Electronic Supplementary Material

[Hexaamminecobalt(III)] Dichloride Permanganate – Structural Features and Heat-Induced Transformations into $M^{II}M^{III}_2O_4$ Spinels (M=Co, Mn, Co:Mn=1:1 and 1:3)

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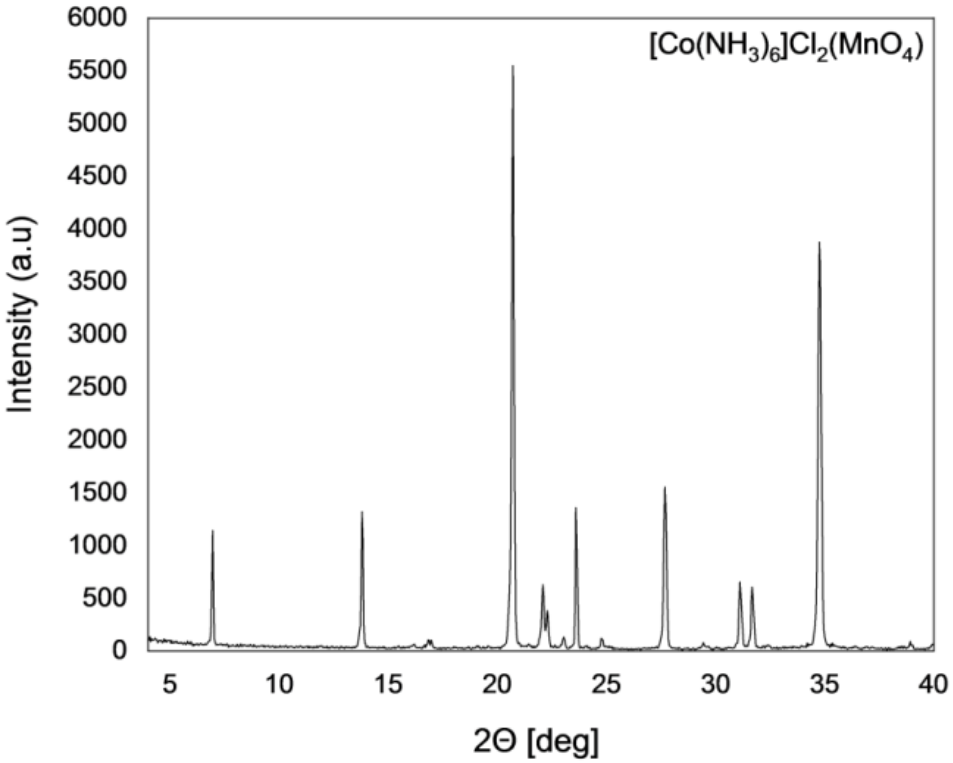
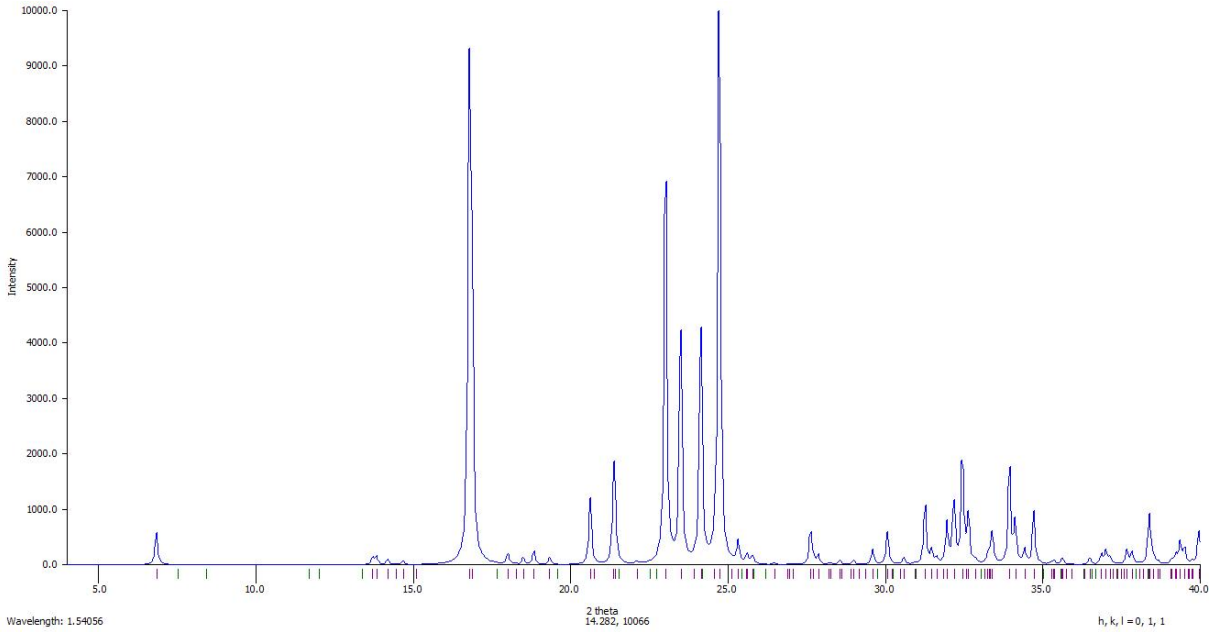


ESI Figure S1. The powder X-ray diffractogram of compound 1.



ESI Figure S2. The calculated (from SXRD data) powder X-ray diffractogram of compound 1.

ESI Table S1. Crystal data and structure refinement.

