Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

For

Hydrazinium lanthanide oxalates: synthesis, structure and thermal reactivity of $N_2H_5[Ln_2(C_2O_4)_4(N_2H_5)].4H_2O$, Ln = Ce, Nd.

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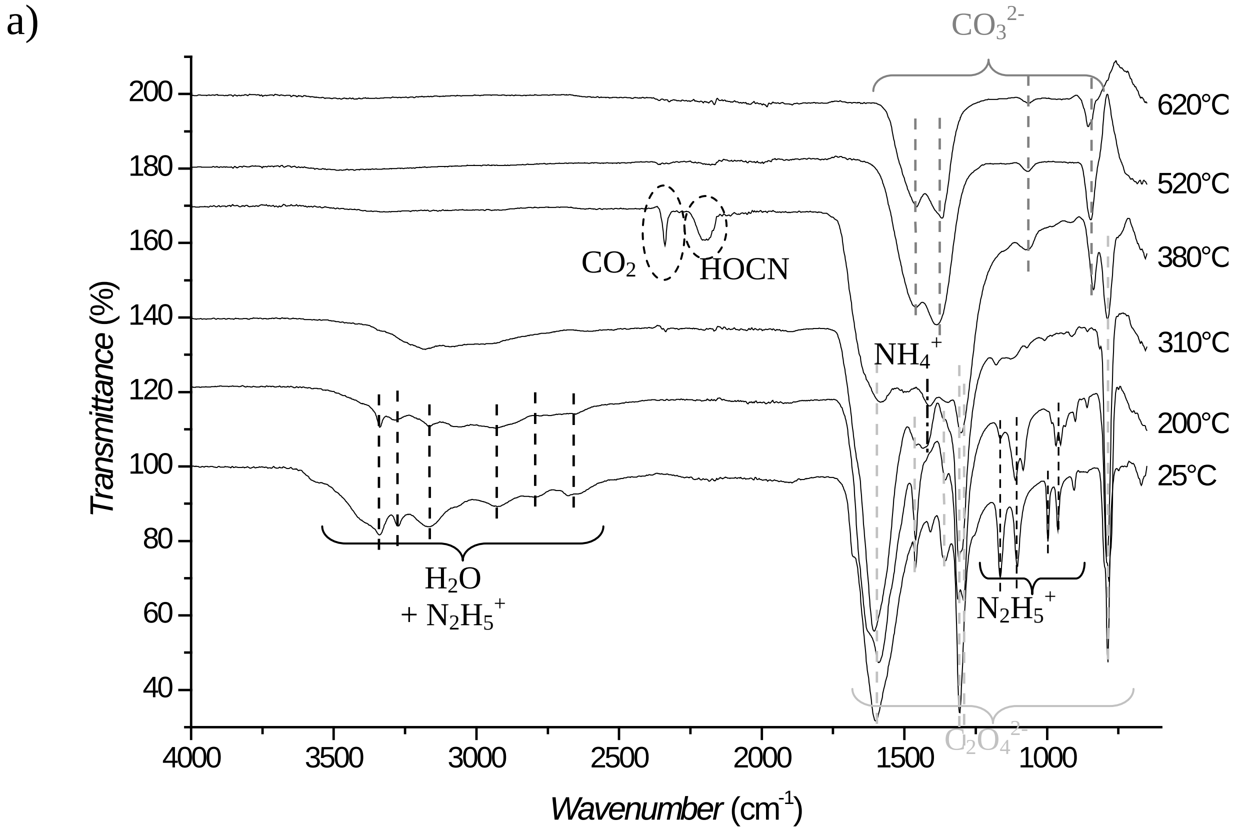
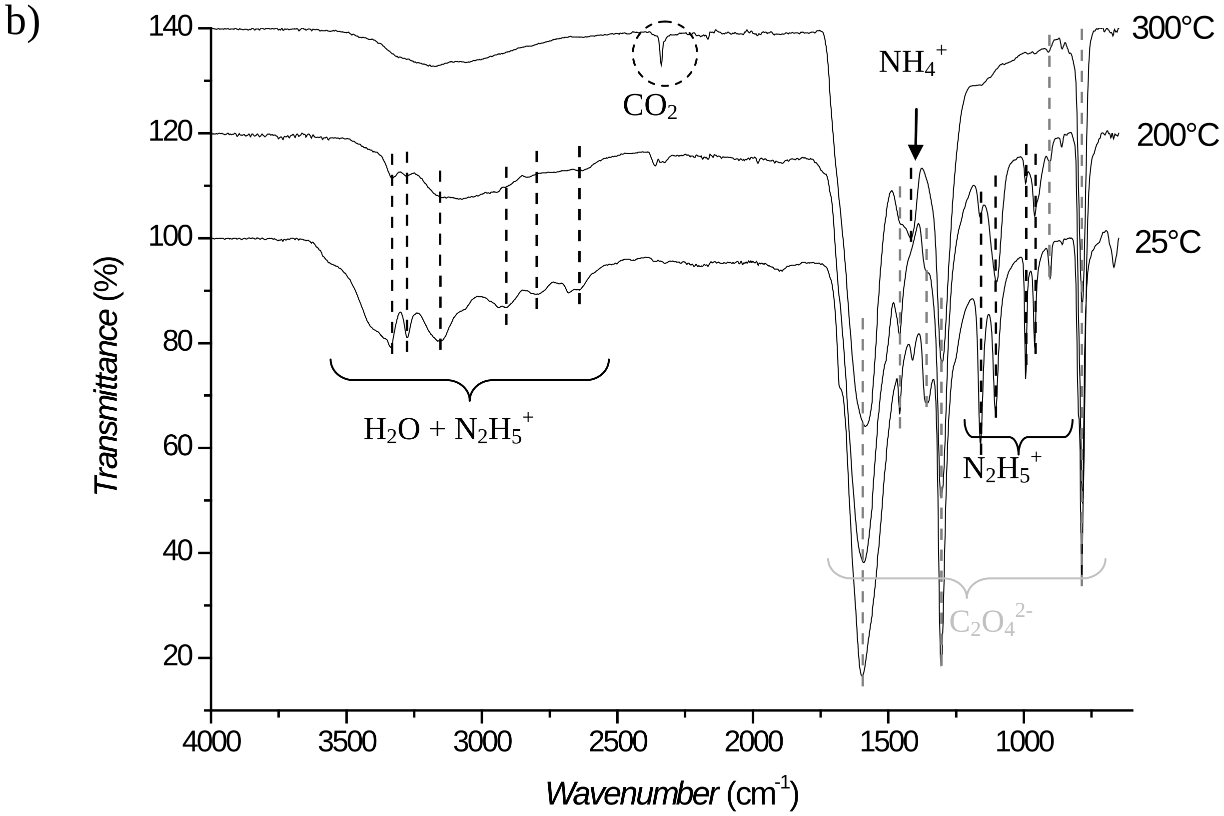

