Electronic Supplementary Material

Structural, Spectroscopic, and Thermal Decomposition Features of [Carbonatotetraamminecobalt(III)] Iodide – Insight into the Simultaneous Solid-phase Quasi-intramolecular Redox Reactions

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Table S1. Crystal data and structure refinement details of $[Co(NH_3)_4CO_3]I$.

Empirical formula	C H12 Co I N4 O3
Formula weight	313.98
Temperature	303.46(10)
Radiation and wavelength	Cu-Kα, λ =1.54184Å
Crystal system	orthorhombic
Space group	*P* n m a
Unit cell dimensions	*a* =17.7359(2)Å
	b =7.77940(10)Å
	c =6.82520(10)Å
	α =90°
	β =90°
	γ =90°
Volume	941.70(2)Å^3
Z	4
Density (calculated)	2.215 Mg/m^3
Absorption coefficient, μ	39.827 mm^{-1}
F(000)	600
Crystal colour	purple
Crystal description	needle
Crystal size	0.120 x 0.060 x 0.040 mm
Absorption correction	analytical
Max. and min. transmission	0.0650.502
θ–range for data collection	4.987 ≤ θ ≤ 75.404°
Index ranges	$-22 \le h \le 22; -9 \le k \le 9; -8 \le l \le 8$
Reflections collected	22097
Completeness to 2θ	1.000
Independent reflections	1046 [*R*(int) =0.0666]
Reflections $I>2\sigma(I)$	1009
Refinement method	full-matrix least-squares on *F*2
Data / restraints / parameters	1046 /0 /56
Goodness-of-fit on *F*2	1.141
Final *R* indices [$I>2\sigma(I)$]	*R*1 =0.0314, *wR*2 =0.0761
R indices (all data)	*R*1 =0.0328, *wR*2 =0.0769
Max. and mean shift/esd	0.000;0.000
Largest diff. peak and hole	1.331;-0.438 e.Å^{-3}

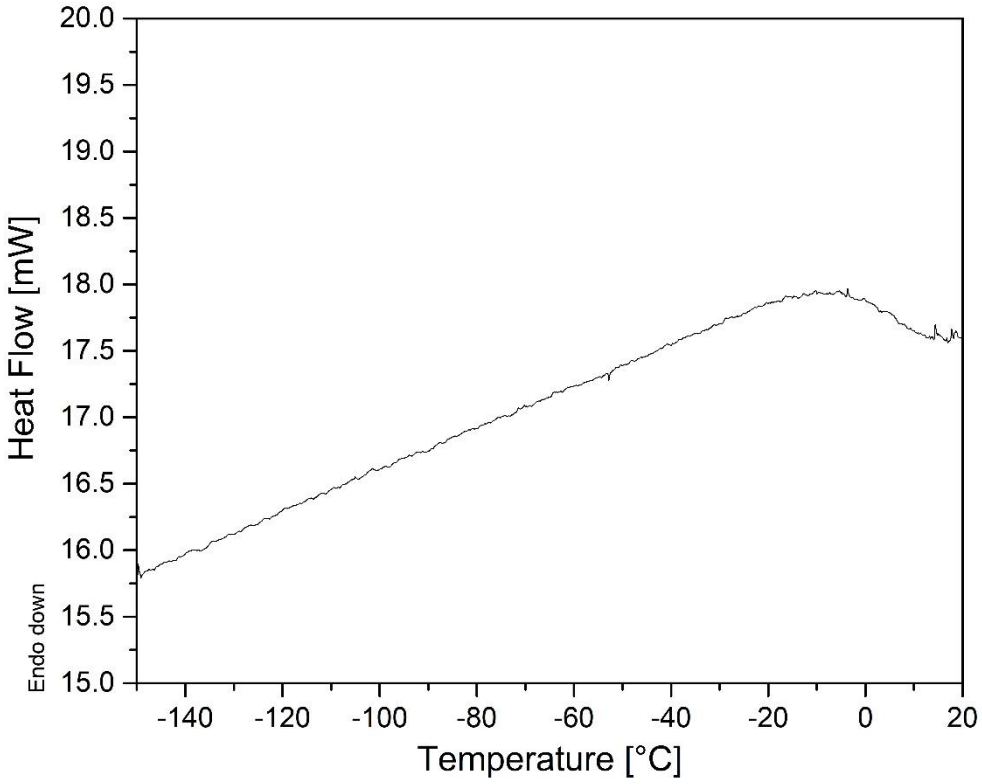

Figure S1. DSC results of compound **1** between -150 °C and room temperature.