Empirical formula	Cl2 Co H18 Mn N6 O4
Formula weight	350.97
Temperature	163(2)
Radiation and wavelength	Mo-Kα, λ =0.71075Å
Crystal system	monoclinic
Space group	*P* 21/c
Unit cell dimensions	*a* =13.6133(7)Å
	b =7.3658(5)Å
	c =12.3682(6)Å
	α =90°
	β =108.547(8)°
	γ =90°
Volume	1175.78(13)Å^3
Z	4
Density (calculated)	1.983 Mg/m^3
Absorption coefficient, μ	2.941 mm^{-1}
F(000)	712
Crystal colour	red
Crystal description	platelet
Crystal size	0.56 x 0.41 x 0.11 mm
Absorption correction	numerical
Max. and min. transmission	0.8680.987
θ–range for data collection	3.157 ≤ θ ≤ 27.473°
Index ranges	-17 ≤ *h* ≤17;-9≤ *k* ≤9;-16 ≤ *l* ≤15
Reflections collected	18320
Completeness to 2θ	1.000
Independent reflections	2684 [*R*(int) =0.0588]
Reflections *I*>2σ(*I*)	2351
Refinement method	full-matrix least-squares on *F*2
Data / restraints / parameters	2684 /0 /136
Goodness-of-fit on *F*2	1.152
Final *R* indices [*I*>2σ(*I*)]	*R*1 =0.0422, *wR*2 =0.0854
R indices (all data)	*R*1 =0.0528, *wR*2 =0.0892
Max. and mean shift/esd	0.000;0.000
Largest diff. peak and hole	1.535;-0.574 e.Å^{-3}

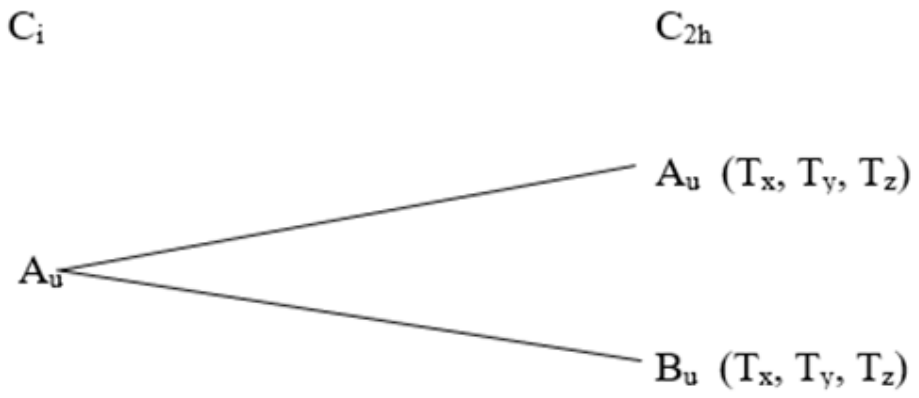
ESI Table S2. The hydrogen bond interactions in the crystal structure of hexamminecobalt(III) dichloro permanganate.

Nr	Donor	--- H....	Acceptor	Symm. code	D – H (Å)	H...A (Å)	D...A (Å)	D - H...A (°)
1	N1	--H1A	..Cl2	x,1/2-y,1/2+z	0.91	2.44	3.289(3)	155
2	N1	--H1A	..O3	x,1/2-y,1/2+z	0.91	2.57	2.952(4)	106
3	N1	--H1B	..Cl1	x,y,z	0.91	2.42	3.327(3)	174
4	N1	--H1C	..Cl1	-x,-y,1-z	0.91	2.60	3.371(3)	143
5	N1	--H1C	..O3	x,1/2-y,1/2+z	0.91	2.59	2.952(4)	104
6	N2	--H2A	..Cl1	-x,1/2+y,1/2-z	0.91	2.42	3.309(4)	166
7	N2	--H2B	..O4	-x,-1/2+y,1/2-z	0.91	2.53	3.208(4)	132
8	N2	--H2C	..Cl1	x,y,z	0.91	2.56	3.399(3)	154
9	N3	--H3A	..Cl1	x,1+y,z	0.91	2.53	3.431(3)	168
10	N3	--H3B	..O3	x,y,z	0.91	2.55	2.941(4)	106
11	N3	--H3B	..Cl1	-x,1/2+y,1/2-z	0.91	2.61	3.408(4)	147
12	N3	--H3C	..O3	x,y,z	0.91	2.57	2.941(4)	105
13	N3	--H3C	..Cl2	x,1/2-y,1/2+z	0.91	2.69	3.541(3)	156
14	N4	--H4A	..Cl2	x,y,z	0.91	2.66	3.561(3)	170
15	N4	--H4B	..O3	x,1/2-y,-1/2+z	0.91	2.49	2.993(4)	115
16	N4	--H4C	..O2	x,3/2-y,-1/2+z	0.91	2.46	3.153(4)	133
17	N5	--H5A	..Cl2	1-x,1/2+y,1/2-z	0.91	2.44	3.316(3)	161
18	N5	--H5B	..Cl2	x,y,z	0.91	2.77	3.338(3)	121
19	N5	--H5B	..O1	1-x,-1/2+y,1/2-z	0.91	2.32	3.146(4)	151
20	N5	--H5C	..O1	x,y,z	0.91	2.37	3.078(4)	135
21	N5	--H5C	..O4	x,y,z	0.91	2.45	3.305(4)	157
22	N6	--H6A	..O4	1-x,1-y,-z	0.91	2.16	3.049(4)	166
23	N6	--H6B	..O1	x,1/2-y,-1/2+z	0.91	2.01	2.895(4)	165
24	N6	--H6C	..O1	1-x,-1/2+y,1/2-z	0.91	2.39	3.212(3)	151
25	N6	--H6C	..O2	1-x,-1/2+y,1/2-z	0.91	2.28	3.035(4)	140