a)
CO3 2-
620°C
520°C
380°C
310°C
200°C
25°C
CO2
HOCN
NH4+
H2O
+ N2H5+
N2H5+
C2O4 2-
Transmittance (%)
Wavenumber (cm-1)


b)
300°C
200°C
25°C
CO2
NH4+
H2O + N2H5+
N2H5+
C2O4 2-
Transmittance (%)
Wavenumber (cm-1)

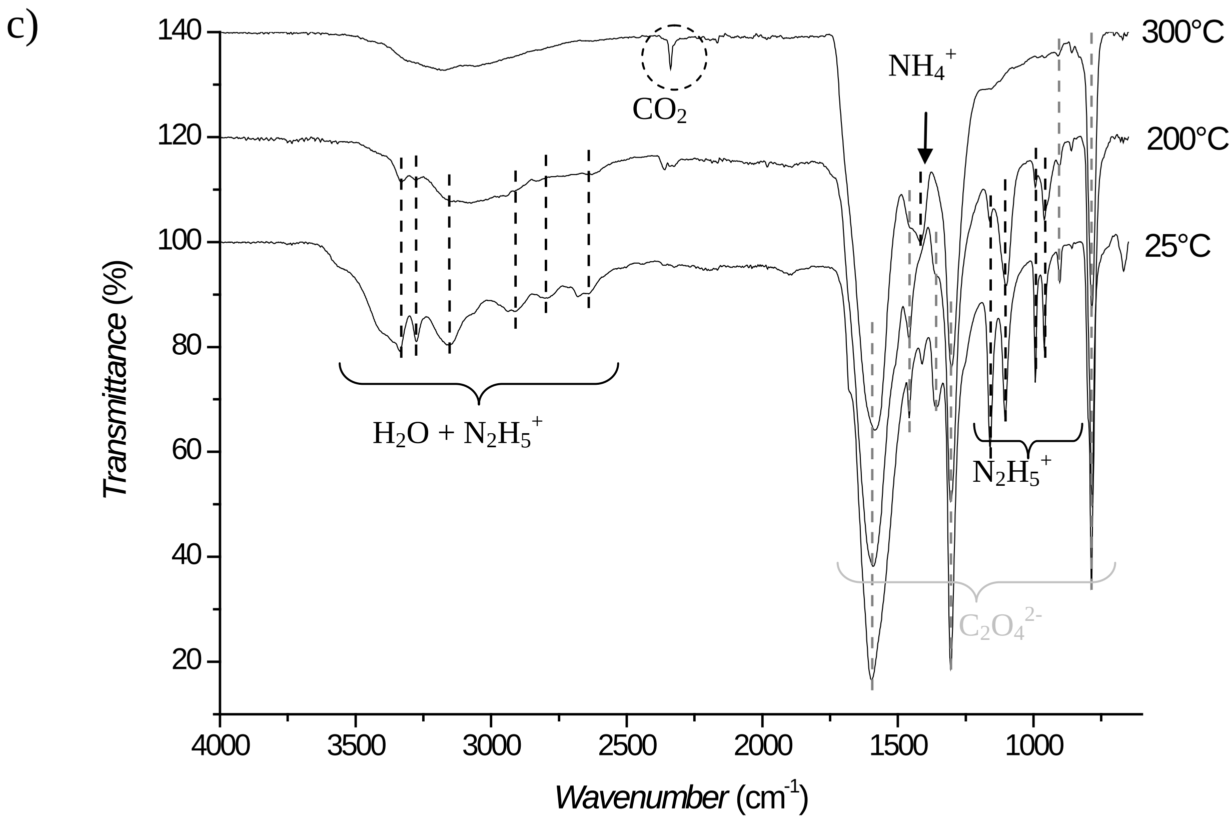


Figure S1. FT-IR spectra of thermal decomposition intermediates in air for the three $N_2H_5[Ln_2(C_2O_4)_4(N_2H_5)].4H_2O$ compounds a) Ce-HyOx, b) Nd-HyOx and c) CeNd-HyOx.