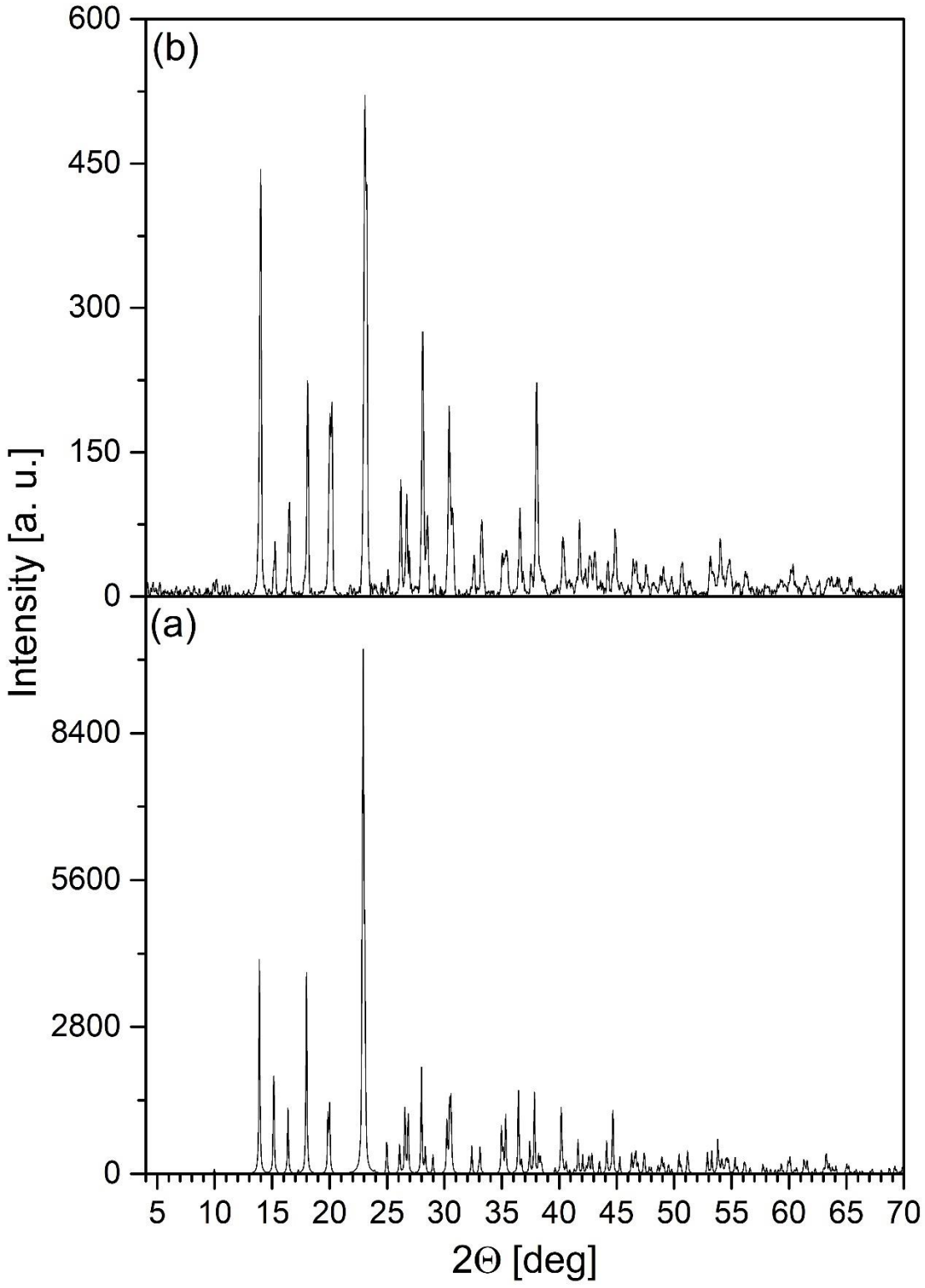

Figure S2. (a) The calculated (from SXRD data) and **(b)** the experimental powder X-ray diffractogram of compound **1**.

Table S2. Bonds lengths in the crystal structure of $[Co(NH_3)_4CO_3]I$ (Symmetry codes to generate equivalent atoms: 1. [8_565] x,-y-1/2+1,z).

Co1-O2#1	1.917(2)	Co1-O2	1.917(2)
Co1-N2	1.953(4)	Co1-N3	1.957(5)
Co1-N1#1	1.959(3)	Co1-N1	1.959(3)
Co1-C1	2.325(5)	C1-O1	1.227(6)
C1-O2	1.308(4)	C1-O2#1	1.308(4)

Table S3. Bonds angles in the crystal structure of $[Co(NH_3)_4CO_3]I$ (Symmetry codes to generate equivalent atoms: 1. [8_565] x,-y-1/2+1,z).

O2#1-Co1-O2	68.4(2)	O2#1-Co1-N2	90.1(1)
O2-Co1-N2	90.1(1)	O2#1-Co1-N3	89.5(1)
O2-Co1-N3	89.5(1)	N2-Co1-N3	179.5(2)
O2#1-Co1-N1#1	167.0(1)	O2-Co1-N1#1	98.6(1)
N2-Co1-N1#1	89.3(1)	N3-Co1-N1#1	91.1(1)
O2#1-Co1-N1	98.6(1)	O2-Co1-N1	167.0(1)
N2-Co1-N1	89.3(1)	N3-Co1-N1	91.1(1)
N1#1-Co1-N1	94.4(2)	O2#1-Co1-C1	34.22(8)
O2-Co1-C1	34.22(8)	N2-Co1-C1	88.7(2)
N3-Co1-C1	90.8(2)	N1#1-Co1-C1	132.7(1)
N1-Co1-C1	132.7(1)	O1-C1-O2	124.5(2)
O1-C1-O2#1	124.5(2)	O2-C1-O2#1	111.0(4)
O1-C1-Co1	175.2(4)	O2-C1-Co1	55.5(2)
O2#1-C1-Co1	55.5(2)	C1-O2-Co1	90.2(2)

Table S4. Analysis of Potential Hydrogen Bonds and Schemes with d(D...A) < R(D)+R(A)+0.50, d(H···A) < R(H)+R(A)-0.12 Ang., D-H···A > 100.0 Deg.

D-H…A	D-H (Å)	H…A (Å)	D…A (Å)	D - H...A(°)	Symmetry operator
N1 --H1AC ..O1	0.89	2.35	3.038(4)	135	x,y,1+z
N1 --H1AA ..O1	0.89	2.42	3.276(4)	163	1-x,1/2+y,1-z
N1 --H1AB ..I1	0.89	2.98	3.733(3)	144	x,y,z
N2 --H2A ..O2	0.89	2.14	2.953(3)	152	1-x,-y,1-z
N2 --H2B ..O1	0.89	2.16	3.004(5)	160	x,y,1+z
N3 --H3B ..I1	0.91	2.88	3.761(5)	164	3/2-x,1-y,1/2+z