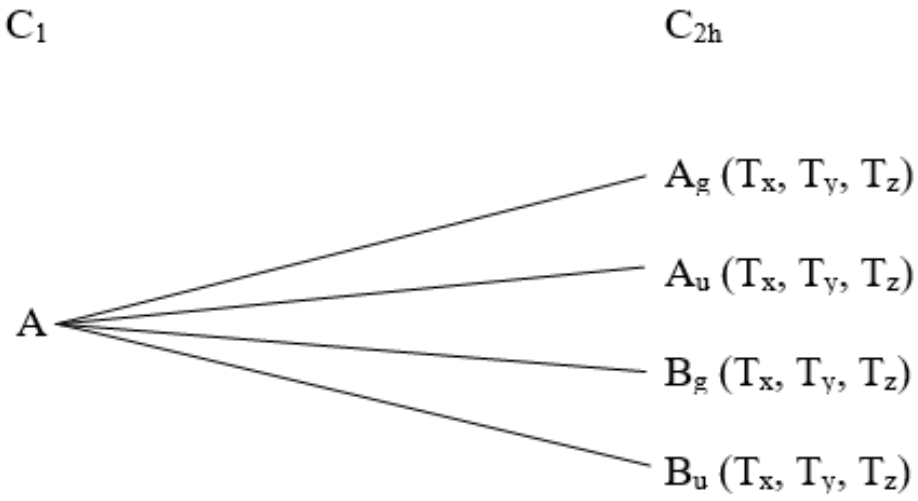
ESI Table S3. The bond lengths (Å) and angles (°) in the crystal structure of hexamminecobalt(III) dichloro permanganate.

Co1-N3	1.949(3)	Co1-N3#1	1.949(3)
Co1-N2	1.952(3)	Co1-N2#1	1.952(3)
Co1-N1	1.961(3)	Co1-N1#1	1.961(3)
Co2-N6	1.953(3)	Co2-N6#2	1.953(3)
Co2-N5	1.956(3)	Co2-N5#2	1.956(3)
Co2-N4	1.975(3)	Co2-N4#2	1.975(3)
Mn3-O3	1.605(2)	Mn3-O2	1.614(2)
Mn3-O1	1.621(3)	Mn3-O4	1.622(3)

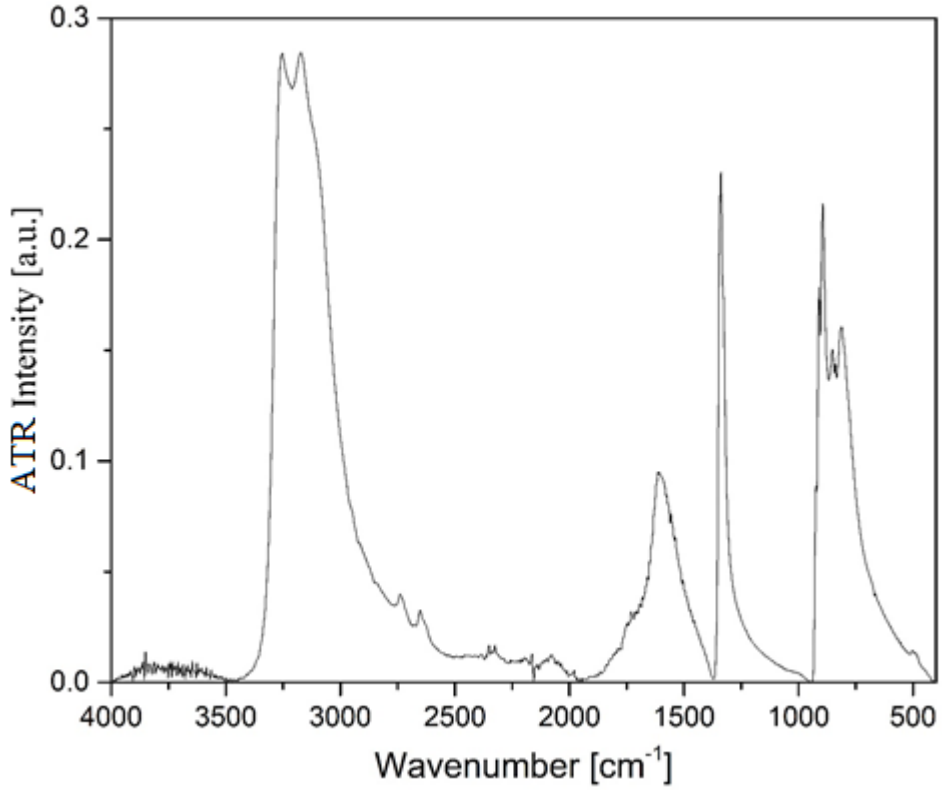
N3-Co1-N3#1	180.0	N3-Co1-N2	91.9(1)
N3#1-Co1-N2	88.1(1)	N3-Co1-N2#1	88.1(1)
N3#1-Co1-N2#1	91.9(1)	N2-Co1-N2#1	180.0
N3-Co1-N1#1	90.3(1)	N3#1-Co1-N1#1	89.8(1)
N2-Co1-N1#1	89.3(1)	N2#1-Co1-N1#1	90.7(1)
N3-Co1-N1	89.8(1)	N3#1-Co1-N1	90.3(1)
N2-Co1-N1	90.7(1)	N2#1-Co1-N1	89.3(1)
N1#1-Co1-N1	180.0	N6#2-Co2-N6	180.0
N6#2-Co2-N5#2	90.4(1)	N6-Co2-N5#2	89.6(1)
N6#2-Co2-N5	89.6(1)	N6-Co2-N5	90.4(1)
N5#2-Co2-N5	180.0	N6#2-Co2-N4	89.2(1)
N6-Co2-N4	90.8(1)	N5#2-Co2-N4	90.8(1)
N5-Co2-N4	89.2(1)	N6#2-Co2-N4#2	90.8(1)
N6-Co2-N4#2	89.2(1)	N5#2-Co2-N4#2	89.2(1)
N5-Co2-N4#2	90.8(1)	N4-Co2-N4#2	180.0
O3-Mn3-O2	109.3(1)	O3-Mn3-O1	109.8(1)
O2-Mn3-O1	107.9(1)	O3-Mn3-O4	110.2(1)
O2-Mn3-O4	109.8(1)	O1-Mn3-O4	109.8(2)



ESI Figure S3. The group analysis for Co atoms in compound **1**.