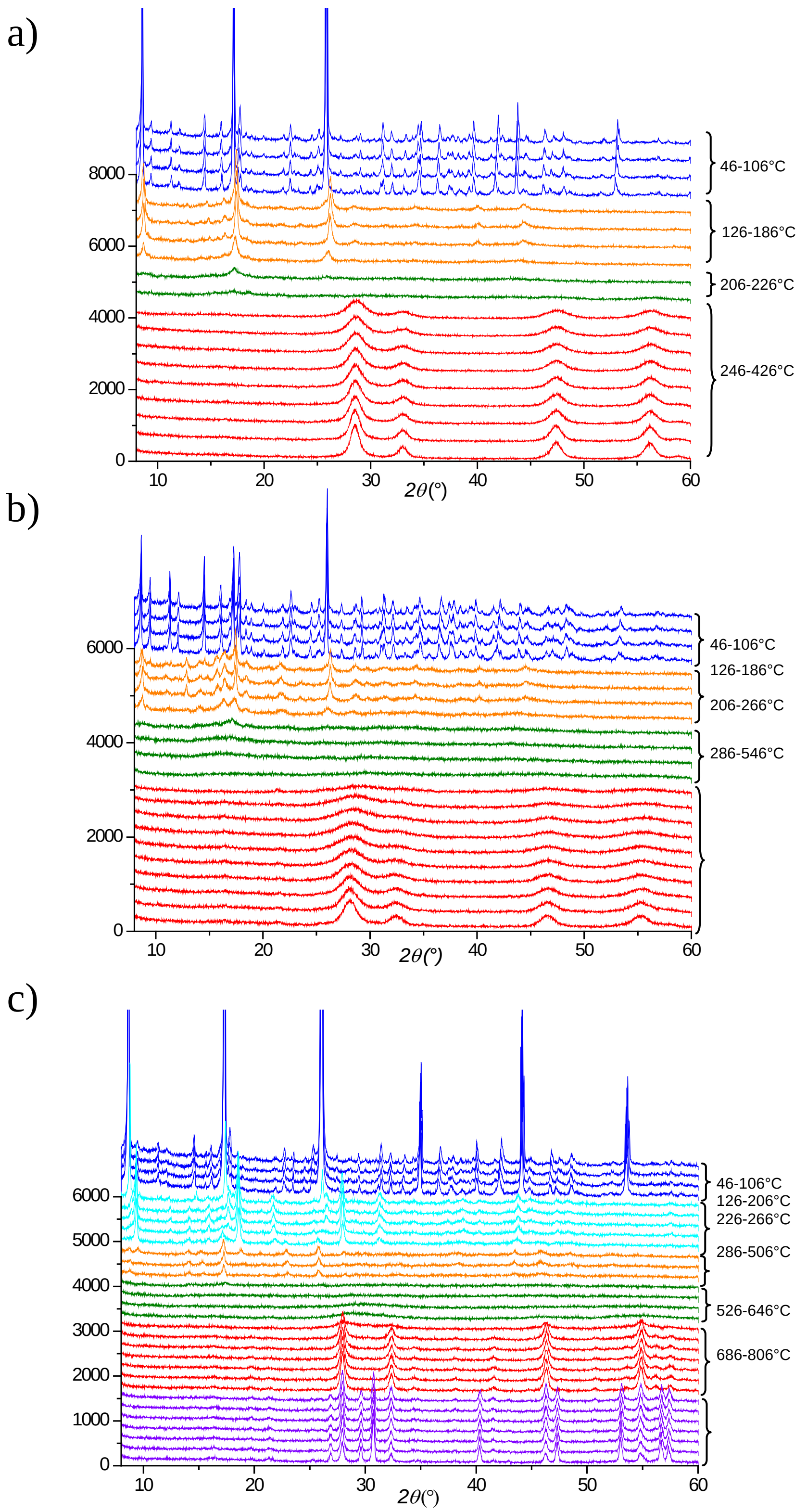


Figure S2. HT-XRD patterns in air of $N_2H_5[Ln_2(C_2O_4)_4(N_2H_5)].4H_2O$ compounds a) Ce-HyOx, b) CeNd-HyOx and c) Nd-HyOx.