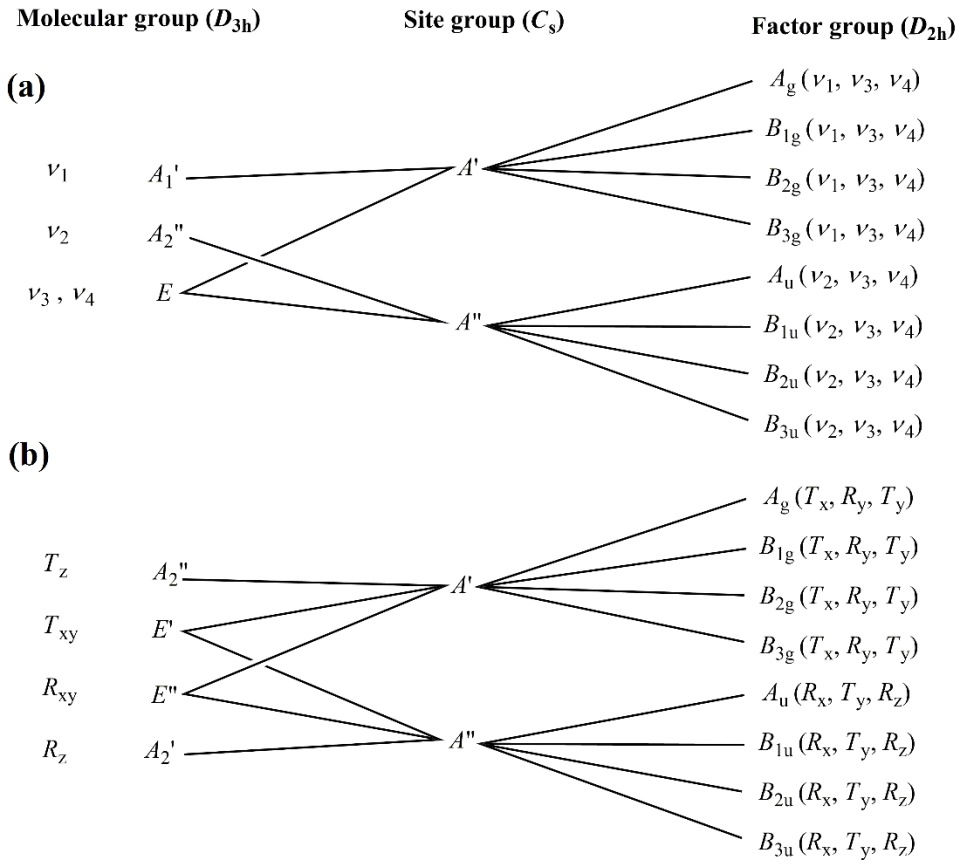

Figure S3. Factor group analysis of **(a)** internal and **(b)** external CO_3^{2-} modes in $[Co(NH_3)_4CO_3]I$.

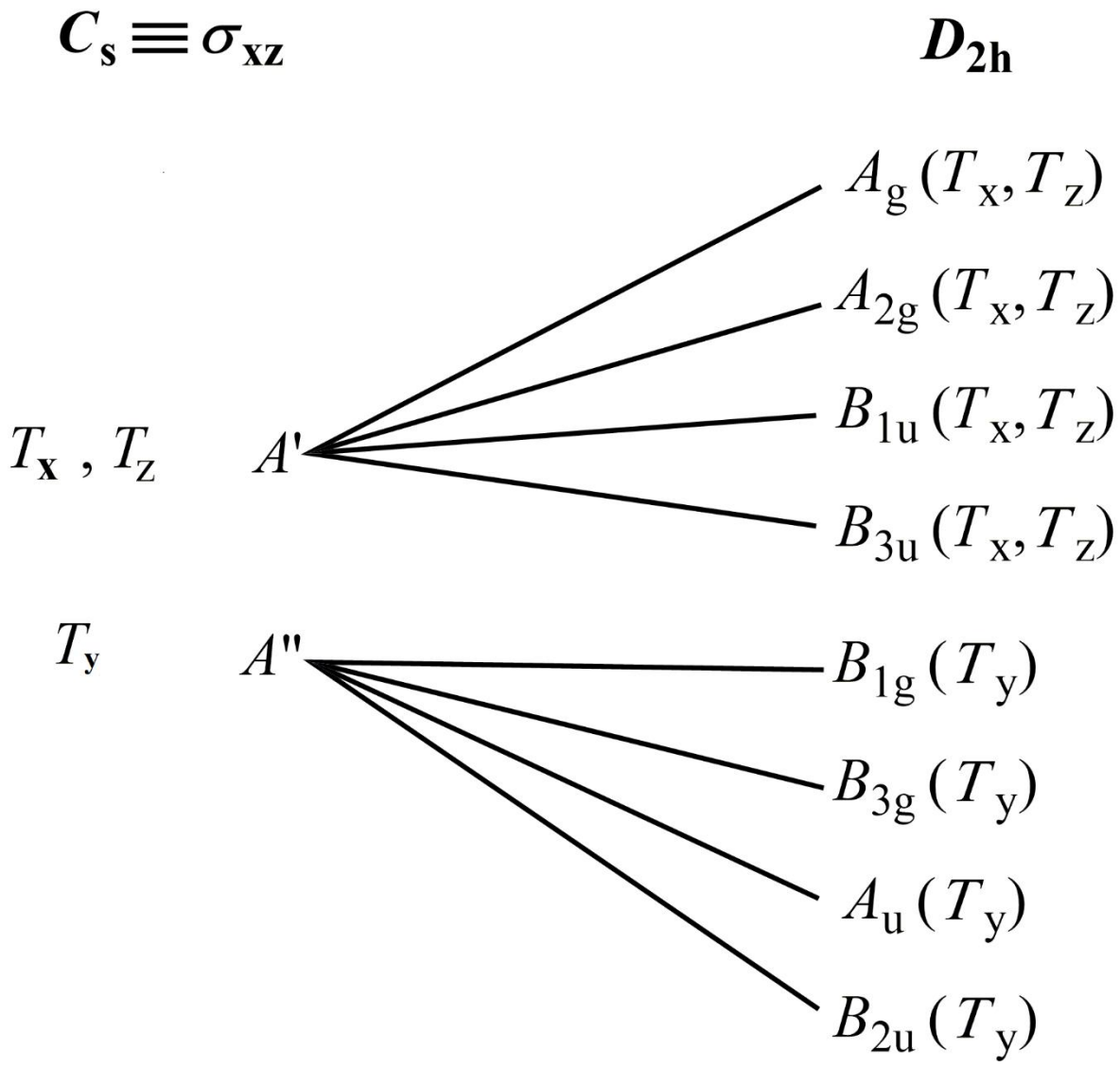

Figure S4. Factor group analysis of hindered translations of monoatomic structural motifs (Co^{3+} or I^-) in $[Co(NH_3)_4CO_3]I$.