ESI Figure S4. The group analysis for Cl atoms in compound **1**.



ESI Figure S5. The IR spectra of compound **1**.

ESI Table S4. The IR and Raman spectral data of permanganate ion in compound **1**.

Band/assignation	Wavenumber		
	IR	Raman (785 nm excitation)	
		298 K	123 K
ν_1(Mn-O), ν_s(A)	852 (w)	843 (vs)	843 (vs)
ν_2(Mn-O), δ_s(E)	350sh	350 (s)	350 (s)
ν_3(Mn-O), ν_{as}(F_2)	924sh, 910, 894(vs)	928 922, 917, 912sh, 897 (m)	927, 922, 917, 912sh, 896 (m)
ν_4(Mn-O), δ_{as}(F_2)	388 (m)	398sh, 391	398sh, 393

vw-very weak, w-weak, m-medium, s-strong., vs-very strong; *might be combined with Co-N modes

ESI Table S5. The IR and Raman spectral data of the ammonia ligand in compound **1**.

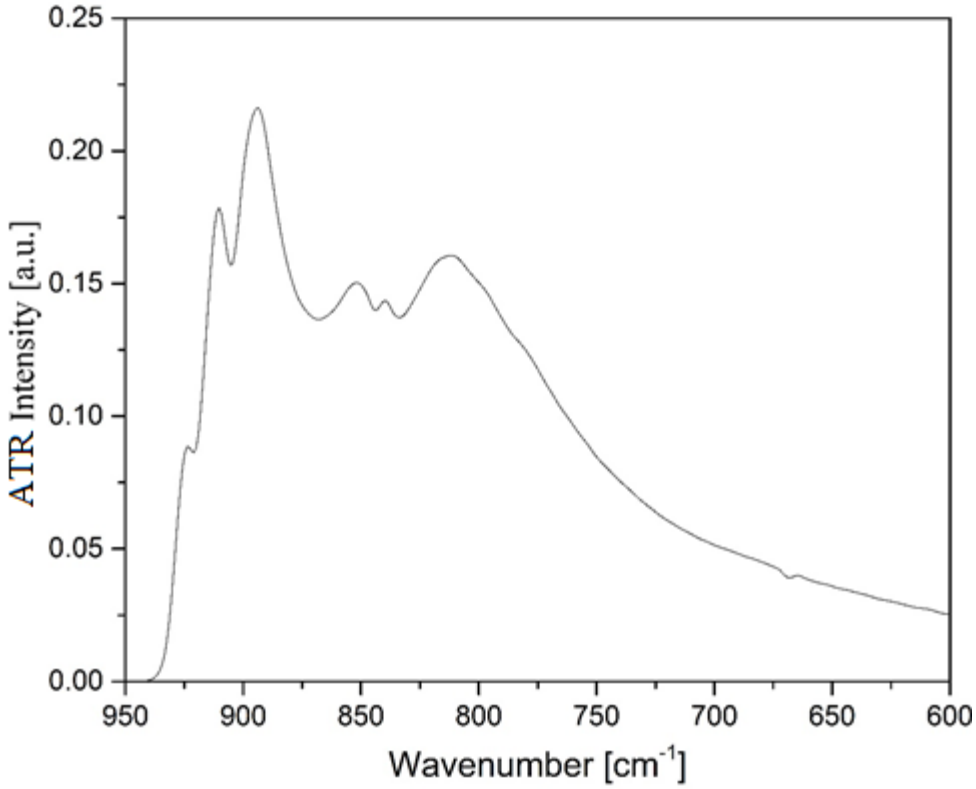
Band/Assignment	Wavenumber, cm^{-1}		
	IR, 298 K	Raman, 785 nm excitation, 298 K	Raman, 785 nm excitation, 123 K
$\rho(NH_3)$	813 (m)	800 (vw)	800 (vw)
$\delta_s(HNH)$	1340 (m), 1327sh	1331, 1324, 1317 (w)	1330, 1323,1305 (w)
$\delta_{as}(HNH)$	1608 (m)	-	-
$\nu_s(NH)$	3174 (vs)	-	-
$\nu_{as}(NH)$	3256 (vs)	-	-

ESI Table S6. The IR and Raman spectral data of the CoN_6 skeleton in compound **1**.

