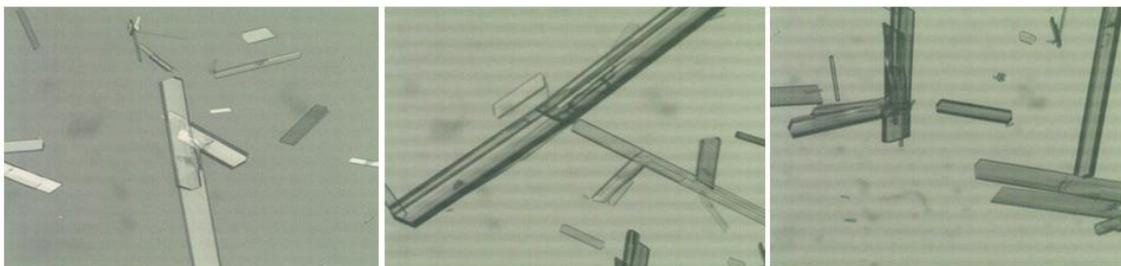
Jeannette Carolina Belmont-Sánchez,¹ Duane Choquesillo-Lazarte,² María Eugenia García-Rubiño,³ Antonio Matilla-Hernández,¹ Juan Nicolás-Gutiérrez,¹ Alfonso Castiñeiras,^{4,*} Antonio Frontera⁵

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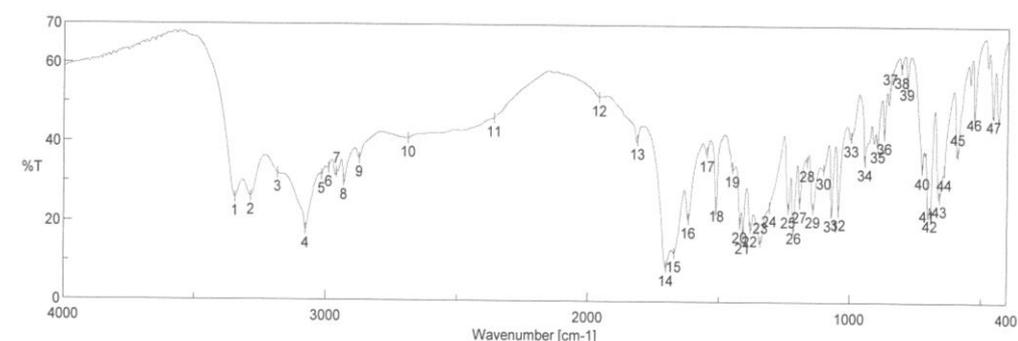
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SM1. Crystals of $[(H_9Heade^+)(Htda^-)]$, **1**.

Three photos taken from dissolution using polarized light.



S2. FT-IR spectrum of $[(\text{H9Heade}^+)(\text{Htda}^-)]$, 1.



[Comments]
 Sample name
 Comment
 User
 Division
 Company

[Measurement Information]
 Model Name FT/IR-6300typeA
 Serial Number A014961024
 Measurement Date 24/09/2020 13:03

[Detailed Information]
 Creation date 24/09/2020 13:04
 Date modified 24/09/2020 13:15

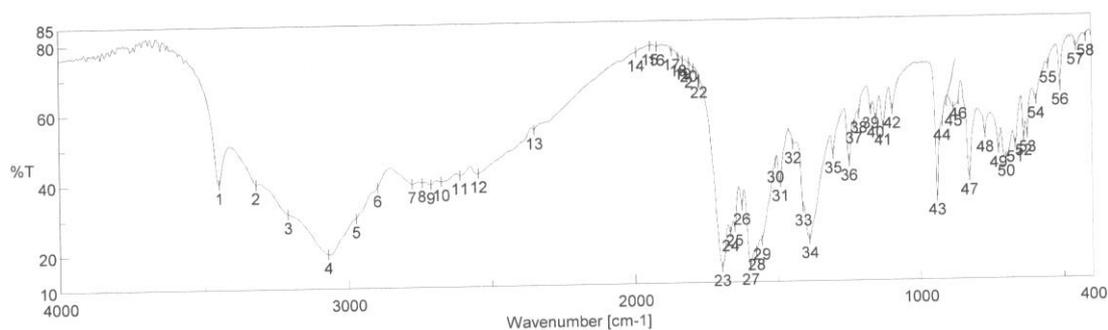
Light Source Standard
 Detector TGS
 Accumulation 250
 Resolution 4 cm-1
 Zero Filling On

Universidad de Granada

[Result of Peak Picking]

No.	Position	Intensity									
1	3346.85	25.8278	2	3286.11	26.1388	3	3183.9	31.9825	4	3077.83	17.822
5	3017.09	31.5049	6	2990.09	33.2463	7	2960.2	32.2425	8	2933.2	30.0184
9	2874.38	35.7607	10	2687.32	40.853	11	2361.41	46.1118	12	1961.25	51.4987
13	1814.69	40.6359	14	1701.87	8.79292	15	1671.98	12.3455	16	1617.98	20.8418
17	1547.59	37.6702	18	1509.99	25.1798	19	1451.17	33.8374	20	1421.28	19.7925
21	1409.71	17.1302	22	1382.71	18.8702	23	1342.21	15.3393	24	1308.46	23.9639
25	1236.15	23.7005	26	1213.97	19.7392	27	1192.76	25.0113	28	1163.83	35.3991
29	1141.65	23.774	30	1100.19	33.5416	31	1071.26	22.8015	32	1044.26	23.1516
33	997.017	41.7009	34	944.949	35.6892	35	896.737	40.3044	36	872.631	42.3984
37	852.382	53.2422	38	808.992	59.2704	39	788.743	56.2663	40	727.996	33.7208
41	709.676	25.4879	42	698.105	22.9798	43	662.428	26.6234	44	644.108	33.369
45	593.968	37.927	46	531.293	48.6719	47	456.082	48.1124			

S3. FT-IR spectrum of $[(\text{H}_2\text{dap}^+)_2(\text{tda}^{2-})]\cdot 2\text{H}_2\text{O}$, 2.

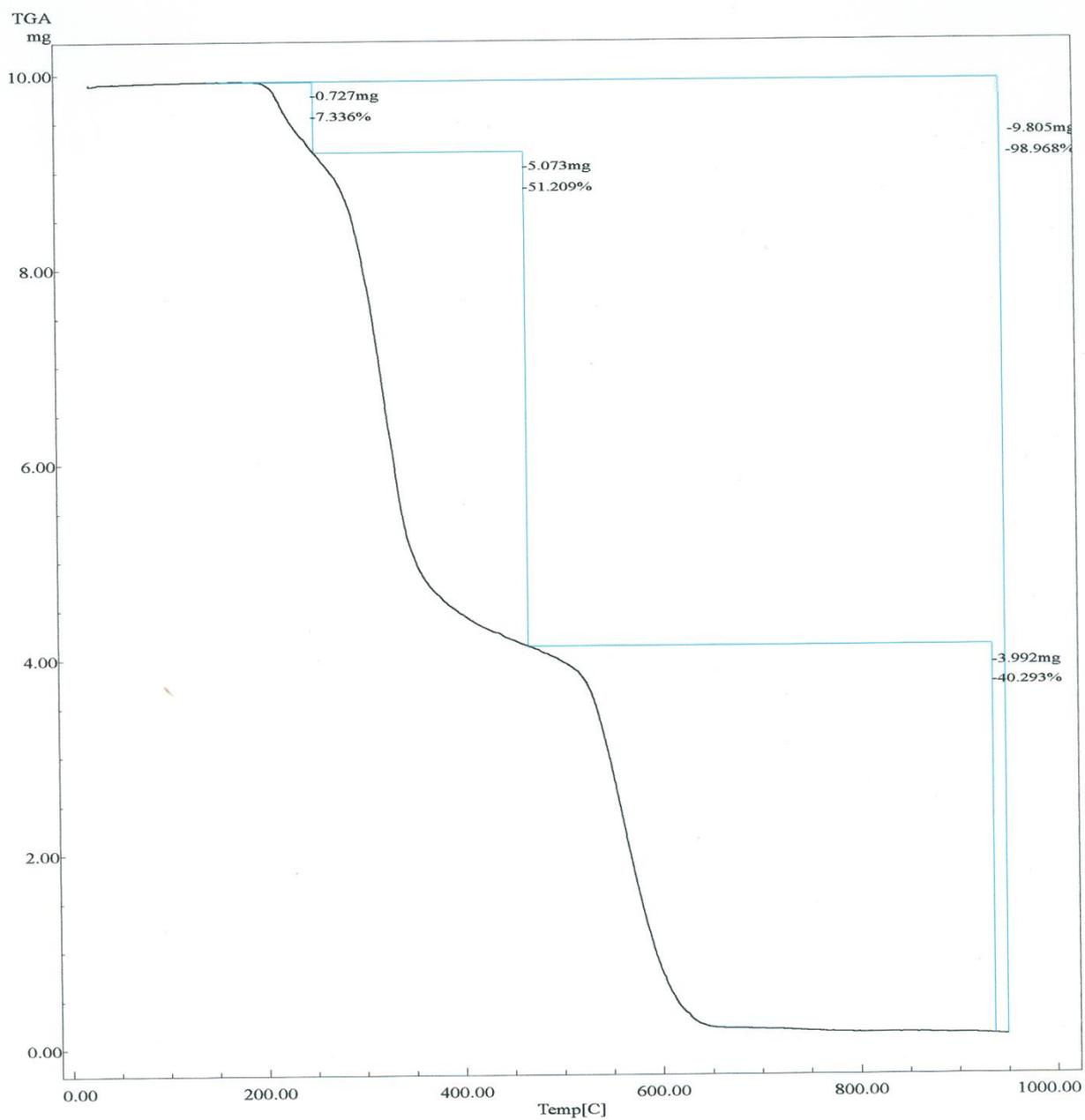


[Result of Peak Picking]