Table S5. The internal vibrational modes of the cis-O_2CoN_4 skeleton and their assignments in the far-IR and Raman spectra of compound **1** (assuming effective C_{2v} symmetry of the skeleton).

Species	Band	Measured, cm^{-1}			Calculated, cm^{-1}	Assignment
		Far-IR		Raman (785 nm)		
		Our	[42]	Our	[42]	
A_1	ν_1	545	524	506	527	ν_{CoN}
	ν_2	430	430	439	430	ν_{CoN}
	ν_3	293	300	300	308	δ
	ν_4	133sh	148	155	149	δ
	ν_5	-	-	-	38	δ
	ν_6	392	392	397	396	ν_{as}(CoO)
B_1	ν_9	490	492	486	496	ν_{CoN}
	ν_{10}	267	278	299	273	δ
	ν_{11}	-	204	-	201	δ
B_2	ν_{12}	430	460	467	459	ν_{CoN}
	ν_{13}	-	182	155	191	δ
	ν_{14}	325	324	323	318	ν_s(CoO)
	ν_{15}	120	148	114	129	δ

Table S6. The assignment of the ammonia vibrational modes in the IR and Raman spectra of compound **1** (classified under C_{3v} symmetry).

Species	Band	Measured/cm^{-1}				Assignment
		IR, 25 °C			Raman, 532 nm, -150 °C	
		[43].	[37]	Our results	Our results	
A_1	ν_1	3170	3190	3174	3183	ν_s(NH)
	ν_2	1318	1314	1316	1314	δ_s(HNH)
E	ν_3	3290	3290	3284,3219	3291, 3228	ν_{as}(NH)
	ν_4	1652	1603	1665	1664	δ_{as}(HNH)
	ν_5	820	834, 825	817, 793sh	839, 818	$\rho(NH_3)$

Table S7. The relative Co-N donor bond strength in the amminecobalt iodide complexes.

Compound	δ_s(HNH), cm^{-1}	Relative bond strength, in %	Ref.
$[Co(NH_3)_4CO_3]I$	1316	0.84	[42]
$[Co(NH_3)_5CO_3]I$	1307	0.82	[42]
$[[Co(NH_3)_6]I_3$	1323	0.86	[44]

Table S8. The κ^2-O,O'-coordinated (chelate-forming) carbonate ion (C_{2v}) vibrational modes and their assignments in compound **1** (a tentative C_{2v} symmetry of the coordinated carbonate anions was assumed).

Species	Band	Measured/cm^{-1}			Calculated values/cm^{-1} [42]	Assignation
		IR [42]	IR (our results)	Raman (785 nm - 150 °C)		
A_1	ν_1	1595	1595	1617	1577	ν_{as}(C=O§)
	ν_2	1044	1045	1049	1052	ν_s(C-O)
	ν_3	763	761	763	771	δ(OCO), in-plane
B_1	ν_4	1284,1267	1283,1263	1275sh, 1264	1274	ν_{as}(CO)
	ν_5	673,667	672		671	δ(OCO§), in-plane
B_2	ν_6	840,834	844sh, 831		859	π, out-of-plane