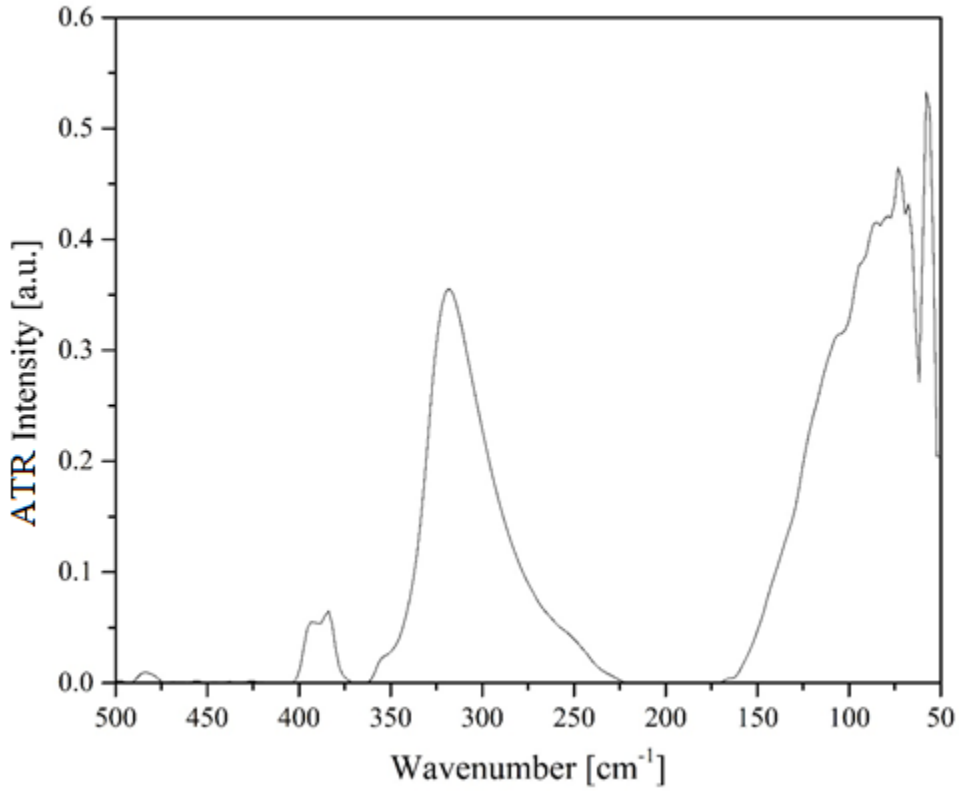
Band/Assignment	Wavenumber, cm^{-1}		
	IR, 298 K	Raman, 785 nm excitation, 298 K	Raman, 785 nm excitation, 123 K
$\nu_1(\nu_{CoN})$	547 (m)	506,500 (m)	507, 499 (m)
$\nu_2(\nu_{as})$		460, 455, 445 (m)	460, 453, 446 (m)
$\nu_3(\nu_s)$	485 (vw)-	-	490 (w)
ν_4 (δ_{as})	317 (vs)	-	320 (vw)
ν_5 (δ_s)		311,306 (w)	311, 306 (w)
ν_6 (δ_{NCoN})	250sh	-	-

ESI Table S7. Electronic transitions (in nm) of the hexaamminecobalt(III) cation in compound **1** and in octahedral and trigonally distorted (compressed) octahedral structures.

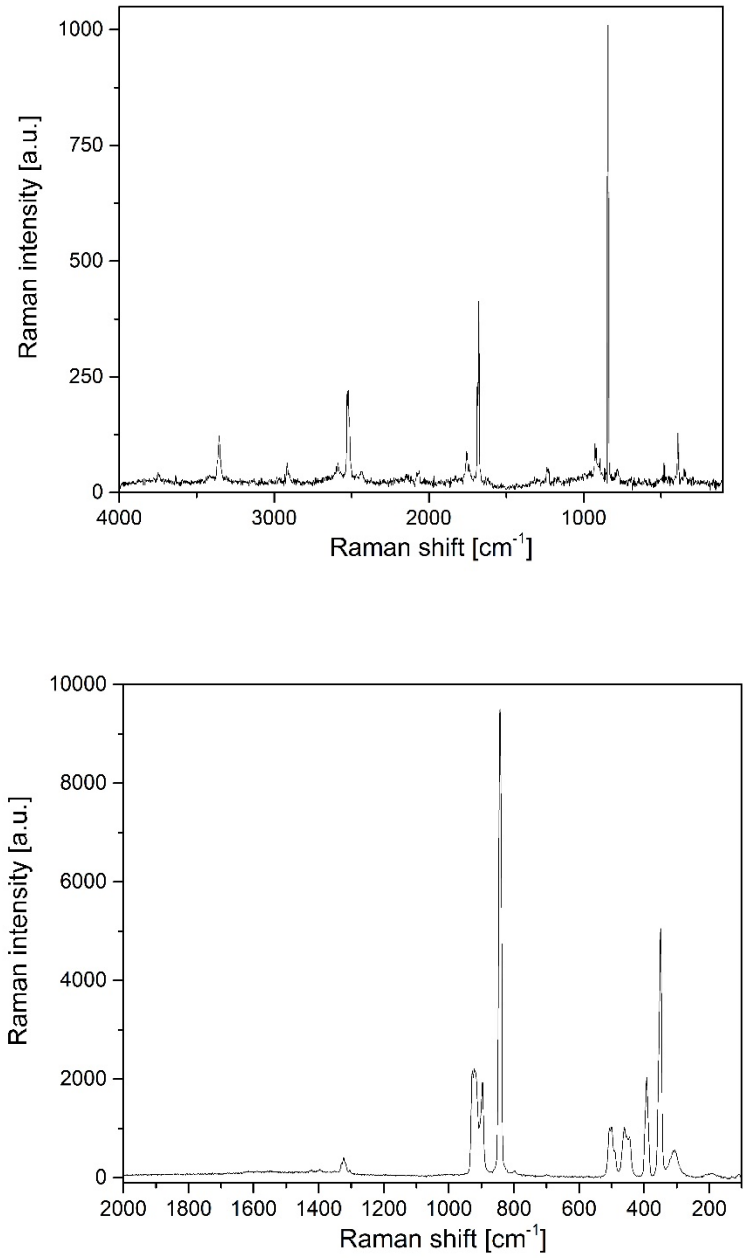
Assignment in O symmetry	Assignment in D_3 symmetry	Compound **1**	Compound **4** [48]	Calculated DFT (LC-BLYP/6-31G]
$^1A_1 \rightarrow {}^3T_1$	$^1A_1 \rightarrow {}^3E$	830	833	806
	$^1A_1 \rightarrow {}^3A_2$			775
$^1A_1 \rightarrow {}^5T_2$	$^1A_1 \rightarrow {}^5E$	727	730	740
	$^1A_1 \rightarrow {}^5A_1$			724
$^1A_1 \rightarrow {}^3T_2$	$^1A_1 \rightarrow {}^3E$	-	617	613
	$^1A_1 \rightarrow {}^3A_1$	575sh	581	585
$^1A_1 \rightarrow {}^1T_1$	$^1A_1 \rightarrow {}^1E$	490	486	465
	$^1A_1 \rightarrow {}^1A_2$	450	444	459
$^1A_1 \rightarrow {}^1T_2$	$^1A_1 \rightarrow {}^1E$	375	367	367
	$^1A_1 \rightarrow {}^1A_1$	343,330sh	324	327