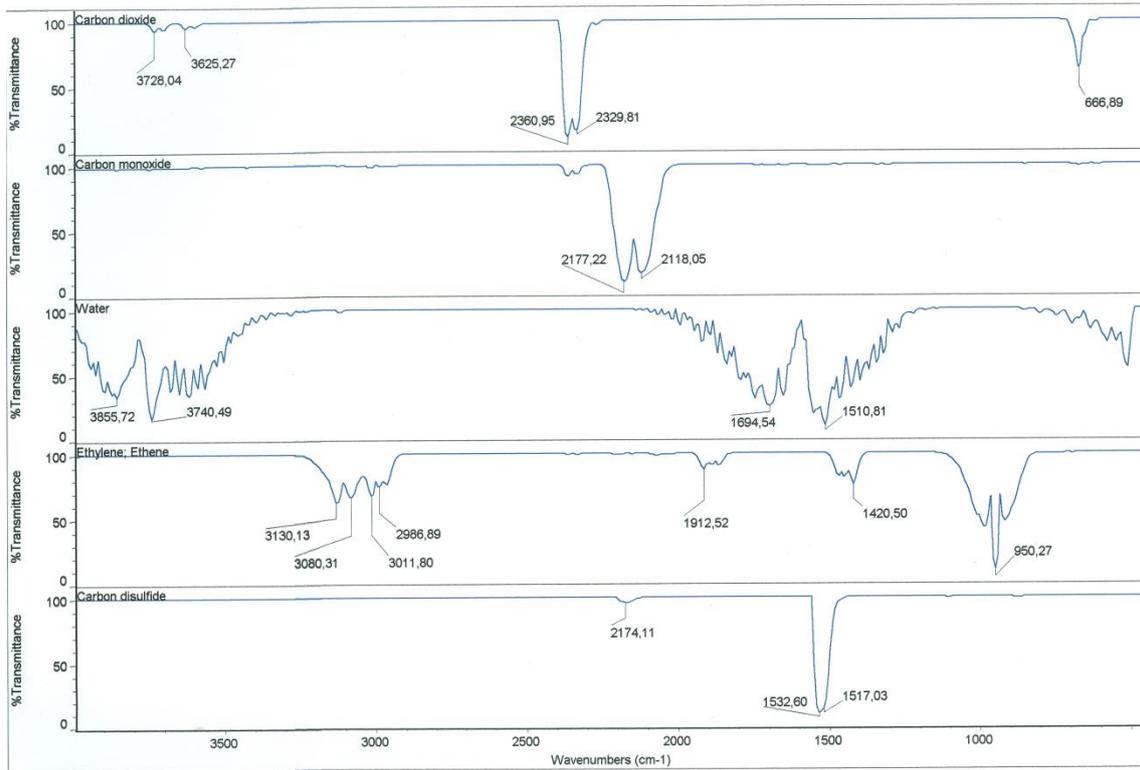
No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
①	3448.1	40.1847	②	3319.86	40.0203	③	3208.97	31.4661
④	3071.08	19.8961	⑤	2972.73	29.997	⑥	2896.56	38.6918
⑦	2776.03	39.5604	8	2742.28	39.9196	9	2711.42	39.3353
10	2674.78	40.1364	11	2610.18	41.8786	12	2545.58	42.2944
13	2348.87	54.3515	14	1992.11	76.0618	15	1942.93	77.7301
16	1920.75	77.612	17	1867.72	76.2356	18	1844.58	74.4644
19	1829.15	73.5038	20	1807.94	72.8565	21	1792.51	71.1755
22	1772.26	68.1629	23	1697.05	14.477	24	1667.16	24.3562
②⑤	1652.7	25.9281	②⑥	1626.66	31.8799	②⑦	1597.73	14.7093
②⑧	1576.52	18.9009	②⑨	1558.2	21.842	③⑩	1508.06	43.7791
31	1491.67	38.4566	32	1446.35	49.1221	33	1412.6	31.3347
③④	1390.42	22.1055	35	1306.54	46.1441	36	1250.61	44.0036
37	1232.29	54.4746	38	1214.93	57.4845	39	1172.51	58.6732
40	1155.15	56.0337	41	1129.12	53.8631	42	1096.33	58.632
④③	940.128	33.8832	44	921.807	54.961	④⑤	882.274	58.944
④⑥	864.917	60.9789	47	829.241	39.4057	48	772.351	51.4607
49	726.068	47.0549	50	700.034	44.4952	51	668.214	48.4501

S4. Thermogravimetric analysis (TGA) of [(H9Heade+)(Htda-)], 1.

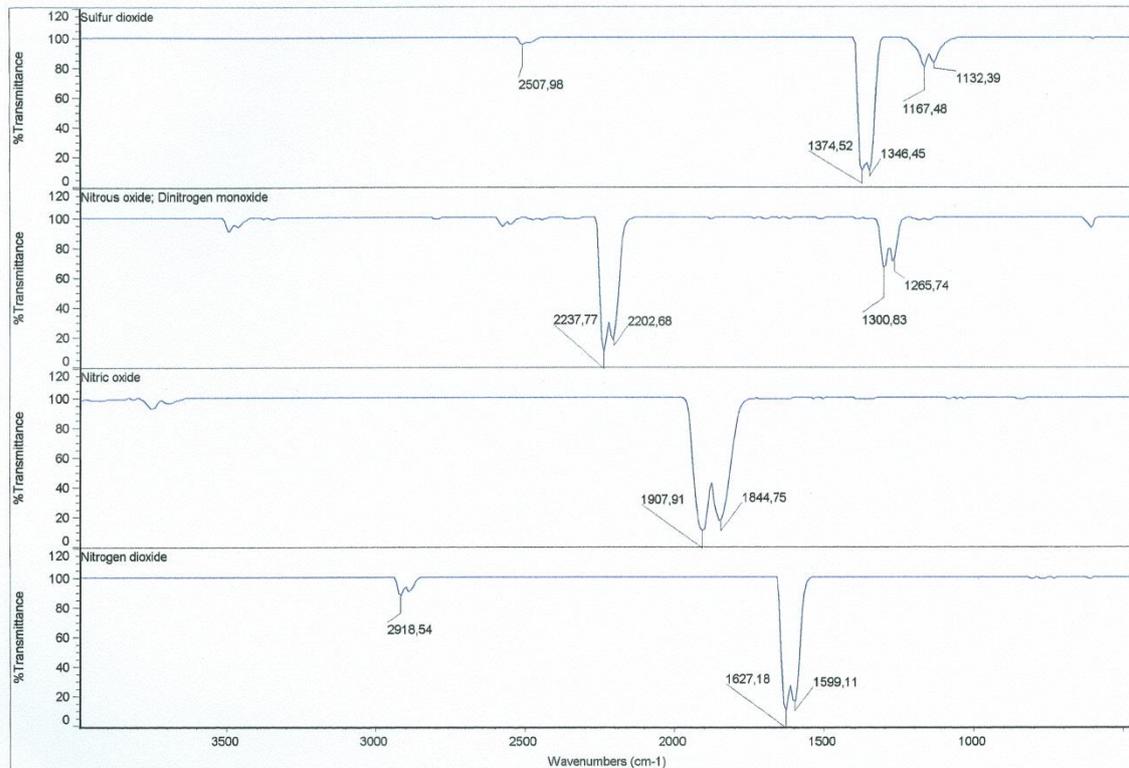
S4.1. Weight loss and data to estimate the final residual for 1.