§O means non-coordinated oxygen atom of carbonate ion

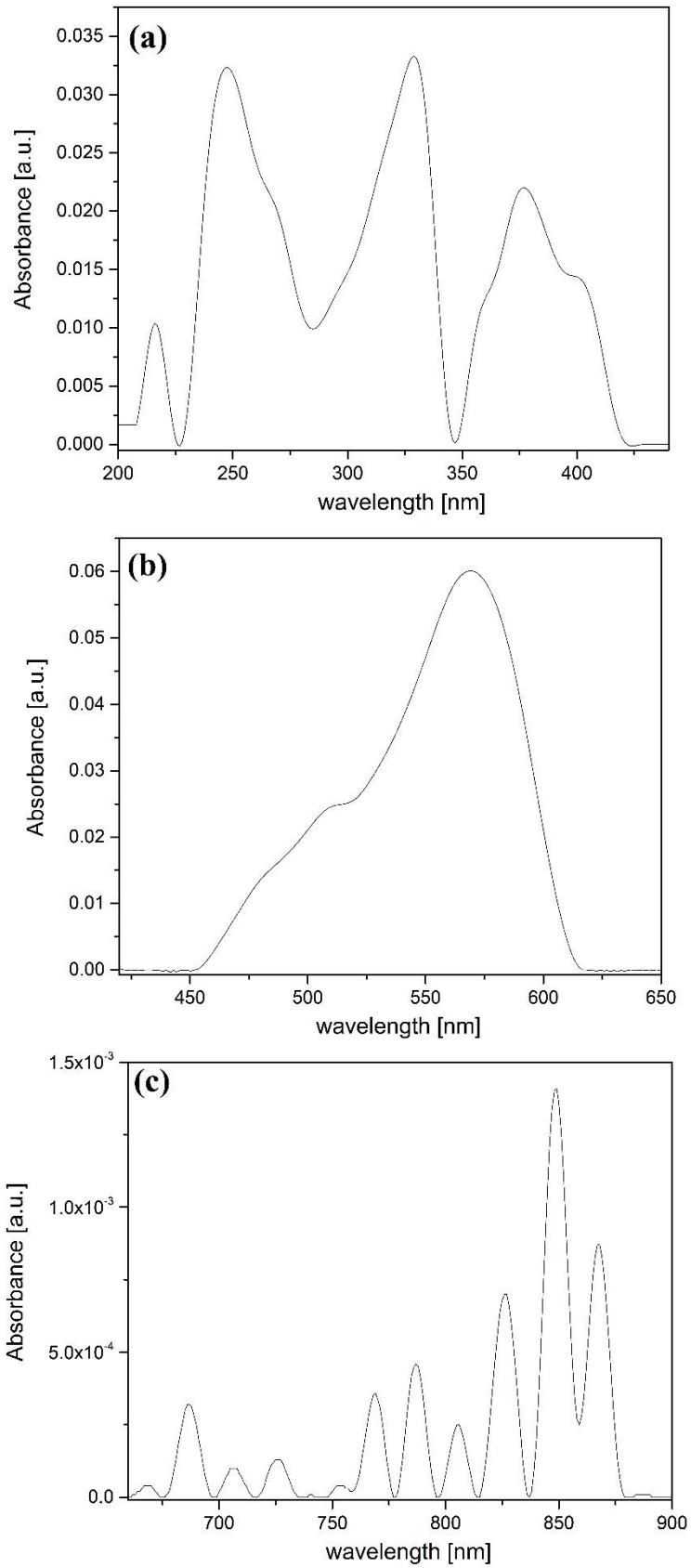

Figure S5. The UV-VIS spectra of compound **1** in **(a)** 200-440 nm range, **(b)** 420-650 nm range and **(c)** 660-900 nm range.

Table S9. Experimental UV–Vis data for compound **1,** $[Co(NH_3)_4CO_3]_2SO_4.3H_2O$, and the calculated data for the $[Co(NH_3)_4CO_3]^+$ ion

Assignment	λ_{max}(in nm)		
	Compound **1**	$[Co(NH_3)_4CO_3]^+$ [43]	$[Co(NH_3)_4CO_3]_2SO_4.3H_2O$ [23]
$^1T_{1g} \leftarrow {}^1A_{1g}$	569	519	537
$^1T_{2g} \leftarrow {}^1A_{1g}$	377	368	380
$^3T_{1g} \leftarrow {}^1A_{1g}$	850	845	834
$^3T_{2g} \leftarrow {}^1A_{1g}$	687	633	653
LMCT π-e_g	246	-	300

Table S10. The main parameters of the decomposition process of compound **1**.

Parameter	Step	In inert atmosphere	In air atmosphere
Peak temperatures (°C)	1A	209.9	210.6
	1B		241.6
	2	575.4	-
Weight loss (%)	1A	69.7	46.1
	1B		30.1
	2	8.4	2.0
Summarized weight loss (%)	1-2	78.1	78.2
Reaction heat (J/g)	1A	47.85	697.64
	1B	-	-181.38
	2	37.00	-
Summarized reaction heat (J/g)	1-2	84.85	516.26

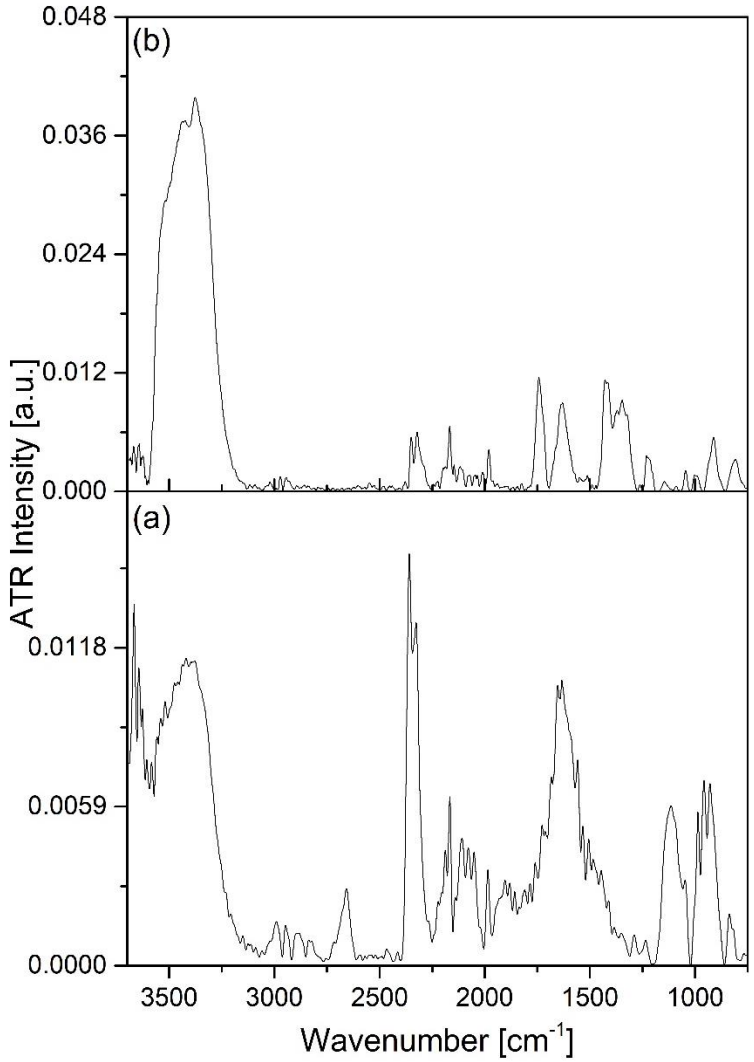

Figure S6. The IR spectrum of the decomposition intermediates formed at 300 °C in air, recorded in the range of 700-3700 cm^{-1} (enlarged part of the IR spectra of the decomposition intermediates formed in He(a) and in air (b), in the N-H and -C(=O)-NH- groups absorption bands range).