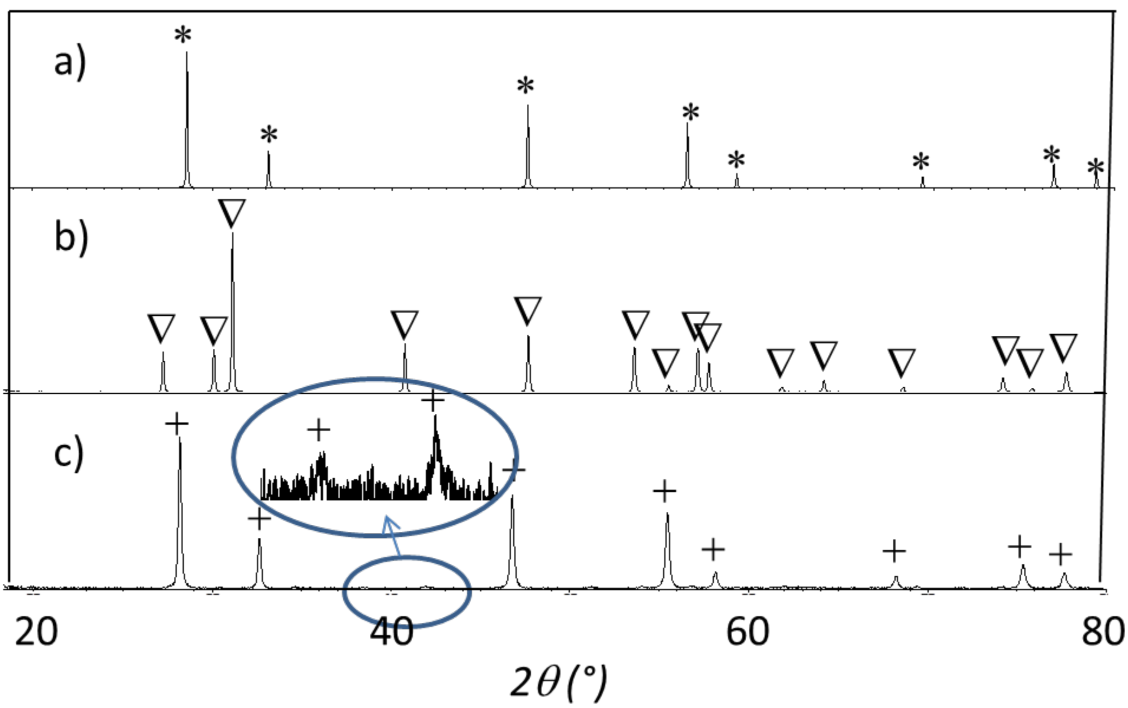


Figure S3. X-ray diffraction patterns of the Ce-HyOx, Nd-HyOx and CeNdHYOX calcinations residues at 1000°C showing the formation of a) CeO_2 (∗, JCPDS 04-013-4361), b) A-Nd_2O_3 (∇, JCPDS 04-015-4998) and c) C-$Ce_{0.5}Nd_{0.5}O_{1.75}$ solid solution (+,JCPDS 04-013-6624).