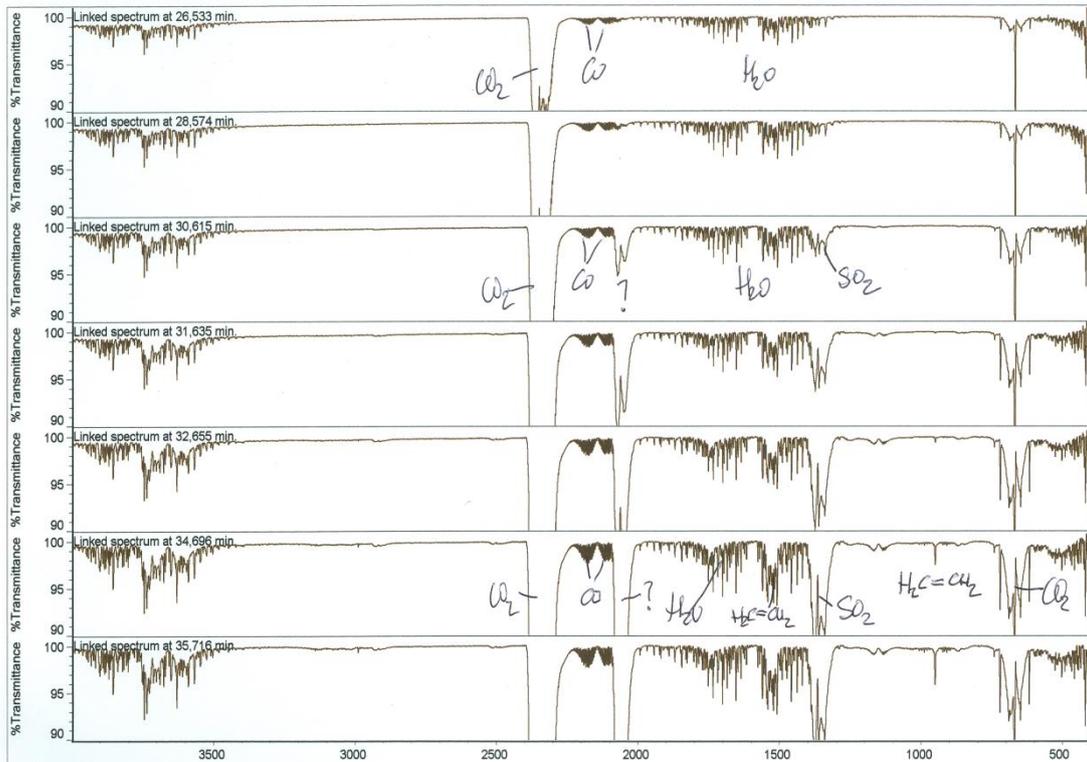
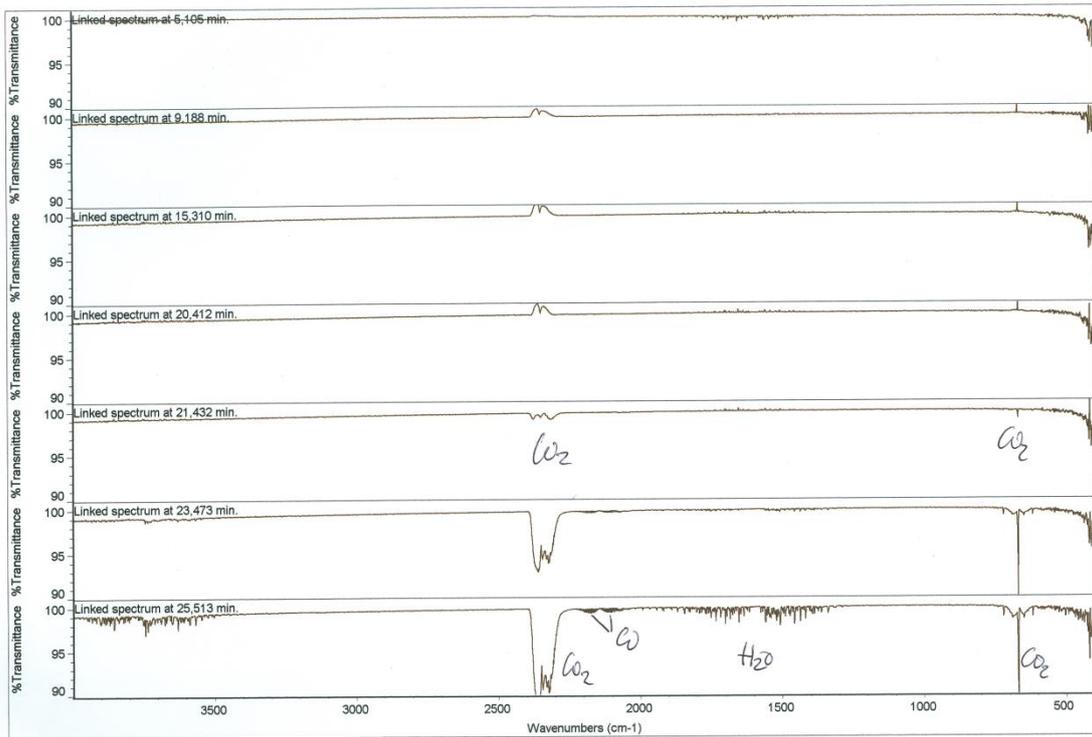
S4.2. FT-IR spectra of standard gases to identify evolved gases in TGA of 1.

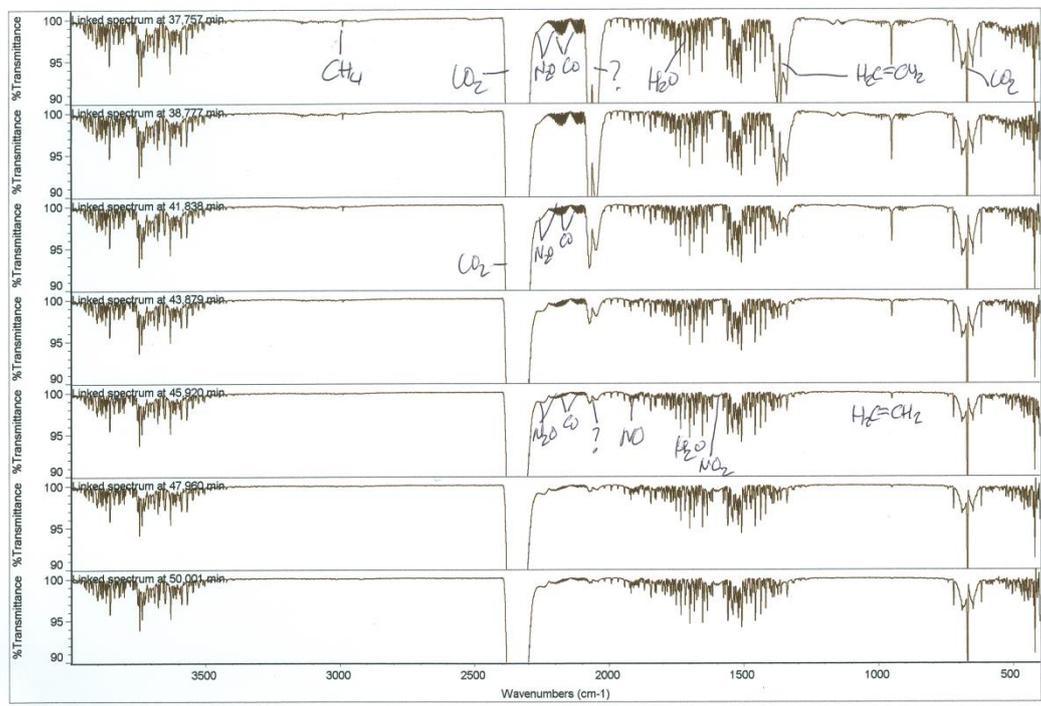
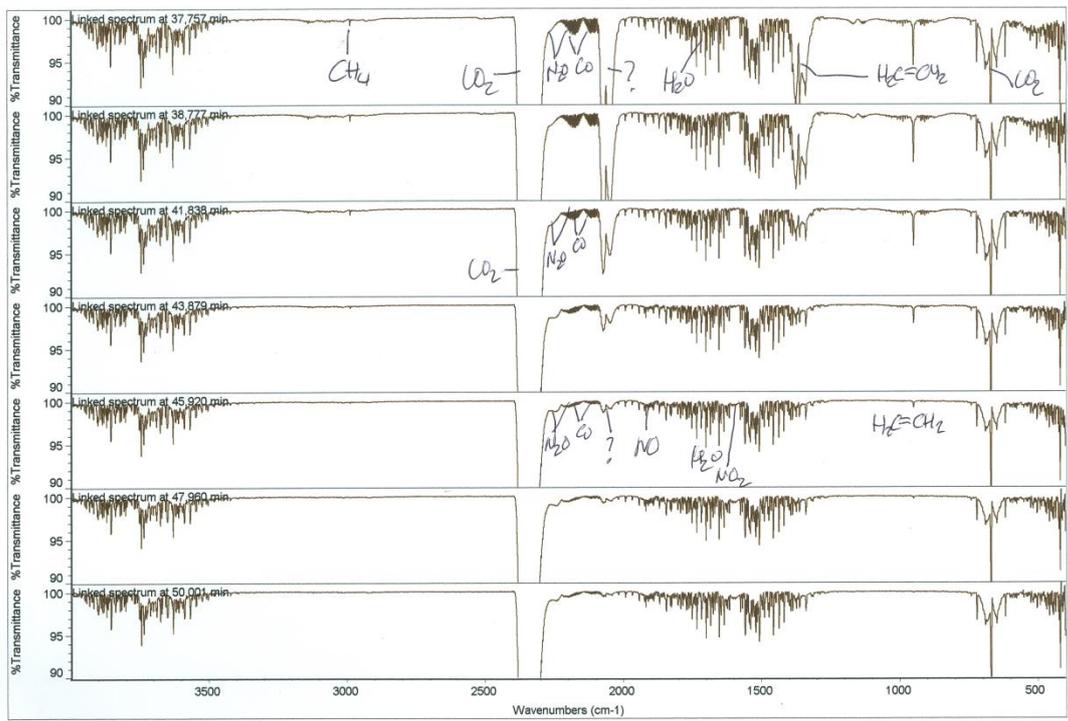