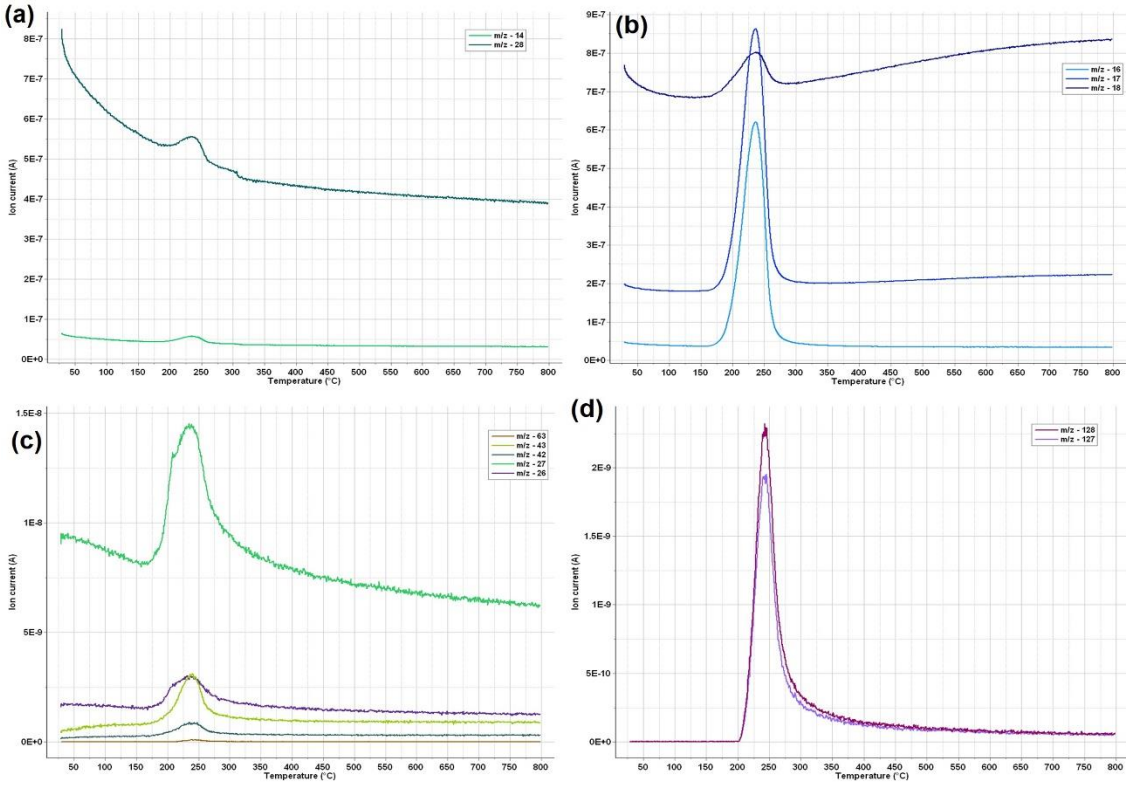

Figure S7. The TG-MS ion intensity curves for curves of *m*/*z*=14,15, 28, 30 and 44 (a), *m*/*z*=15,16,17, and 18 (b), *m*/*z*= 26,27,42 and 43 (c) and *m*/*z*= 127 and 128 ions.

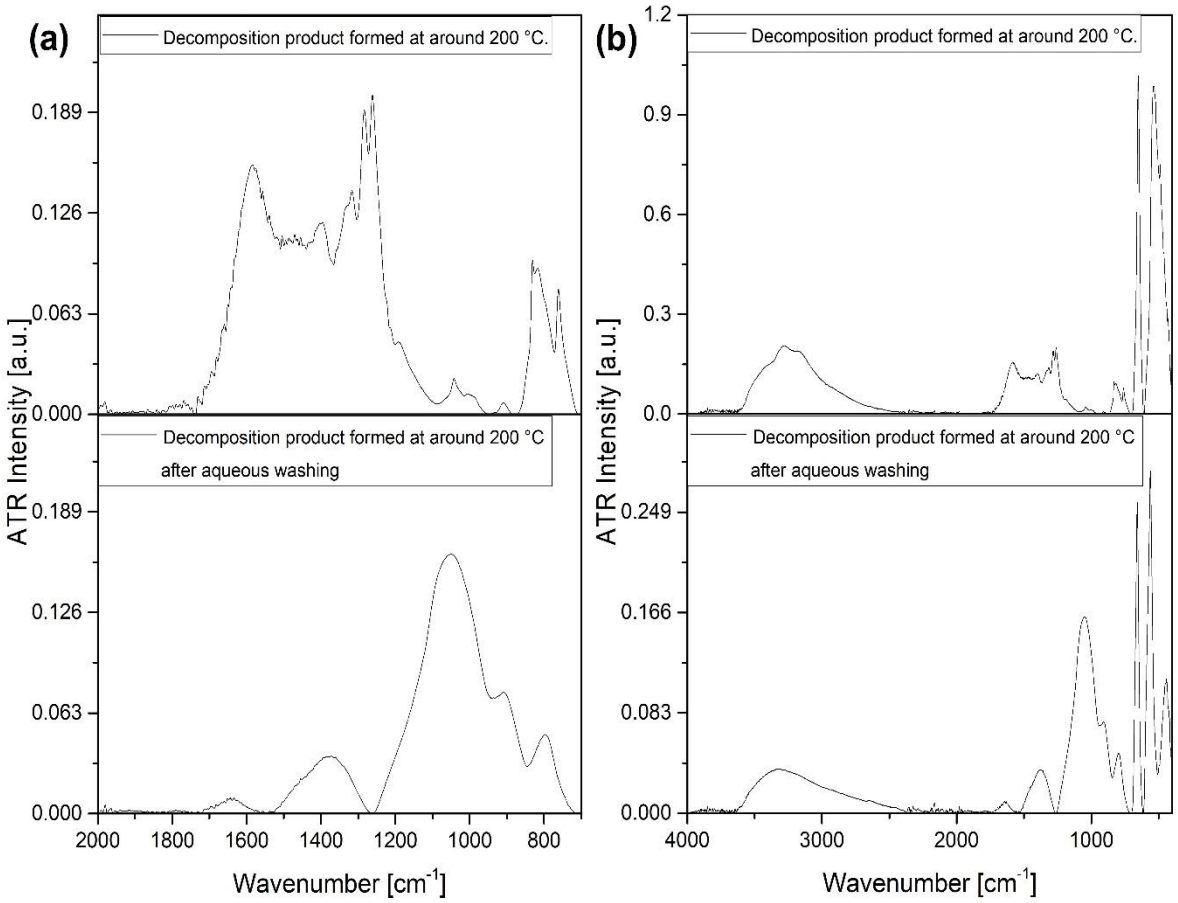

Figure S8. The IR spectra of the decomposition product of compound **1** formed under isotherm conditions at around ~200 °C, **(a)** in range 2000 to 700 cm^{-1} an (b) in range 4000 to 400 cm^{-1}.

