Crystal structure of the octahedral iron(III)-nitrate complexes with isomer dimethylurea ligands

Kende Attila Béres[1,2], Zoltán Homonnay[3], Laura Bereczki[1,4], Zsolt Dürvanger[5,6], Vladimir M. Petruševski[7], Attila Farkas[8] and László Kótai[1,9]*

[1]Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Magyar Tudósok krt. 2., H-1117 Budapest, Hungary;
[2]György Hevesy PhD School of Chemistry, ELTE Eötvös Loránd University, Pázmány Péter s. 1/A, H-1117 Budapest, Hungary
[3]Institute of Chemistry, ELTE Eötvös Loránd University, Pázmány Péter s. 1/A, H-1117 Budapest, Hungary
[4]Centre for Structural Science, Research Centre for Natural Sciences, Magyar Tudósok krt. 2., 1117 Budapest, Hungary
[5]ELKH-ELTE Protein Modelling Research Group, Pázmány Péter s. 1/A, H-1117 Budapest, Hungary
[6]Structural Chemistry and Biology Laboratory, Institute of Chemistry, ELTE Eötvös Loránd University, Pázmány Péter s. 1/A, H-1117 Budapest, Hungary
[7]Faculty of Natural Sciences and Mathematics, Ss. Cyril and Methodius University, Skopje, MK-1000, North Macedonia
[8]Department of Organic Chemistry and Technology, Faculty of Chemical Technology and Biotechnology, Budapest University of Technology and Economics, Műegyetem rkp. 3., H-1111 Budapest, Hungary
[9]Deuton-X Ltd., Selmeci u. 89, H-2030, Érd, Hungary
*Correspondence: kotai.laszlo@ttk.hu

ESI Table S1. Crystal data and structure refinement of compounds **1**, **2** and **3**

Label	Compound 1	Compound **2**	Compound **3**
Compound	$[Fe(N,N'\text{-}DMU)_6](NO_3)_3$	$[Fe(N,N\text{-}DMU)_4(H_2O)_2](NO_3)_3$	$[Fe(N,N\text{-}DMU)_6](NO_3)_3.3H_2O$
Empirical formula	$C_{18}H_{48}FeN_{14}O_{12}$	$C_{12}H_{36}FeN_{11}O_{15}$	$C_{18}H_{54}FeN_{15}O_{18}$
Formula weight	708.55	630.37	824.61
Temperature	100.00(10) K	113(2)	105(2) K
Radiation and wavelength	Cu-Kα, λ =1.54184 Å	Mo-Kα, λ =0.71073Å	Cu-Kα, λ =1.54184 Å
Crystal system	Trigonal	triclinic	Trigonal
Space group	*R*-3	*P*-1	*R*-3
Unit cell dimensions	a = 12.1232(2) Å b = 12.1232(2) Å c = 22.5665(4) Å α= 90° β = 90° γ = 120°	*a* =9.8655(6)Å *b* =10.5568(7)Å *c* =15.5569(10)Å α =77.658(5)° β =76.538(5)° γ =62.239(4)°	a = 22.0051(3) Å b = 22.0051(3) Å c = 13.9132(2) Å α= 90° β = 90° γ = 120°
Volume	2872.30(11) $Å^3$	1383.86(16)$Å^3$	5834.51(18) $Å^3$
Z	3	2	6
Density (calculated)	1.229 Mg/m^3	1.513 Mg/m^3	1.408 Mg/m^3
Absorption coefficient, μ	3.737 mm^{-1}	0.629 mm^{-1}	3.887 mm^{-1}
F(000)	1128	662	2622
Crystal colour	orange	orange	orange
Crystal description	block	prism	rod
Crystal size	0.387 x 0.369 x 0.293 mm^3	0.37 x 0.33 x 0.32 mm^3	0.197 x 0.066 x 0.049 mm^3
Absorption correction	Gaussian	numerical	Gaussian
Max. and min. transmission	1.0000.166	0.9070.962	1.0000.569
θ–range for data collection	4.645 ≤ θ ≤ 75.409°	5.116 ≤ θ ≤ 25.349°	3.934 to 75.583°
Index ranges	-15<=h<=15, -15<=k<=14, -28<=l<=28	$-11 \le h \le 11$;$-12 \le k \le 12$;$-18 \le l \le 18$	-27<=h<=27, -27<=k<=27, -17<=l<=17
Reflections collected	13522	22946	27109
Completeness to 2θ	100.0 %	0.990	100.0 %
Independent reflections	1321 [R(int) = 0.0395]	5030 [*R*(int) =0.0547]	2672 [R(int) = 0.0466]
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data / restraints / parameters	1321 / 0 / 74	5030 /1 /363	2672 / 0 / 164
Goodness-of-fit on F^2	1.145	1.114	1.088
Final *R* indices [$I>2\sigma(I)$]	R1 = 0.0387, wR2 = 0.1152	*R*1 =0.0504, *wR*2 =0.1032	R1 = 0.0417, wR2 = 0.1233
R indices (all data)	R1 = 0.0388, wR2 = 0.1154	*R*1 =0.0660, *wR*2 =0.1089	R1 = 0.0427, wR2 = 0.1242
Largest diff. peak and hole	0.283 and -0.502 e.$Å^{-3}$	0.445;-0.326 e.$Å^{-3}$	0.522 and -0.376 e.$Å^{-3}$

ESI Table S2. Bond lengths [Å] and angles [°] of compound **1**.