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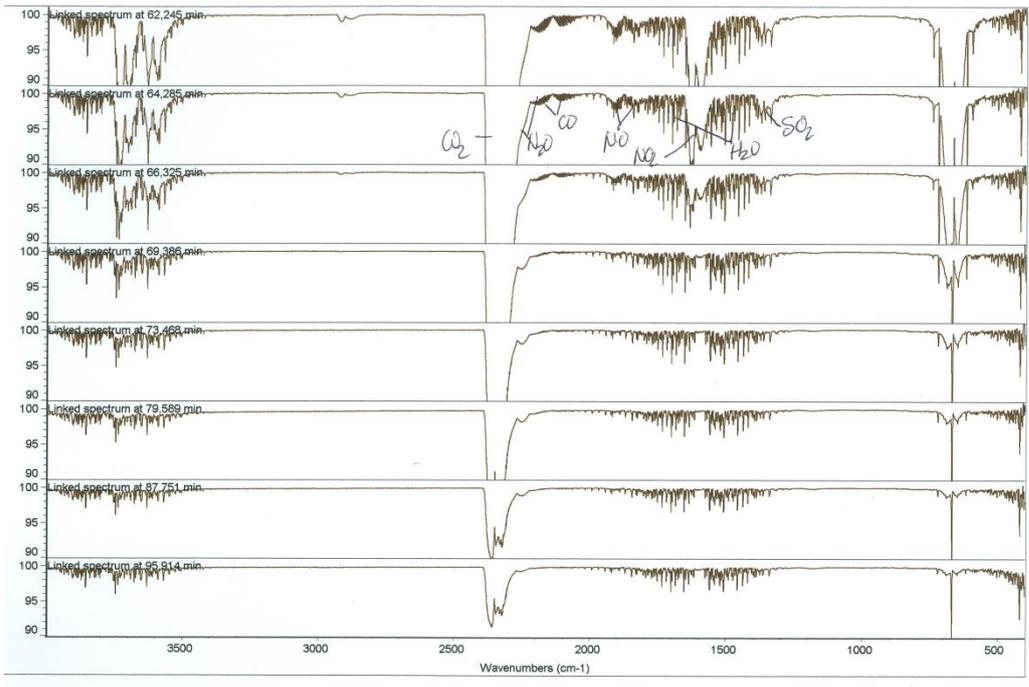


S4.3. Time-spaced FT-IR spectra to identify the evolved gases in the TGA of 1.

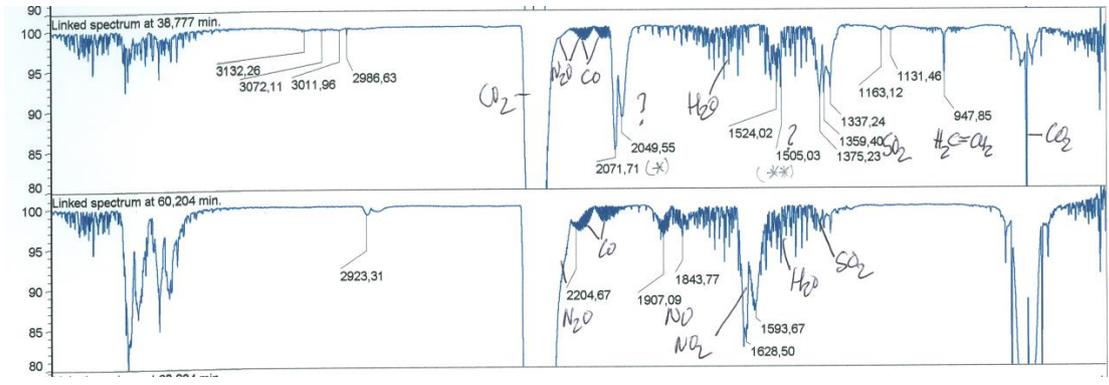




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S4.4. Selected FT-IR spectra to identify the evolved gases in the TGA of 1. Second (up) and third (down) steps.



S4.5. Summary of results and Comments on TGA of **1**.

Step	Temperature	Time	Lost weight (%)	Gases or final residue
	°C	min	Observed	
1	180-250	14-23	7.336	H ₂ O, CO ₂
2	250-465	23-44	51.209	H ₂ O, CO ₂ , CO, X**, SO ₂ , H ₂ C=CH ₂ , N ₂ O (t*)
3	465-650	44-66	40.293	H ₂ O, CO ₂ , CO, N ₂ O, NO, NO ₂
Residue	650-950	93	1.032	Undetermined

* t = Trace amounts. ** X = Unidentified gas.

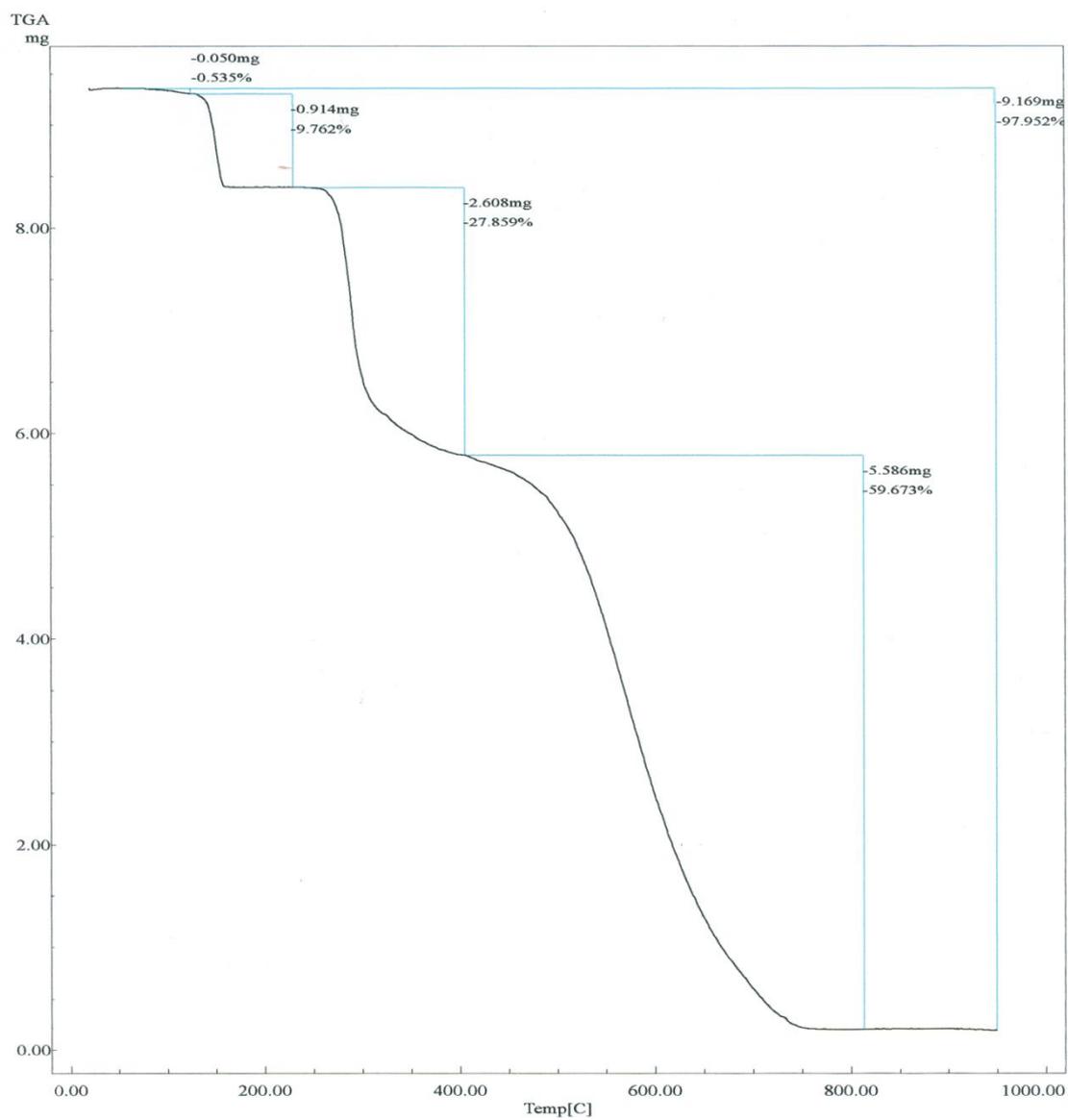
Comments:

Compound **1** is rather stable. Its decomposition begins at 180 °C, step 1 only giving of H₂O and CO₂. The evolved gases during the step 2 mainly suggest the burning of Htda⁻ counter-anion, with perhaps a partial decomposition of the N9-(2-hydroxyethyl) arm from the H9heade⁺ cation, related to the production of ethylene and small amounts of N₂O. Finally, the last step produces (among others gases) the three common N-oxides, mostly due to the burning of the purine moiety from 9heade. A pair of typical peaks near to 970 and 930 cm⁻¹ related to the loss of ammonia have not been observed. Moreover, this should not be attributed to the high temperatures (> 450 °C) of step 3, which the three favor the formation of N-oxides. Indeed the thermogravimetric analysis of *molecular* 9heade (here not shown) revealed a first weight loss > 96% (215-420 °C) evolving H₂O, CO₂, CO and N₂O (without produce ammonia!) and a second step (420-625 °C) with production such gases plus NO and NO₂. Most of compound **1** weight loss occurs below 700 °C. In addition, the chemical purity of the tested sample agrees of the low final residue (~1 %) at 950 °C!