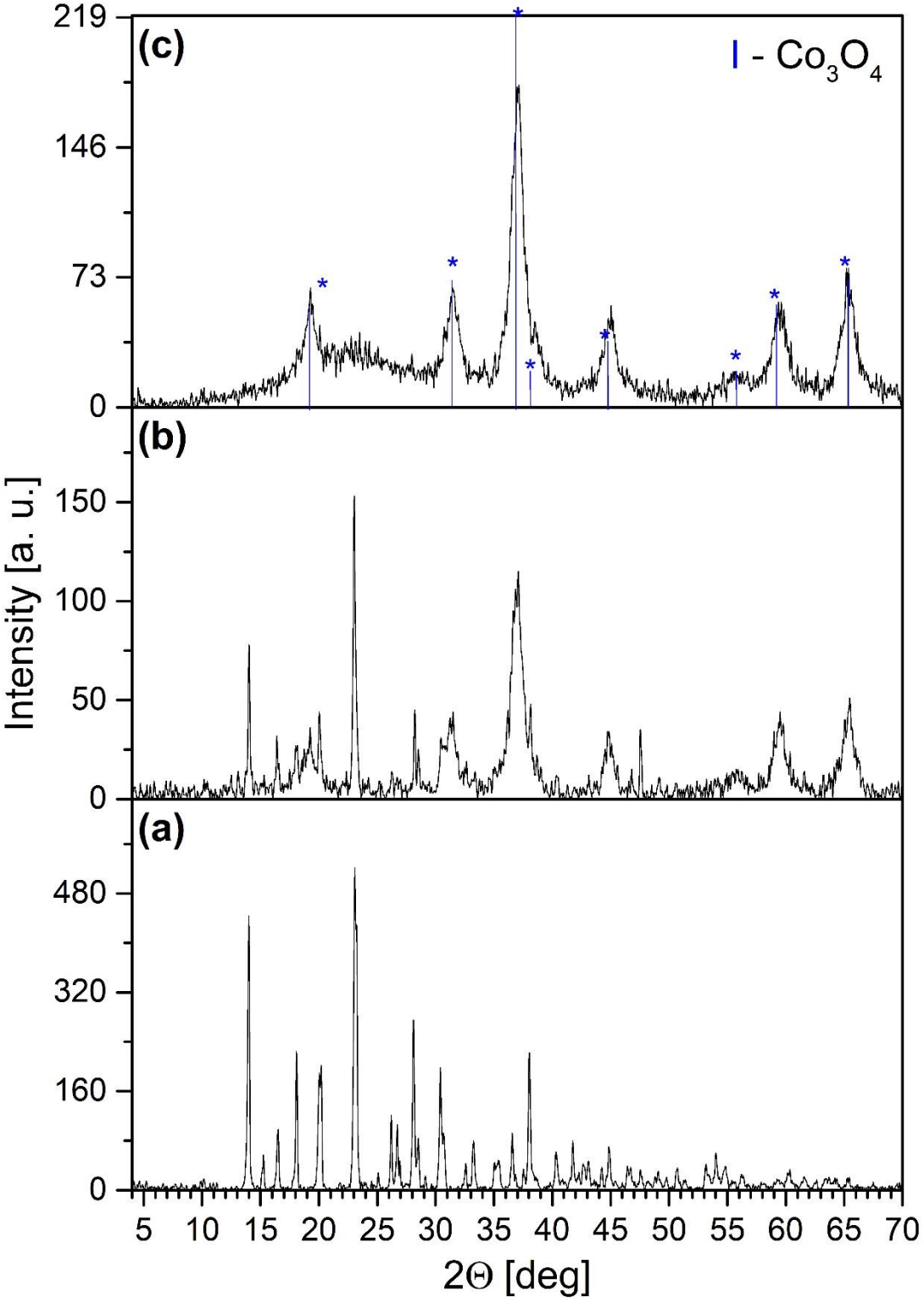

Figure S9. The powder-XRD of the decomposition product of compound **1** formed under isotherm conditions at around ~200 °C: **(a)** compound **1**, **(b)** decomposition product of compound **1** under isotherm conditions at around ~200 °C and **(c)** the (b) after aqueous washing.