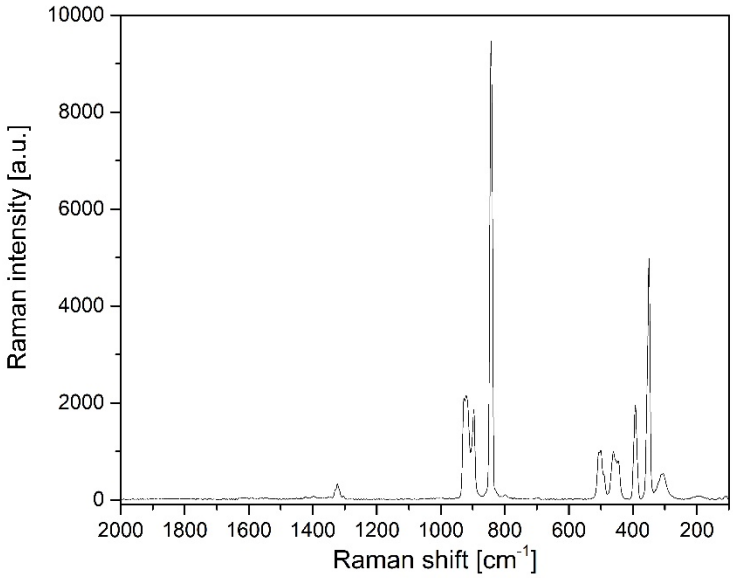
ESI Figure S6. The IR spectra of compound **1** between 950 cm^{-1} and 600 cm^{-1}.

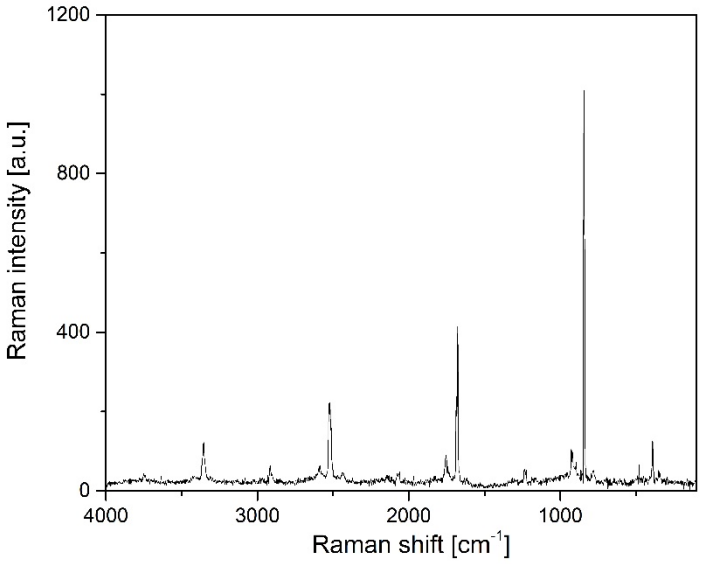


ESI Figure S7. The far-range IR spectra of compound **1**.

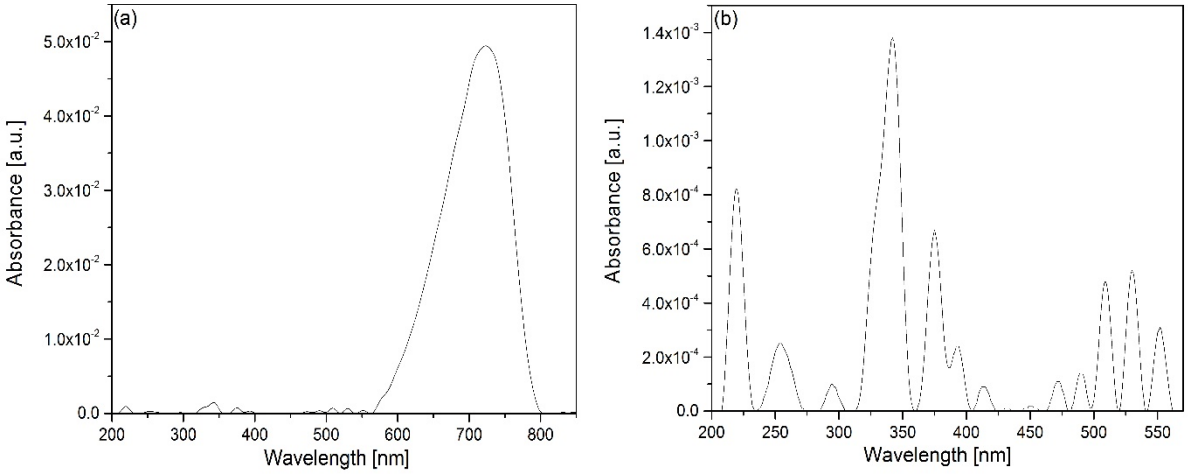


ESI Figure S8. The Raman spectra (at room temperature) of compound **1** with (a) 532 and (b) 785 nm excitation.