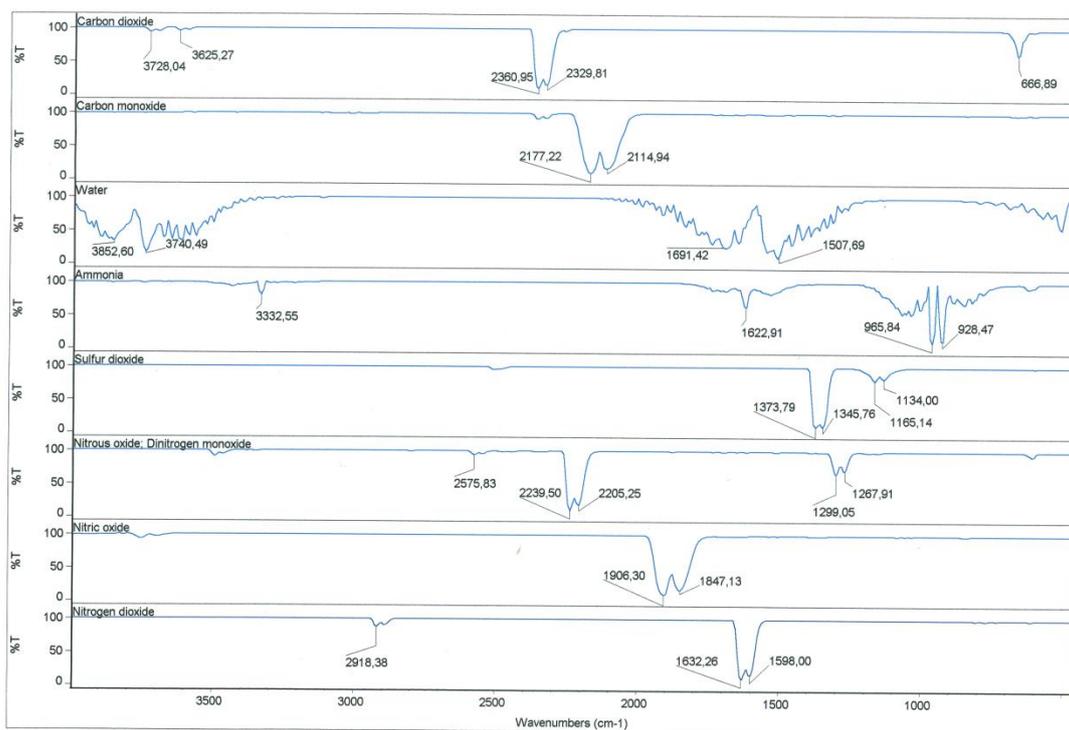
Comments:

*Compound **1** start the decomposition (180-250 °C, 7.34% of weight loss) evolving H₂O and CO₂, followed by a sharp step (250-465 °C, 51.12 % of weight loss) with formation of H₂O, CO₂, CO, SO₂, H₂C=CH₂ and probably HSCN plus some N₂O. A third step 465-650°C, 40.19% of weight loss) yields H₂O, CO₂, CO, and N-oxides (N₂O, NO and NO₂) but not NH₃. A stable but small residue is formed (1.16% or 1.03% at 650 or 950 °C). This data are consistent to a partial overlapped burning of the both ligands as well as the expected stability of the purine moiety of 9heade.

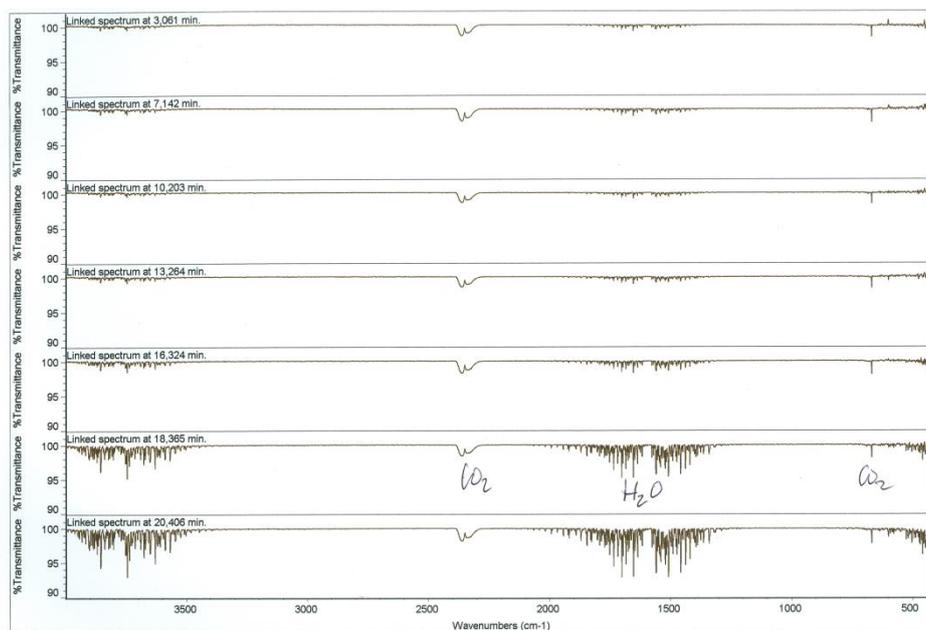
S5. Thermogravimetric analysis (TGA) $[(\text{H}_2\text{dap}^+)_2(\text{tda}^{2-})]\cdot 2\text{H}_2\text{O}$ (2).