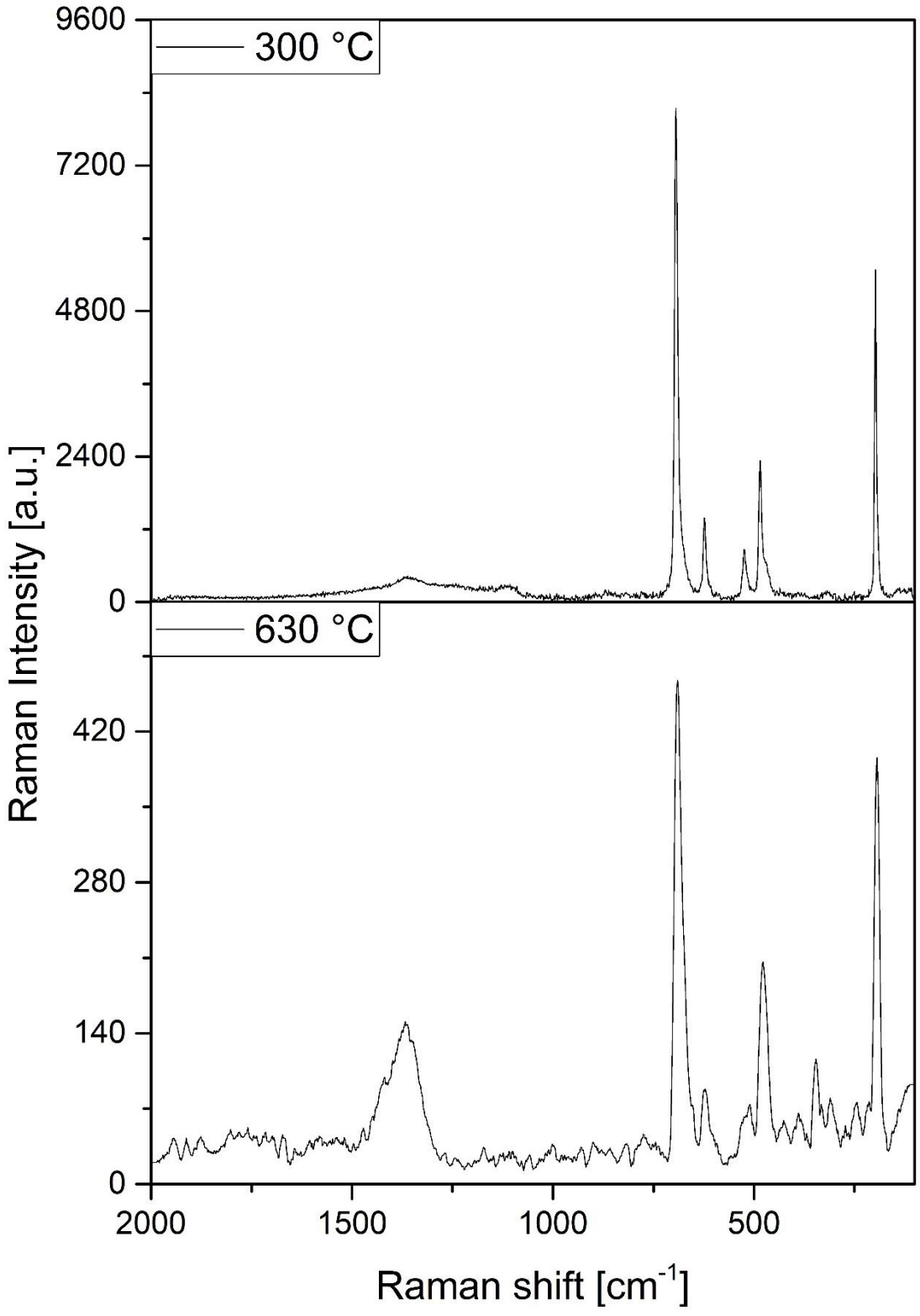

Figure S10. The Raman spectra of decomposition products of compound **1** formed at 300 and 630 °C in air.

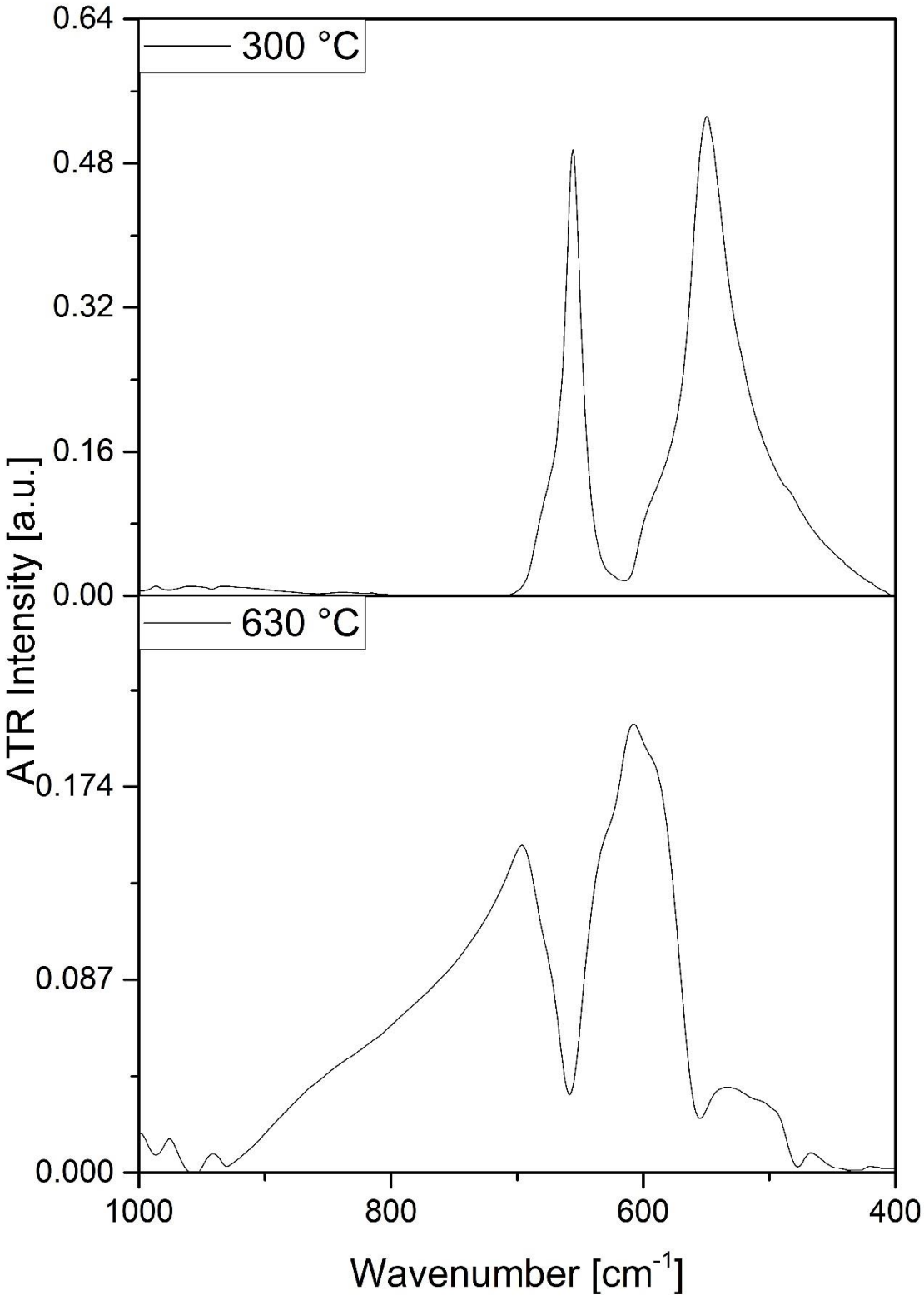

Figure S11. The IR spectra of decomposition products of compound **1** formed at 300 and 630 °C in inert atmosphere.