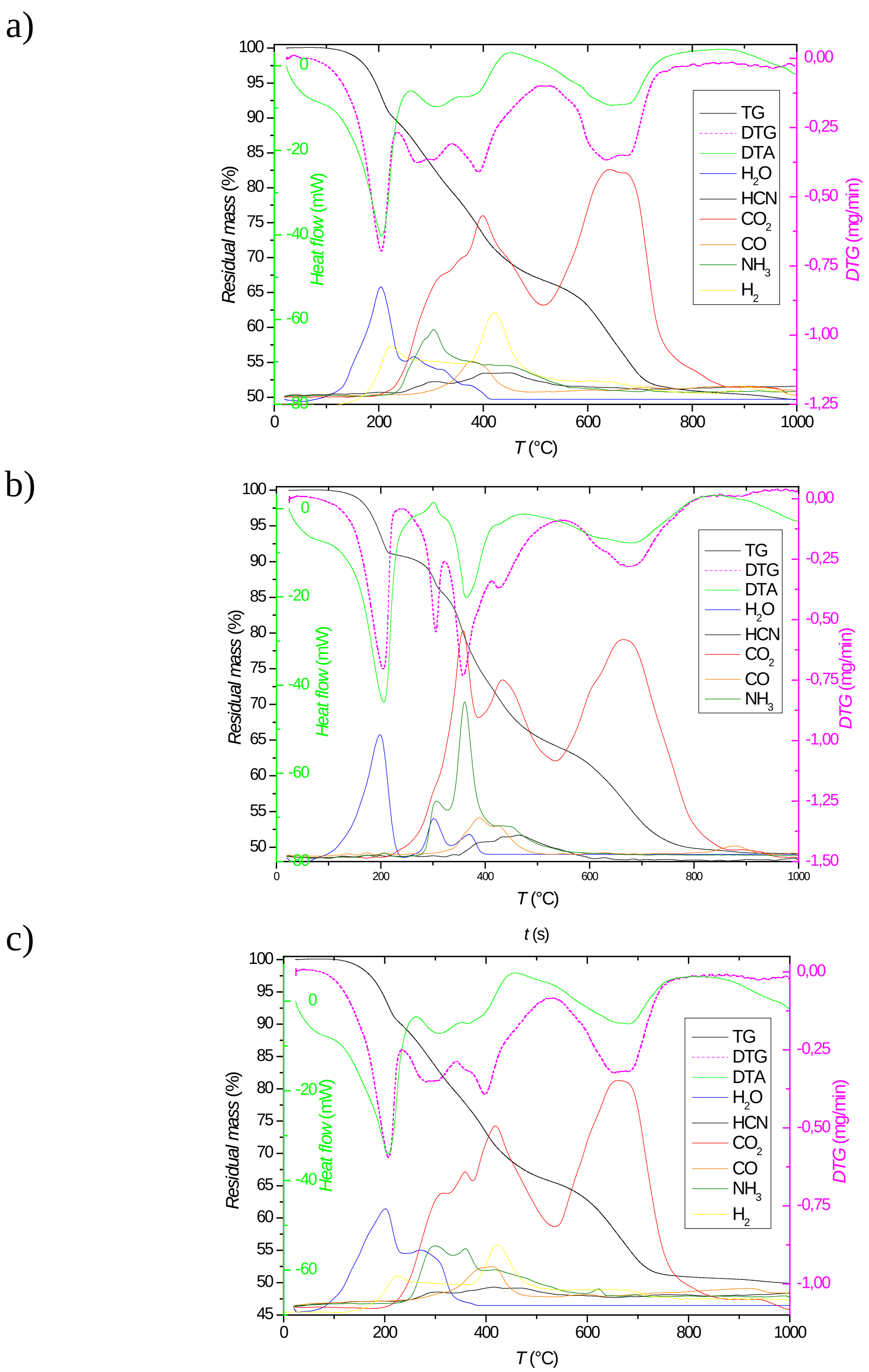
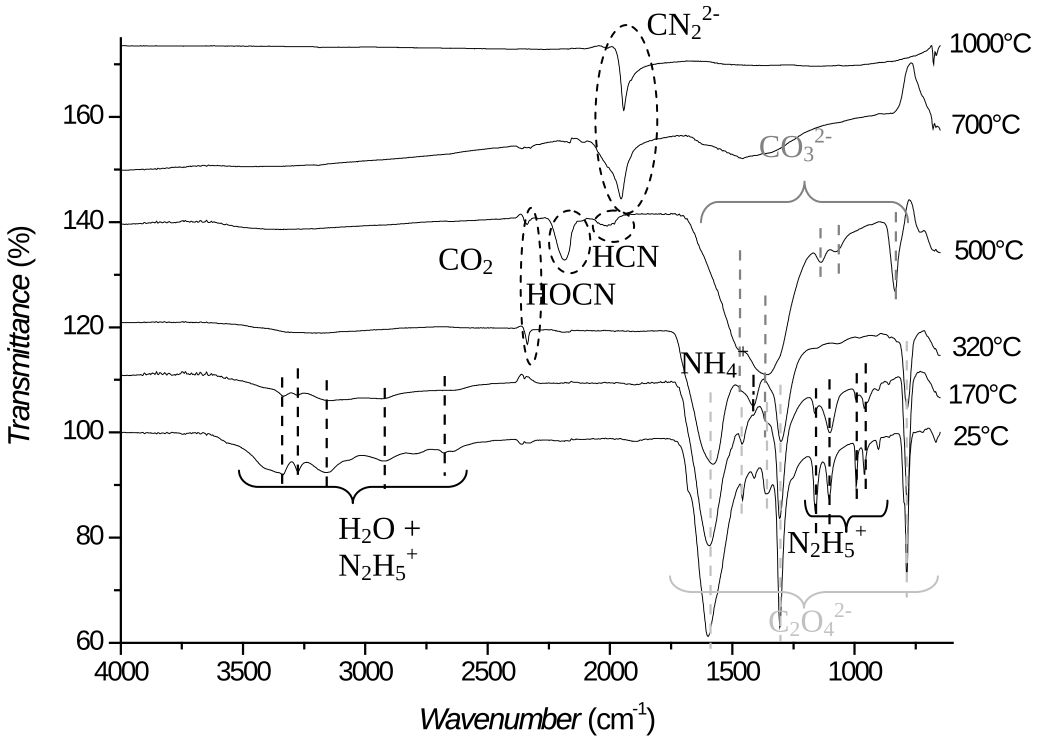
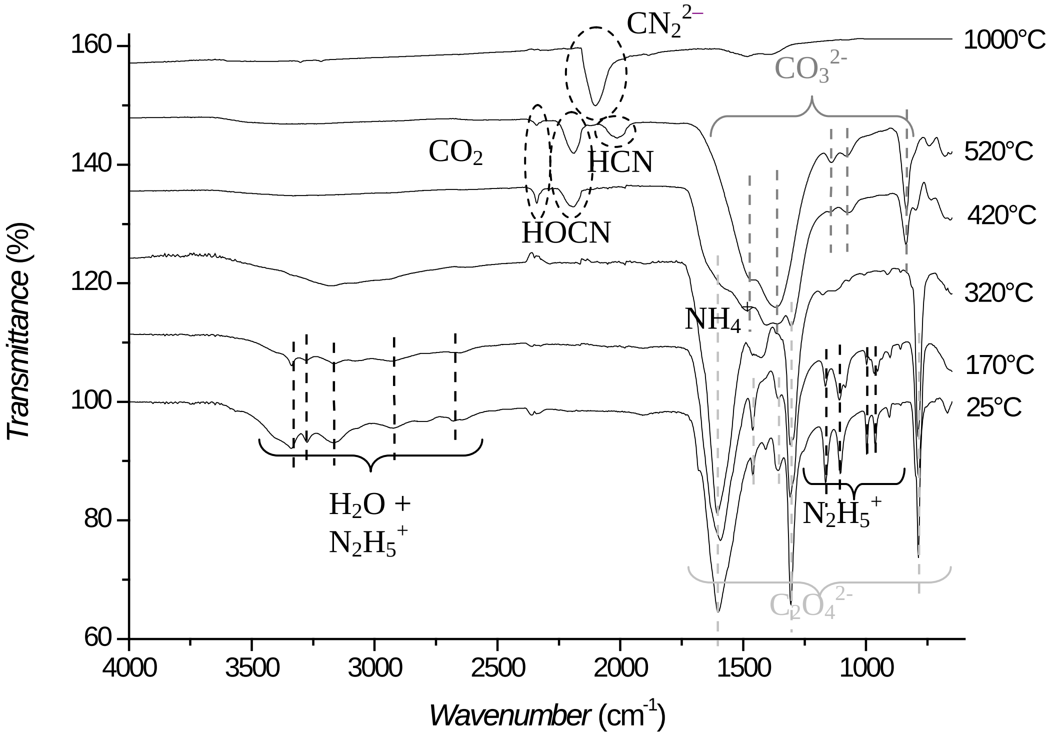