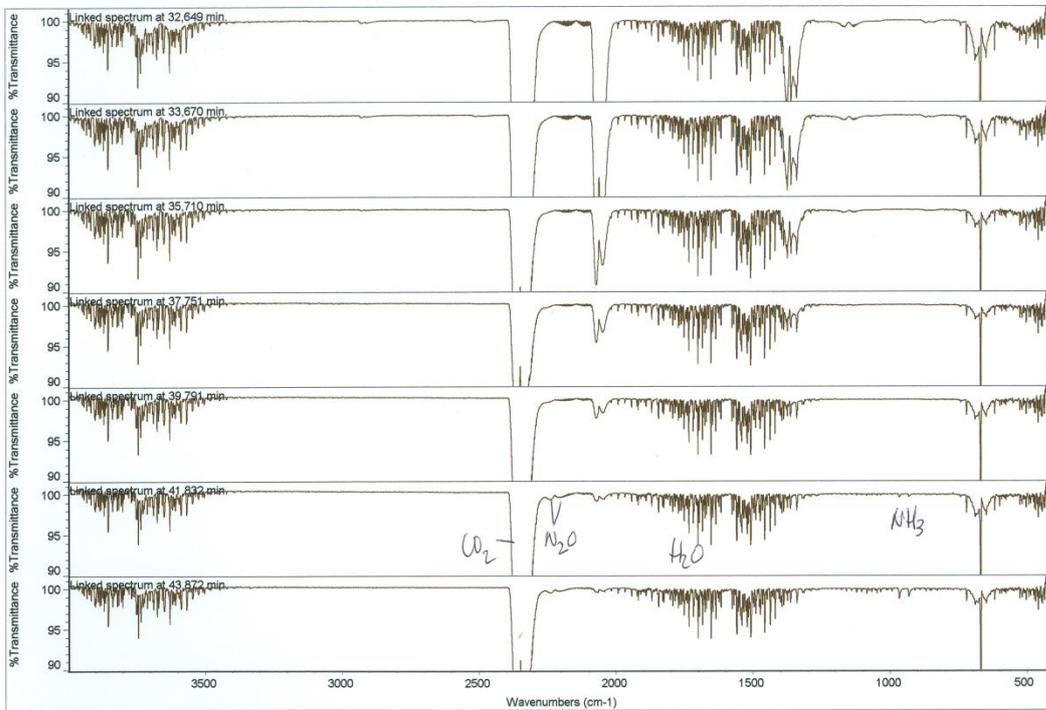
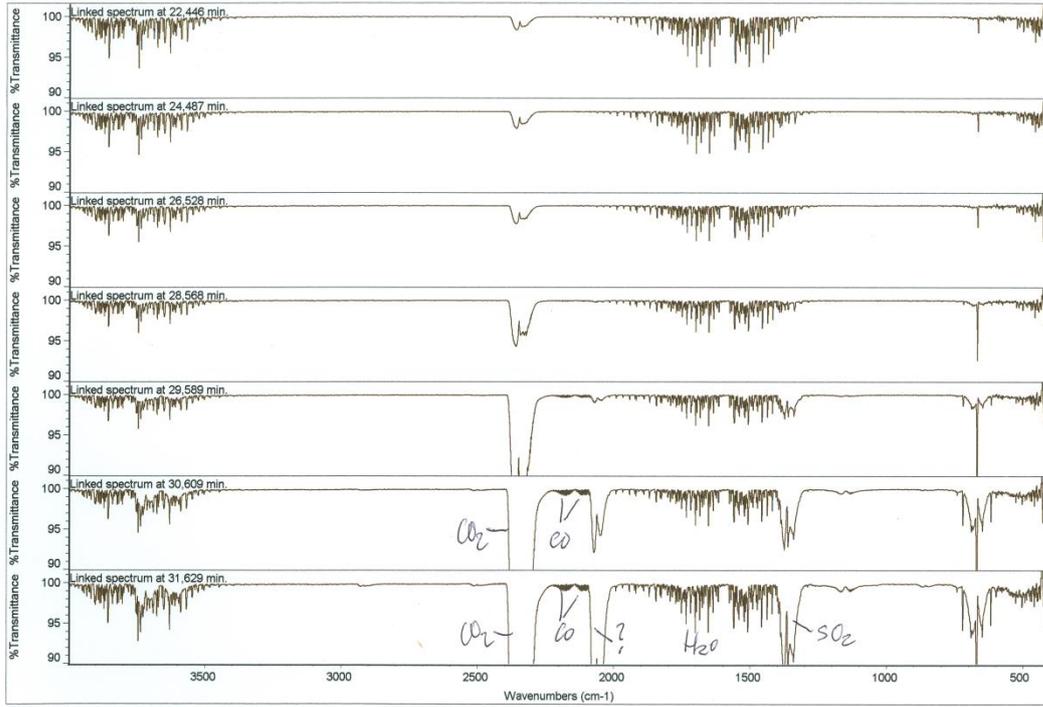


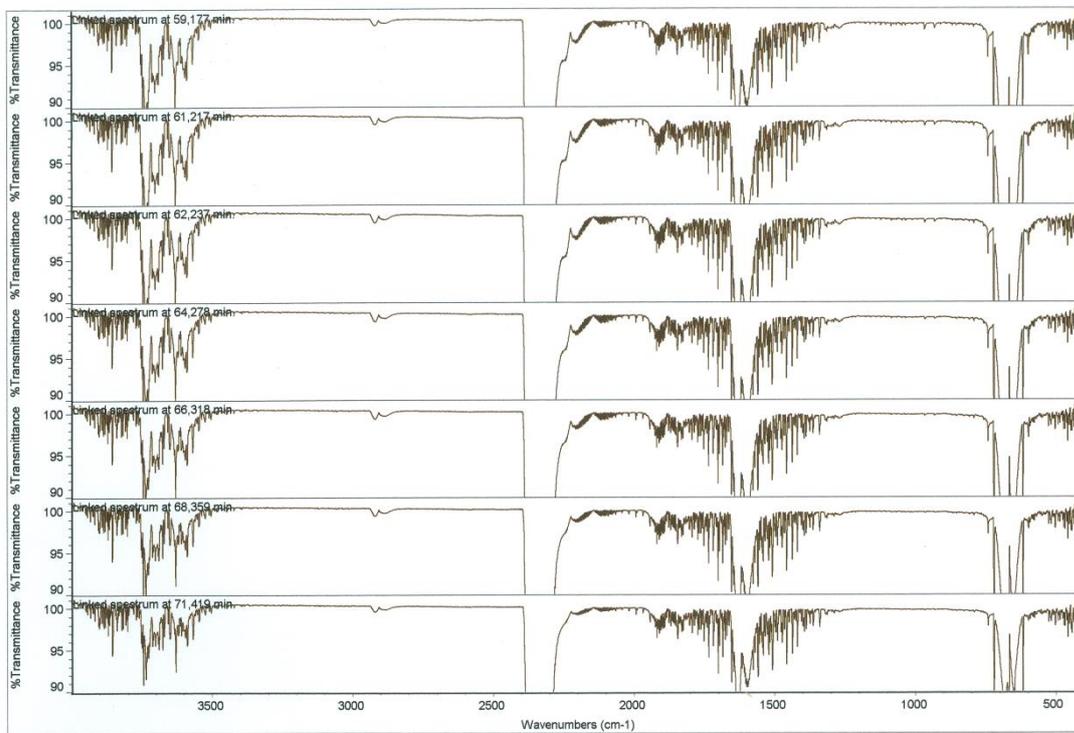
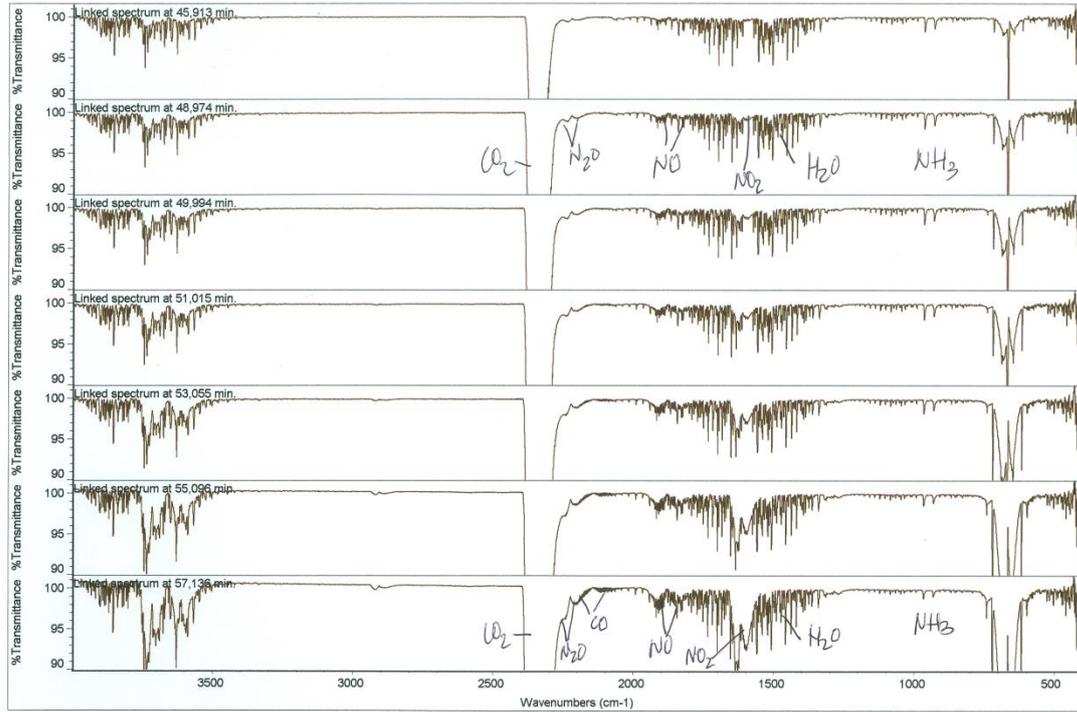
S5.2. FT-IR spectra of standard gases to identify evolved gases in TGA of 2.