Fe(1)-O(2)	2.0048(11)
Fe(1)-O(2)#1	2.0048(11)
Fe(1)-O(2)#2	2.0048(11)
Fe(1)-O(2)#3	2.0048(11)
Fe(1)-O(2)#4	2.0048(11)
Fe(1)-O(2)#5	2.0048(11)
O(2)-C(3)	1.282(2)
O(9)-N(8)	1.2500(12)
N(6)-C(3)	1.333(2)
N(6)-C(7)	1.447(2)
N(6)-H(6)	0.8800
N(4)-C(3)	1.322(2)
N(4)-C(5)	1.462(2)
N(4)-H(4)	0.8800
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
O(2)-Fe(1)-O(2)#1	92.17(5)
O(2)-Fe(1)-O(2)#2	180.0
O(2)#1-Fe(1)-O(2)#2	87.83(5)
O(2)-Fe(1)-O(2)#3	87.83(5)
O(2)#1-Fe(1)-O(2)#3	180.00(7)
O(2)#2-Fe(1)-O(2)#3	92.17(5)
O(2)-Fe(1)-O(2)#4	92.17(5)
O(2)#1-Fe(1)-O(2)#4	92.17(5)
O(2)#2-Fe(1)-O(2)#4	87.83(5)
O(2)#3-Fe(1)-O(2)#4	87.83(5)
O(2)-Fe(1)-O(2)#5	87.83(5)
O(2)#1-Fe(1)-O(2)#5	87.83(5)
O(2)#2-Fe(1)-O(2)#5	92.17(5)
O(2)#3-Fe(1)-O(2)#5	92.17(5)
O(2)#4-Fe(1)-O(2)#5	180.0
C(3)-O(2)-Fe(1)	133.63(10)
O(9)#6-N(8)-O(9)	120.000(3)
O(9)#6-N(8)-O(9)#7	119.998(3)
O(9)-N(8)-O(9)#7	119.996(3)
C(3)-N(6)-C(7)	125.07(14)
C(3)-N(6)-H(6)	117.5
C(7)-N(6)-H(6)	117.5
C(3)-N(4)-C(5)	122.11(16)
C(3)-N(4)-H(4)	118.9
C(5)-N(4)-H(4)	118.9
O(2)-C(3)-N(4)	119.32(15)
O(2)-C(3)-N(6)	120.20(14)
N(4)-C(3)-N(6)	120.49(15)
N(6)-C(7)-H(7A)	109.5
N(6)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
N(6)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
N(4)-C(5)-H(5A)	109.5
N(4)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
N(4)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5

Symmetry transformations used to generate equivalent atoms:
#1 -x+y+1,-x+2,z #2 -x+2,-y+2,-z+1 #3 x-y+1,x,-z+1
#4 -y+2,x-y+1,z #5 y,-x+y+1,-z+1 #6 -y+1,x-y+1,z
#7 -x+y,-x+1,z

ESI Table S3. Torsion angles for compound **1** [°]

Fe(1)-O(2)-C(3)-N(4)	-144.18(14)
Fe(1)-O(2)-C(3)-N(6)	35.8(2)
C(5)-N(4)-C(3)-O(2)	4.5(3)
C(5)-N(4)-C(3)-N(6)	-175.56(19)
C(7)-N(6)-C(3)-O(2)	177.72(16)
C(7)-N(6)-C(3)-N(4)	-2.3(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x+y+1,-x+2,z #2 -x+2,-y+2,-z+1 #3 x-y+1,x,-z+1
#4 -y+2,x-y+1,z #5 y,-x+y+1,-z+1 #6 -y+1,x-y+1,z
#7 -x+y,-x+1,z

ESI Table S4. Bond lengths [Å] and angles [°] of compound **2**.