Figure S4. Thermal decomposition of the $N_2H_5[Ln_2(C_2O_4)_4(N_2H_5)].4H_2O$ compounds, a) Ce-HyOx, b) Nd-HyOx, c) CeNd-HyOx, under streaming argon (250 mL/min) on heating at 10°C/min – TG, DTA and evolved gases recorded by FT-IR (except for the H_2 signal recorded by MS), displayed with arbitrary units.

a)


CN$_2^{2-}$
1000°C
700°C
CO$_3^{2-}$
500°C
CO$_2$
HCN
HOCN
NH$_4^+$
320°C
170°C
25°C
H$_2$O +
N$_2$H$_5^+$
N$_2$H$_5^+$
C$_2$O$_4^{2-}$
Transmittance (%)
Wavenumber (cm^{-1})

b)


CN$_2^{2-}$
1000°C
CO$_3^{2-}$
CO$_2$
HCN
520°C
420°C
HOCN
320°C
NH$_4^+$
170°C
25°C
H$_2$O +
N$_2$H$_5^+$
N$_2$H$_5^+$
C$_2$O$_4^{2-}$
Transmittance (%)
Wavenumber (cm^{-1})

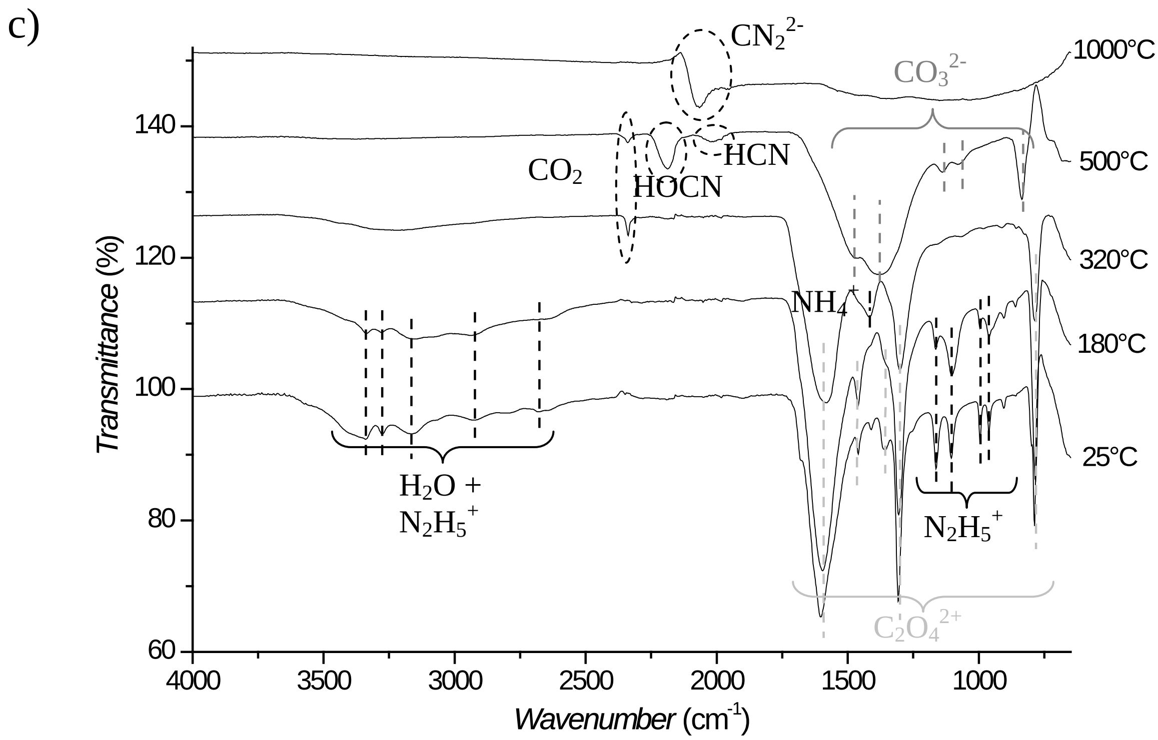


Figure S5. FT-IR spectra of thermal decomposition intermediates under argon flow for $N_2H_5[Ln_2(C_2O_4)_4(N_2H_5)].4H_2O$ compounds, a) Ce-HyOx, b) Nd-HyOx and c) CeNdHyOx.