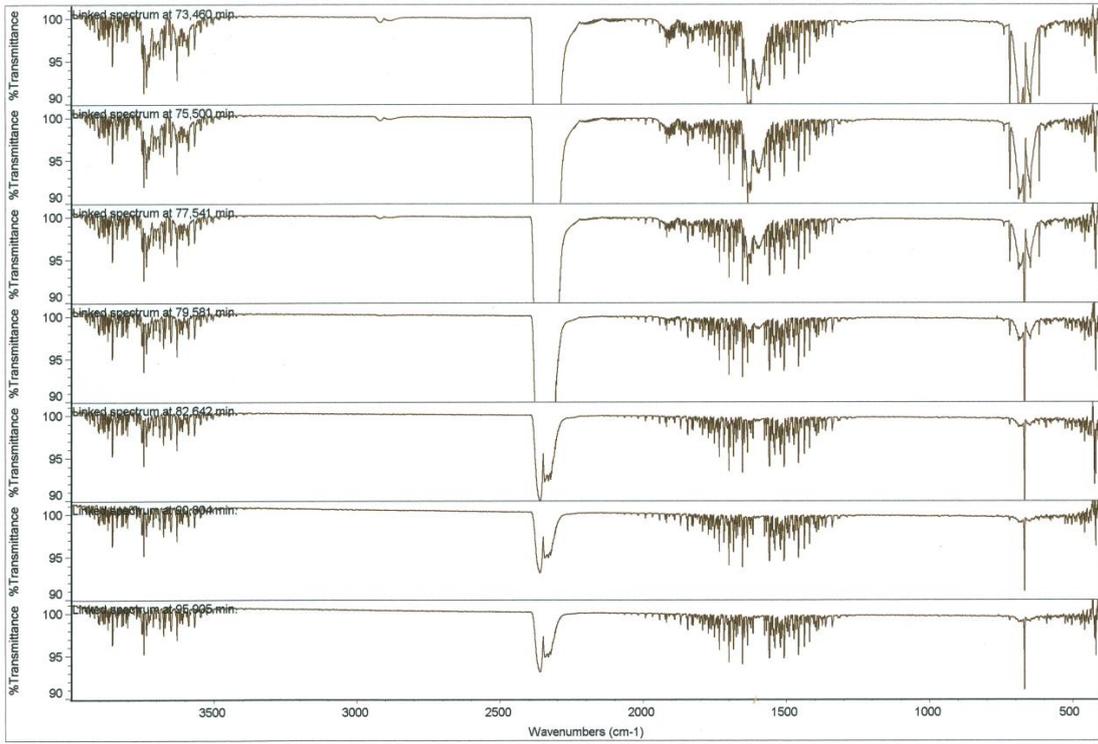


S5.3. Time-spaced FT-IR spectra to identify the evolved gases in the TGA of 1.

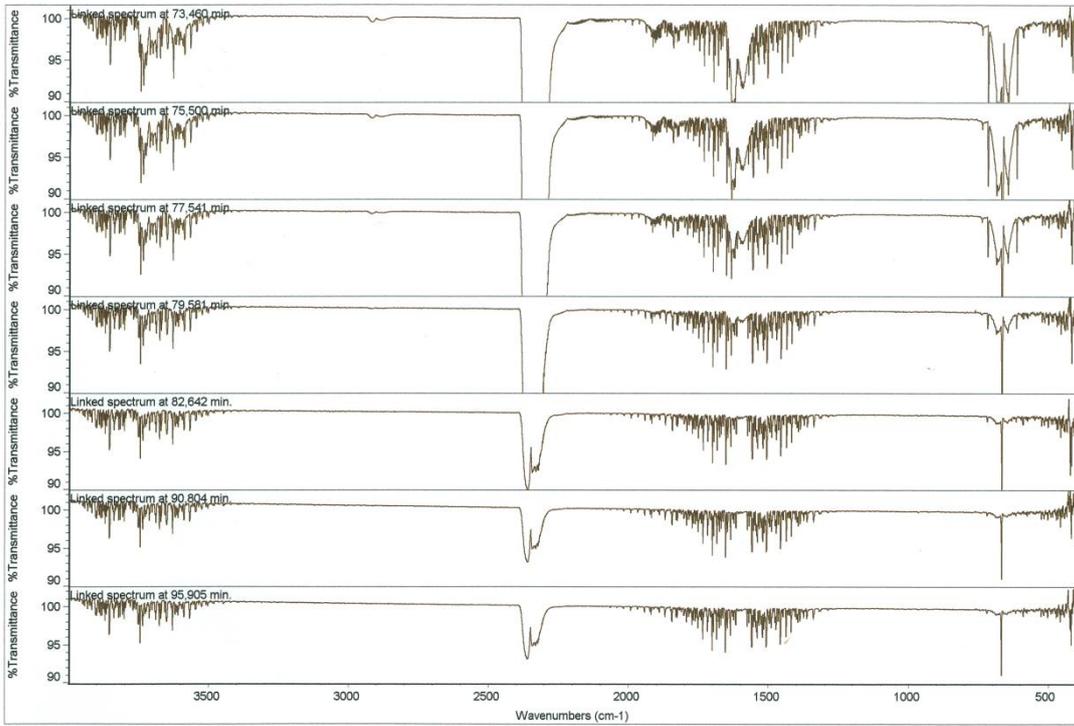




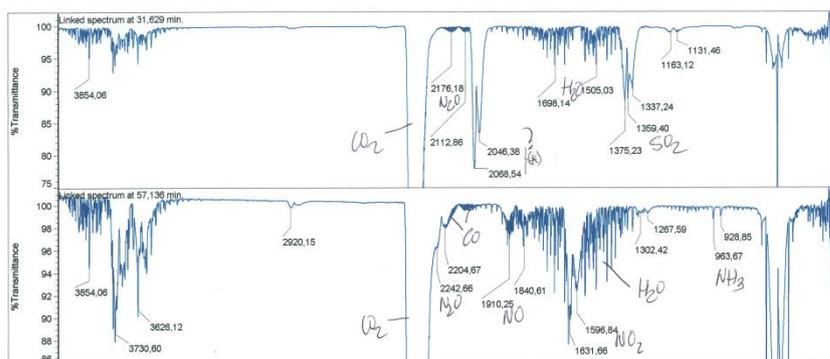




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S5.4. Selected FT-IR spectra to identify the evolved gases in the TGA of 2.
Second (up) and third (down) steps.



S5.5 Summary of results and Comments on TGA of 2.

Step	Temperature °C	Time min	Lost weight (%)		Gases or final residue
			Observed	Calculated	
0	r.t.- 135	0-12	0.535	<i>Humidity</i>	H ₂ O, CO ₂ (t*)
1	135-180	12-18	9.762	7.047	2 H ₂ O, CO ₂ (t*)
2	180-400	18-39	27.859	30.452	H ₂ O, CO ₂ , CO, X**, SO ₂
3	400~800	39-82	59.673	62.142	H ₂ O, CO ₂ , CO, NH ₃ , N ₂ O, NO, NO ₂
Residue	950	93	2.048	0	Undetermined

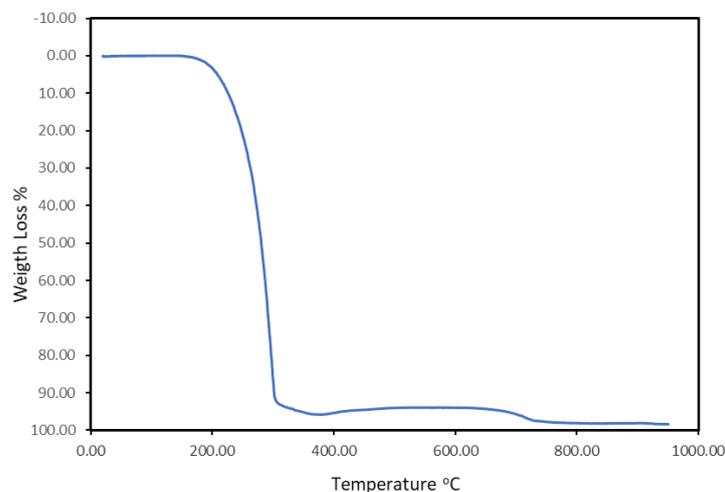
* t = Trace amounts. ** X = Unidentified gas.

Comments:

Initially, the studied sample of compound **2** (9.361 mg) leaves a little amount of weight (so-called step 0, perhaps humidity < 0.6 %). The thermal decomposition of compound **1** mainly starts removing its well retained water (step 1, 135-180 °C, calculated data only for 2 H₂O). The burning of organics occurs in two additional steps. The first one (step 2, 180-400 °C) represents a weight loss close to the expected for the burning of tda²⁻ ion (30.45 %) and the evolved gasses also agree reasonably. Indeed, during this step an unidentified X gas is evolved and we have verified that it is also leaved in the thermogravimetric analysis of free H₂tda acid (here not shown). The weight loss during last step 3 (400-800 °C) is also close to the estimated value for 2 H₂dap⁺ ions (62.142 %). Again, the evolved gasses are in accordance to this suggestion. These steps leave a final residue of 2 % (at 900 °C). The weight loss of steps 1-3 plus the final residue (at 950 °C) nearly represent (99.342 %) the total sample weight estimated for compound **2** (without humidity).

S.6. Thermogravimetric analyses (TGA) of used reagents in this wok.

S6.1.TGA of 2,2'-Thiodiacetic acid, H₂tda (powder sample, 98%).