Fe1-O2	1.970(2)	Fe1-O2#1	1.970(2)
Fe1-O1#1	2.009(2)	Fe1-O1	2.009(2)
Fe1-O1W	2.026(2)	Fe1-O1W#1	2.026(2)
O1-C1	1.292(3)	O2-C4	1.282(4)
N1-C1	1.329(4)	N1-C3	1.458(4)
N1-C2	1.460(4)	N2-C1	1.329(4)
N3-C4	1.331(4)	N4-C4	1.332(4)
N4-C5	1.453(4)	N4-C6	1.458(4)
Fe2-O4	1.960(2)	Fe2-O4#2	1.960(2)
Fe2-O3#2	2.002(2)	Fe2-O3	2.002(2)
Fe2-O2W	2.033(2)	Fe2-O2W#2	2.033(2)
O3-C7	1.285(3)	O4-C10	1.275(4)
N5-C7	1.330(4)	N5-C8	1.452(4)
N5-C9	1.462(4)	N6-C7	1.322(4)
N7-C10	1.337(4)	N8-C10	1.323(4)
N8-C12	1.452(4)	N8-C11	1.455(4)
O5-N9	1.260(3)	O6-N9	1.240(3)
O7-N9	1.214(4)	O8-N10	1.253(3)
O9-N10	1.249(3)	O10-N10	1.245(3)
O11-N11	1.215(4)	O12-N11	1.225(4)
O13-N11	1.260(3)		

O2-Fe1-O2#1	180.0	O2-Fe1-O1#1	88.67(8)
O2#1-Fe1-O1#1	91.33(8)	O2-Fe1-O1	91.33(8)
O2#1-Fe1-O1	88.67(8)	O1#1-Fe1-O1	180.0
O2-Fe1-O1W	90.03(8)	O2#1-Fe1-O1W	89.97(8)
O1#1-Fe1-O1W	90.69(8)	O1-Fe1-O1W	89.31(8)
O2-Fe1-O1W#1	89.97(8)	O2#1-Fe1-O1W#1	90.03(8)
O1#1-Fe1-O1W#1	89.31(8)	O1-Fe1-O1W#1	90.69(8)
O1W-Fe1-O1W#1	180.0	C1-O1-Fe1	131.8(2)
C4-O2-Fe1	136.5(2)	C1-N1-C3	122.6(3)
C1-N1-C2	120.7(3)	C3-N1-C2	116.6(3)
C4-N4-C5	121.2(3)	C4-N4-C6	120.4(3)
C5-N4-C6	116.9(3)	O1-C1-N1	120.0(3)
O1-C1-N2	119.2(3)	N1-C1-N2	120.8(3)
O2-C4-N3	120.7(3)	O2-C4-N4	119.5(3)
N3-C4-N4	119.8(3)	O4-Fe2-O4#2	180.0
O4-Fe2-O3#2	88.62(8)	O4#2-Fe2-O3#2	91.38(8)
O4-Fe2-O3	91.38(8)	O4#2-Fe2-O3	88.62(8)
O3#2-Fe2-O3	180.0	O4-Fe2-O2W	91.25(9)
O4#2-Fe2-O2W	88.75(9)	O3#2-Fe2-O2W	90.19(9)
O3-Fe2-O2W	89.81(9)	O4-Fe2-O2W#2	88.75(9)
O4#2-Fe2-O2W#2	91.26(9)	O3#2-Fe2-O2W#2	89.81(9)
O3-Fe2-O2W#2	90.19(9)	O2W-Fe2-O2W#2	180.0
C7-O3-Fe2	133.7(2)	C10-O4-Fe2	141.4(2)
C7-N5-C8	120.6(3)	C7-N5-C9	121.6(3)
C8-N5-C9	117.1(3)	C10-N8-C12	121.9(3)
C10-N8-C11	120.8(3)	C12-N8-C11	117.1(3)
O3-C7-N6	120.2(3)	O3-C7-N5	119.5(3)
N6-C7-N5	120.2(3)	O4-C10-N8	119.5(3)
O4-C10-N7	120.1(3)	N8-C10-N7	120.4(3)
O7-N9-O6	120.6(3)	O7-N9-O5	119.8(3)
O6-N9-O5	119.6(3)	O10-N10-O9	119.9(3)
O10-N10-O8	120.4(3)	O9-N10-O8	119.7(3)
O11-N11-O12	122.4(3)	O11-N11-O13	117.8(3)
O12-N11-O13	119.7(3)		

Symmetry codes to generate equivalent atoms:

1. [2_756] -x+2,-y,-z+1
2. [2_665] -x+1,-y+1,-z

ESI Table S5. Torsion angles [°] of compound **2**.