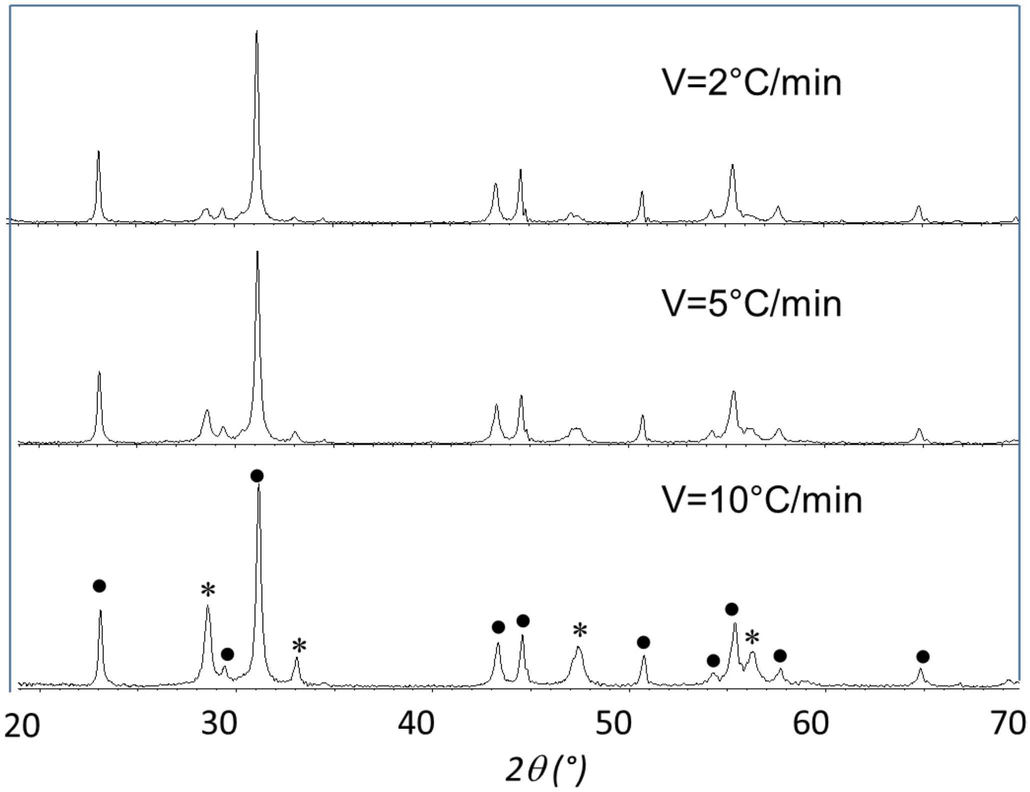


Figure S6. XRD patterns of the residues after calcination under argon at 1000°C, showing the presence of cubic CeO_2 (∗,JCPDS 04-013-4361) and tetragonal $Ce_2O_2CN_2$ (•, JCPDS 00-049-1163) for Ce-HyOx with an increase of the oxide/oxycyanamide ratio with an increase of the heating rate of the thermal analysis.

Table S1. Characteristics of the strongest hydrogen bonds

N2 – Ow2	2.711(11)	N2 – H1	0.870(4)	H1 --- Ow2	1.867(8)	N2-H1---Ow2	165.2(4)
N2 – O7 (2x)	2.961(5)	N2 – H2	0.870(3)	H2 --- O7	2.186(2)	N2-H2---O7	148.2(6)
Ow1 – O5	2.769(5)	Ow1 – H1	0.83(6)	H1 --- O5	1.95(6)	Ow1-H1---O5	167(5)
Ow1 – O8	2.761(5)	Ow1 – H2	0.82(3)	H1 --- O8	1.97(3)	Ow1-H2---O8	161(3)
Ow2 – Ow3/N3 (2x)	2.881(5)	Ow2 – H1	0.81(4)	H1 --- O/N	2.116(4)	Ow2-H---O/N	156(4)

Table S1. **Decomposition scheme of Ce-HyOx in air.**

1. $(N_2H_5)[Ce_2(N_2H_5)(C_2O_4)_4].4H_2O \xrightarrow{100-220°C} 2\ (N_2H_5)Ce(C_2O_4)_2 + 4\ H_2O$

2. $2\ (N_2H_5)Ce(C_2O_4)_2 \xrightarrow{220-300°C} 2$ "$(NH_4)_{0.8}Ce(C_2O_4)_{1.9}$" $+ 1.2\ NH_3 + 0.4\ CO_2 + 0.6\ N_2$