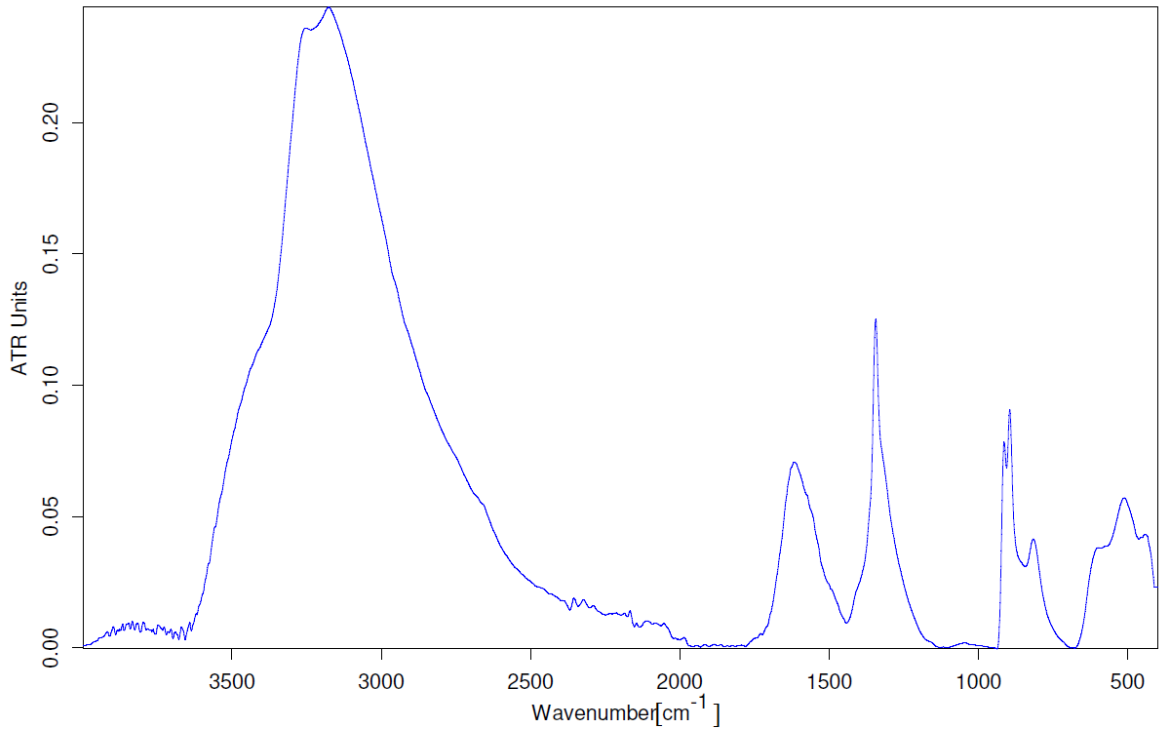




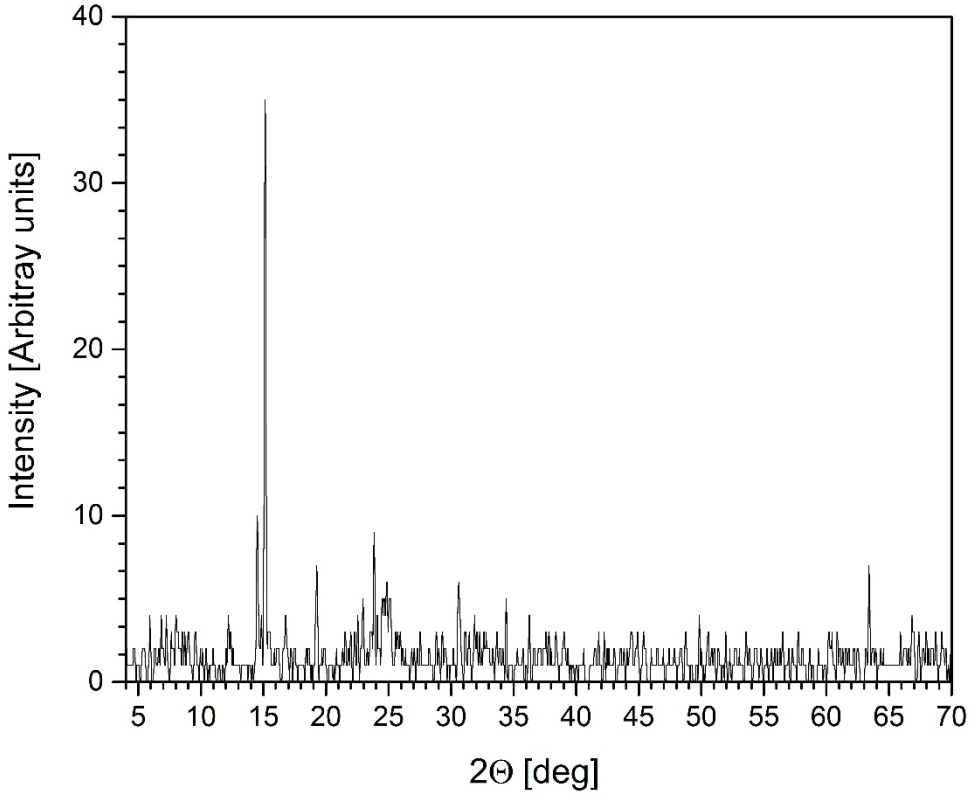
ESI Figure S9. The Raman spectra (at 123K) of compound 1 with (a) 532 and (b) 785 nm excitation.