Step or Residue	Temperature °C	Time Minutes	Weight loss (%)	Gases or Residue (R)
1	130-325	12-31	-93.886	H ₂ O, CO ₂ , CO, SO ₂ , CS ₂ , X**
2	325-380	31-36	-1.851	H ₂ O, CO ₂ , CO, H ₂ CO, SO ₂ , CS ₂ , X**
R-380	380	36	-4.263	
3	380-550	36-54	+ 1.855	H ₂ O, CO ₂ , CO, H ₂ CO, SO ₂ , CS ₂ , X**
4	550-830	54-83	-1.222	H ₂ O, CO ₂ , CO, H ₂ CO, SO ₂
R-830	830	83	-1.89	Unidentified
R-950	950	93	-1.64	Unidentified

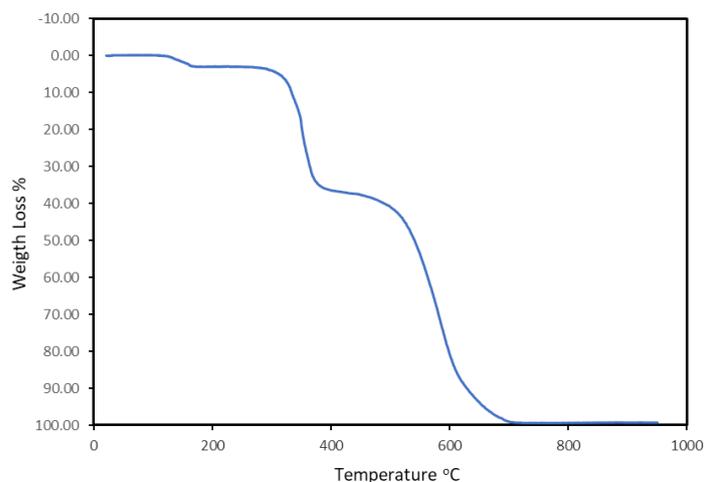
* Lost (-) or gained (+) weight. ** Unidentified gas.

Comments:

The TGA analysis of this compound shows a first step with a loss of weight ~94%, where at least the formation of CS₂ and SO₂ were identified as S-gases. The observed saw-tooth plot for the first derivative of loss weight plot versus temperature agrees to the melting point reported for this acid (128-131 C). During the second step formalin was also observed. The remaining material (~ 4.2 %) gains some weight and then follows its decomposition to yield a final residue (< 2%) in good agreement of the claimed purity by the supplier.

Selected reference: Vinciguerra¹, V., Bucci, R., Marini, F., Napoli, A., Thermal behaviour of iminodiacetic, oxydiacetic and thiodiacetic acids. *J. Therm. Anal. Calorim.* 83, 475–478 (2006). <https://doi.org/10.1007/s10973-005-6939-6>

S6.2. TGA of 2,6-diaminopurine, Hdap (powder sample, 98%).

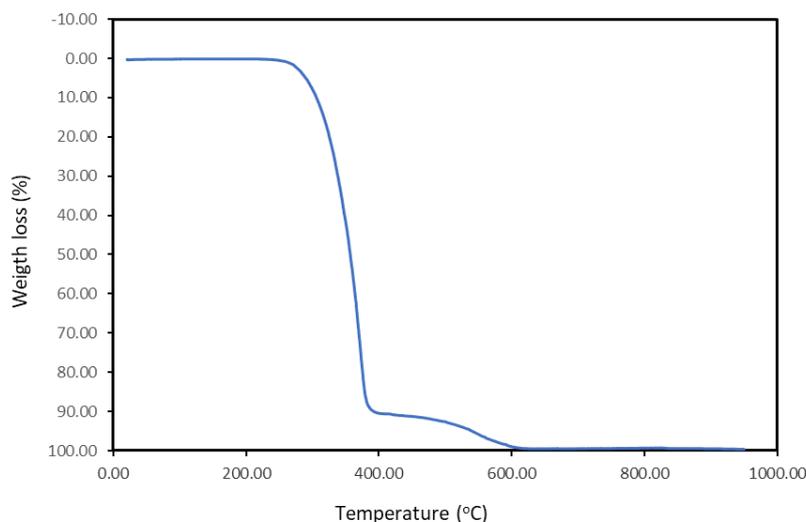


Step or Residue	Temperature °C	Time Minutes	Weight* (%)	Gases or Residue (R)
1	115-220	9-16	- 3.119	H ₂ O, CO ₂ (t),
2	240-335	16-33	- 9.097	H ₂ O, CO ₂
3	335-435	36-54	- 25.226	H ₂ O, CO ₂ , CO(t), NH ₃ , N ₂ O
4	435-775	54-83	- 61.288	H ₂ O, CO ₂ , CO(t), NH ₃ , N ₂ O, NO, NO ₂
R-830	775	83	0.712	Unidentified

Comments:

A first step shows water loss (with some CO₂). The second step starts over 240 °C, without appreciable production of N-gases. In this step the loss weight become relevant at about 300 °C, according to its reported melting point (302 °C). Other steps yield water, CO₂, some CO, NH₃ and N-oxides. Our results also shown that steps 3 plus 4 (> 85 % of weight loss) produce remarkable N-gases (including ammonia) and yield < 1 % of residue. We conclude that the studies sample has ~3 % of water.

S6.3. TGA of N9-(2-hydroxyethyl)adenine, 9heade (powder sample, 98%).



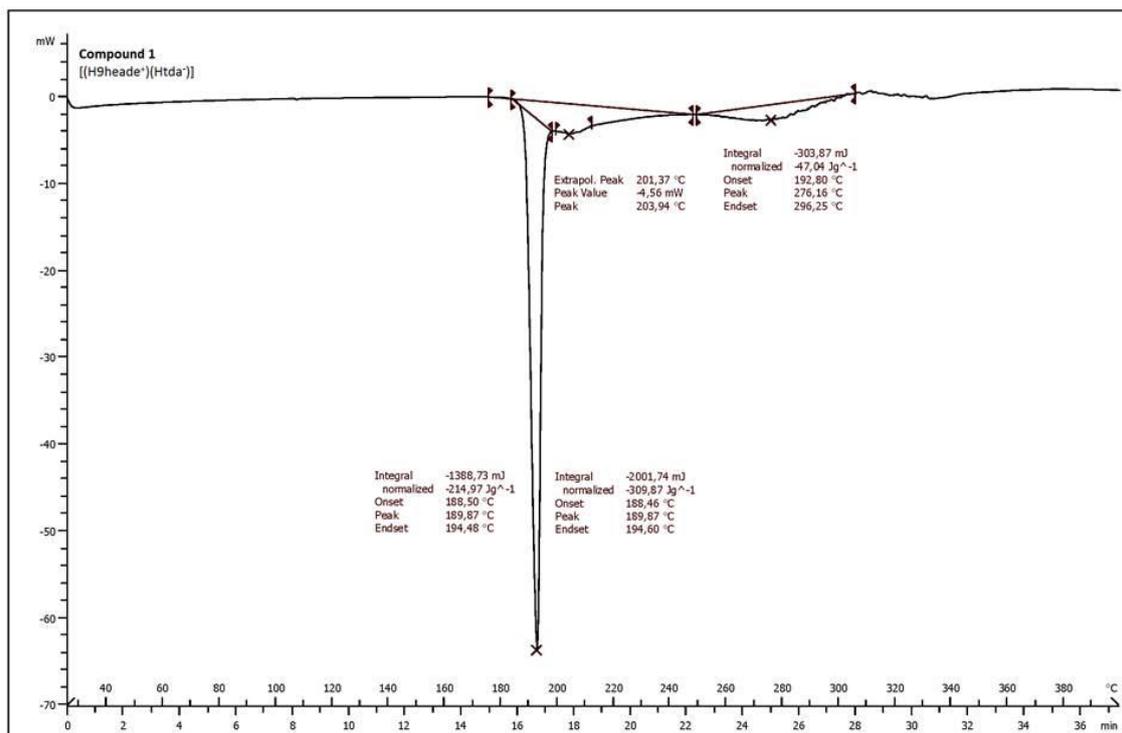
Step or Residue	Temperature °C	Time Minutes	Weight* (%)	Gases or Residue (R)
1	215-420	18-39	- 96.431	H ₂ O, CO ₂ , CO, N ₂ O (t)
2	420-625	39-63	- 3.380	H ₂ O, CO ₂ , CO(t), N ₂ O, NO,NO ₂
R-625	625	63	0.176	Unidentified
3	625-950	63-95	+0.679	H ₂ O, CO ₂ , CO(t), N ₂ O, NO,NO ₂ , SO ₂ (i)
R-950	950	95	0.855	Unidentified

(t) = Small quantity. (i) Unexpected gas, attributed to impurity.

Comments:

Almost the entire sample (> 96 %) melts and decomposes in the first step, in good agreement to reported melting point for 9heade (243 °C). Again the saw-tooth plot for the first derivative of loss weight plot versus temperature agrees to the melting point reported for this synthetic purine nucleoside (242 or 240-244 °C). The resulting material(s) follows the nearly complete decomposition to a residue (< 0.2 %) at 625 °C. This material gains weight up to a final residue (< 1 %) at 950 °C. In this last step the production of SO₂ from an *impurity* or *contaminant* is also observed. In any case, our results agree with the purity guaranteed by the supplier (98%). Interestingly, no ammonia is observed. No ammonia is observed among the evolved gases, in contrast to that usual featured in the TGA of adenine or 2,6-diaminopurine (see S6.2) and almost all of its metal complexes.

S7. DSC curve for [(H9Heade⁺)(Htda⁻)], 1.



S8. DSC curve for $[(\text{H}_2\text{dap}^+)_2(\text{tda}^{2-})]\cdot 2\text{H}_2\text{O}$, 2.