3. 2 "$(NH_4)_{0.8}Ce(C_2O_4)_{1.9}$" $\xrightarrow{300-400°C} 2\ CeO_2 + 3.6\ CO_2 + 4\ CO + 1.6\ NH_3 + 0.8\ H_2$

Table S2. **Decomposition scheme of Nd-HyOx in air.**

1. $(N_2H_5)(H_2O)[Nd_2(N_2H_5)(C_2O_4)_4].3H_2O \xrightarrow{100-200°C} 2\ (N_2H_5)Nd(C_2O_4)_2 + 4\ H_2O$

2. $2\ (N_2H_5)Nd(C_2O_4)_2 \xrightarrow{200-300°C} 2$ "$(NH_4)_{0.85}Nd(C_2O_4)_{1.925}$" $+ NH_3 + 0.3\ CO_2 + 0.65\ N_2 + 0.1\ H_2$

$$NH_3 + ¾\ O_2 \longrightarrow ½\ N_2 + \tfrac{3}{2}\ H_2O$$

3. 2 "$(NH_4)_{0.85}Nd(C_2O_4)_{1.925}$" $\xrightarrow{300-400°C} (NH_4)Nd_2(C_2O_4)_2(CO_3)_{1.5} + 0.7\ CO_2 + 1.5\ CO + 0.7\ NH_3 + 0.35\ H_2$

$$CO + ½\ O_2 \longrightarrow CO_2;\ NH_3 + O_2 \longrightarrow ½\ N_2O + \tfrac{3}{2}\ H_2O$$

4. $(NH_4)Nd_2(C_2O_4)_2(CO_3)_{1.5} \xrightarrow{400-500°C} Nd_2O(CO_3)_2 + 2\ CO_2 + 1.5\ CO + NH_3 + 0.5\ H_2$

5. $Nd_2O(CO_3)_2 \xrightarrow{500-600°C} Nd_2O_2CO_3 + CO_2$

6. $Nd_2O_2CO_3 \xrightarrow{600\text{–}800°C} Nd_2O_3 + CO_2$

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Table S3. Decomposition scheme of the Ln-HyOx compounds in air and in argon.

Air			**Argon**		
Ce	*Nd*	*Ce-Nd*	*Ce*	*Nd*	*Ce-Nd*
$N_2H_5[Ln_2(C_2O_4)_4(N_2H_5)].4H_2O$					
100-200[1]					
9.4/9.3[2] 205±20[3]	9.3/9.2[2] 270±20[3]	9.7/9.3[2] 215±20[3]	9.8/9.3[2] 315±20[3]	9.3/9.2[2] 350±20[3]	9.1/9.3[2] 330±20[3]
2 $N_2H_5[Ln(C_2O_4)_2]$					
220-300[1] 6.6/7.1[2] -35±5[3]	200-300[1] 6.3/6.2[2] -20±5[3]	200-280[1] 7.1/7.1[2] -20±5[3]	200-350[1] 11.9/11.9[2] 20±5[3]	200-300[1] 5.4/5.4[2] -10±2[3]	200-350[1] 12.1/11.9[2] 20±5[3]
$(NH_4)_{1.6}Ce_2(C_2O_4)_{3.8}$	$(NH_4)_{1.7}Nd_2(C_2O_4)_{3.85}$	$(NH_4)_{1.6}CeNd(C_2O_4)_{3.8}$	$(NH_4)Ce_2(C_2O_4)_{3.5}$	$NH_4)_{1.8}Nd_2(C_2O_4)_{3.9}$	$(NH_4)CeNd(C_2O_4)_{3.5}$
300-400[1] 38.1/38.8[2] -1095±30[3]	200-400[1] 11.0/11.0[2] 56±5[3]	280-320[1] 4.2/4.1[2] -25±5[3]	350-500[1] 12.0/*[2] 20±5[3]	300-400[1] 13.4/13.6[2] 125±10	350-500[1] 12.1/*[2] 25±5[3]
	$(NH_4)Nd_2(C_2O_4)_2(CO_3)_{1.5}$	$(NH_4)_{1.4}CeNd(C_2O_4)_3(CO_3)_{0.7}$		$(NH_4)Nd_2(C_2O_4)_{1.5}(CO_3)_2$	
	400-500[1] 18.8/19.0[2] -860±30[3]	320-600[1] 34.2/35.5[2] -770±30[3]		400-520[1] 7.3/*[2] ≈0[3]	
	$Nd_2O(CO_3)_2$		Carbonate intermediate		
	500-600[1] 6.0/5.7[2] -20±5[3]		500-850[1] 18.2/*[2] 260±20[3]	520-900[1] 15.6/*[2] 150±20[3]	500-850[1] 16.2/*[2] 170±20[3]
	$Nd_2O_2CO_3$				
	600-800[1] 4.6/5.7[2] 30±5[3]				
2 CeO_2	A-Nd_2O_3	$CeNdO_{3.5}$	CeO_2 + T-$Ce_2O_2CN_2$	A-Nd_2O_3 + H-$Nd_2O_2CN_2$	A-$(Ce,Nd)_2O_3$ + H-$(Ce,Nd)_2O_2CN_2$

Notes. [1]Transition temperature in °C. [2]Mass loss exp/calc. in %. [3] Reaction heat in kJ/mol.