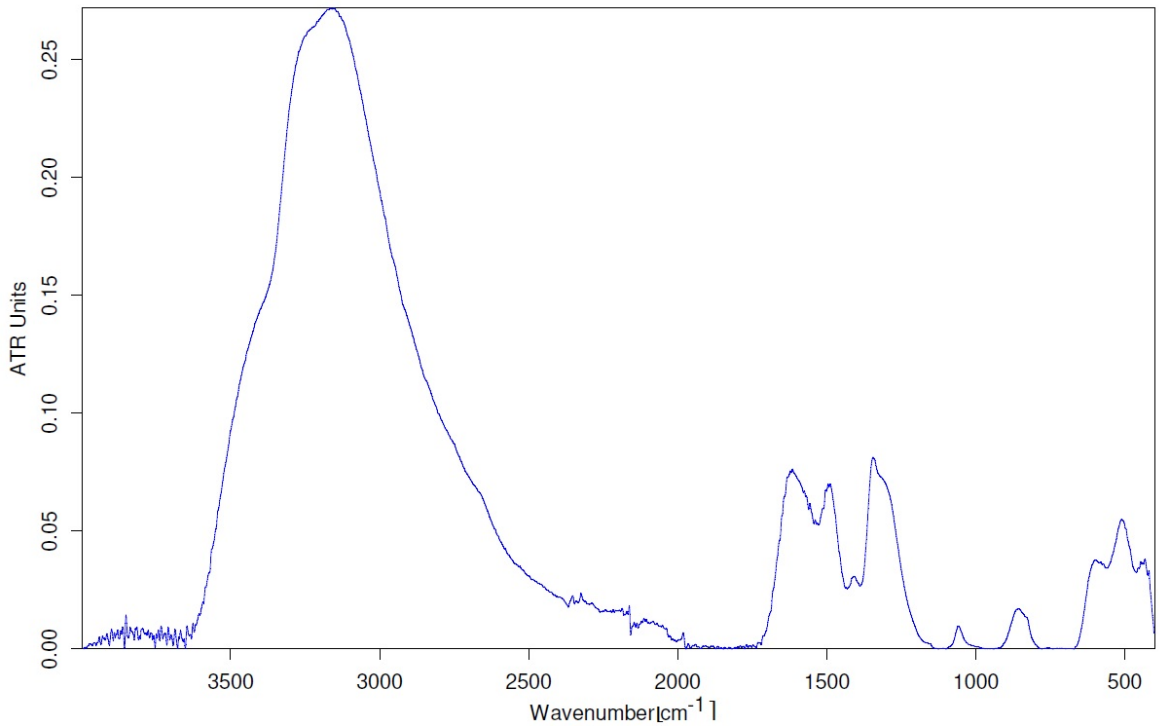
ESI Figure S10. The (a) full range and (b) 200-570 nm range UV-VIS spectra of compound 1.



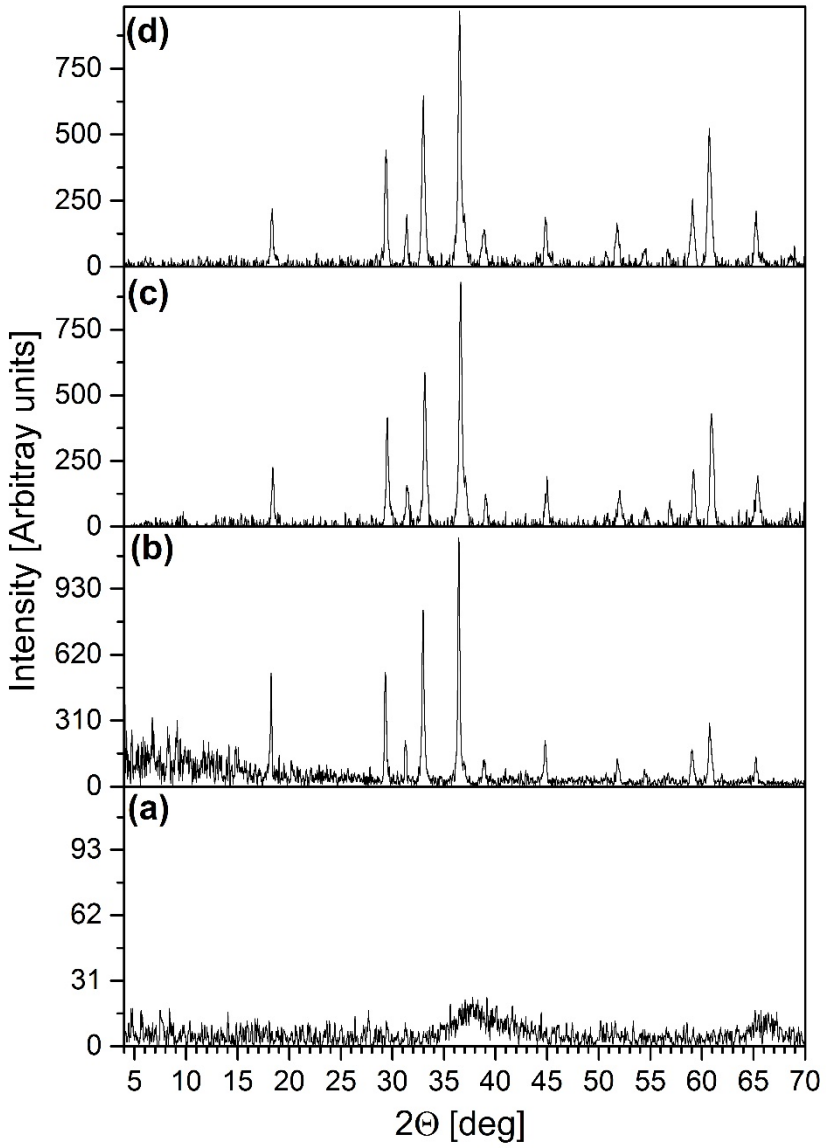
ESI Figure S11. The IR spectra of the evaporation residue from the aqueous extract of the decomposition intermediate made in boiling toluene from compound **1**.



ESI Figure S12. The powder XRD of the evaporation residue from the aqueous extract of the decomposition intermediate made in boiling toluene from compound **1**.



ESI Figure S13. The IR spectra of the water-insoluble decomposition residue of the decomposition intermediate made in boiling toluene from compound **1**.



ESI Figure 14. The powder X-ray diffractograms of the decomposition intermediates and products of compound **2**: **(a)** made by heat-treatment in toluene at 110 °C, **(b)** made by the heat treatment of compound **1** at 500 °C in air and **(c)** made from the water insoluble part of the decomposition intermediate of compound **1** made in toluene by heating at 500 °C and **(d)** made from the decomposition intermediate of compound **1** made in toluene by heating at 500 °C .