Fe1-O1-C1-N1	-106.6(3)	Fe1-O1-C1-N2	75.6(3)
C3-N1-C1-O1	-176.3(3)	C2-N1-C1-O1	3.0(4)
C3-N1-C1-N2	1.5(5)	C2-N1-C1-N2	-179.2(3)
Fe1-O2-C4-N3	28.7(4)	Fe1-O2-C4-N4	-154.1(2)
C5-N4-C4-O2	14.5(4)	C6-N4-C4-O2	180.0(3)
C5-N4-C4-N3	-168.3(3)	C6-N4-C4-N3	-2.8(4)
Fe2-O3-C7-N6	-78.7(4)	Fe2-O3-C7-N5	103.6(3)
C8-N5-C7-O3	2.5(5)	C9-N5-C7-O3	172.7(3)
C8-N5-C7-N6	-175.2(3)	C9-N5-C7-N6	-5.0(5)
Fe2-O4-C10-N8	169.6(2)	Fe2-O4-C10-N7	-12.7(5)
C12-N8-C10-O4	-177.9(3)	C11-N8-C10-O4	-3.8(5)
C12-N8-C10-N7	4.4(5)	C11-N8-C10-N7	178.5(3)

ESI Table S6. Bond lengths [Å] and angles [°] of compound **3**.

Fe(1)-O(2)#1	2.0094(13)
Fe(1)-O(2)#2	2.0094(13)
Fe(1)-O(2)	2.0094(13)
Fe(1)-O(8)#2	2.0169(13)
Fe(1)-O(8)#1	2.0169(13)
Fe(1)-O(8)	2.0169(13)
O(8)-C(9)	1.285(2)
O(2)-C(3)	1.279(2)
O(16)-N(14)	1.243(2)
N(11)-C(9)	1.330(2)
N(11)-C(12)	1.462(2)
N(11)-C(13)	1.463(2)
O(17)-N(14)	1.251(2)
N(14)-O(15)	1.244(2)
N(10)-C(9)	1.336(2)
N(4)-C(3)	1.330(3)
N(5)-C(3)	1.335(3)
N(5)-C(6)	1.452(3)
N(5)-C(7)	1.463(3)
O(2)#1-Fe(1)-O(2)#2	90.36(6)
O(2)#1-Fe(1)-O(2)	90.36(6)
O(2)#2-Fe(1)-O(2)	90.36(6)
O(2)#1-Fe(1)-O(8)#2	89.76(5)
O(2)#2-Fe(1)-O(8)#2	88.70(5)
O(2)-Fe(1)-O(8)#2	179.05(5)
O(2)#1-Fe(1)-O(8)#1	88.70(5)
O(2)#2-Fe(1)-O(8)#1	179.05(5)
O(2)-Fe(1)-O(8)#1	89.76(5)
O(8)#2-Fe(1)-O(8)#1	91.19(6)
O(2)#1-Fe(1)-O(8)	179.05(5)
O(2)#2-Fe(1)-O(8)	89.76(5)
O(2)-Fe(1)-O(8)	88.70(5)
O(8)#2-Fe(1)-O(8)	91.19(6)
O(8)#1-Fe(1)-O(8)	91.19(6)
C(9)-O(8)-Fe(1)	132.23(11)
C(3)-O(2)-Fe(1)	131.72(12)
C(9)-N(11)-C(12)	120.55(14)
C(9)-N(11)-C(13)	121.02(15)
C(12)-N(11)-C(13)	118.43(14)
O(16)-N(14)-O(15)	120.91(17)
O(16)-N(14)-O(17)	120.35(17)
O(15)-N(14)-O(17)	118.74(17)
C(3)-N(5)-C(6)	120.50(18)
C(3)-N(5)-C(7)	121.3(2)
C(6)-N(5)-C(7)	118.1(2)
O(8)-C(9)-N(11)	119.51(15)
O(8)-C(9)-N(10)	120.40(15)
N(11)-C(9)-N(10)	120.08(15)
O(2)-C(3)-N(4)	120.27(17)
O(2)-C(3)-N(5)	118.66(18)
N(4)-C(3)-N(5)	121.05(18)

Symmetry transformations used to generate equivalent atoms:
#1 -y+1,x-y+1,z #2 -x+y,-x+1,z

ESI Table S7. Torsion angles [°] of compound **3**.

Fe(1)-O(8)-C(9)-N(11)	-145.74(14)
Fe(1)-O(8)-C(9)-N(10)	34.8(3)
C(12)-N(11)-C(9)-O(8)	-179.66(17)
C(13)-N(11)-C(9)-O(8)	1.0(3)
C(12)-N(11)-C(9)-N(10)	-0.2(3)
C(13)-N(11)-C(9)-N(10)	-179.53(18)
Fe(1)-O(2)-C(3)-N(4)	39.4(3)
Fe(1)-O(2)-C(3)-N(5)	-141.98(15)
C(6)-N(5)-C(3)-O(2)	2.3(3)
C(7)-N(5)-C(3)-O(2)	180.0(2)
C(6)-N(5)-C(3)-N(4)	-179.1(2)
C(7)-N(5)-C(3)-N(4)	-1.4(3)

Symmetry transformations used to generate equivalent atoms:
#1 -y+1,x-y+1,z #2 -x+y,-x+1,z

ESI Table S8. 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 in compound **1**

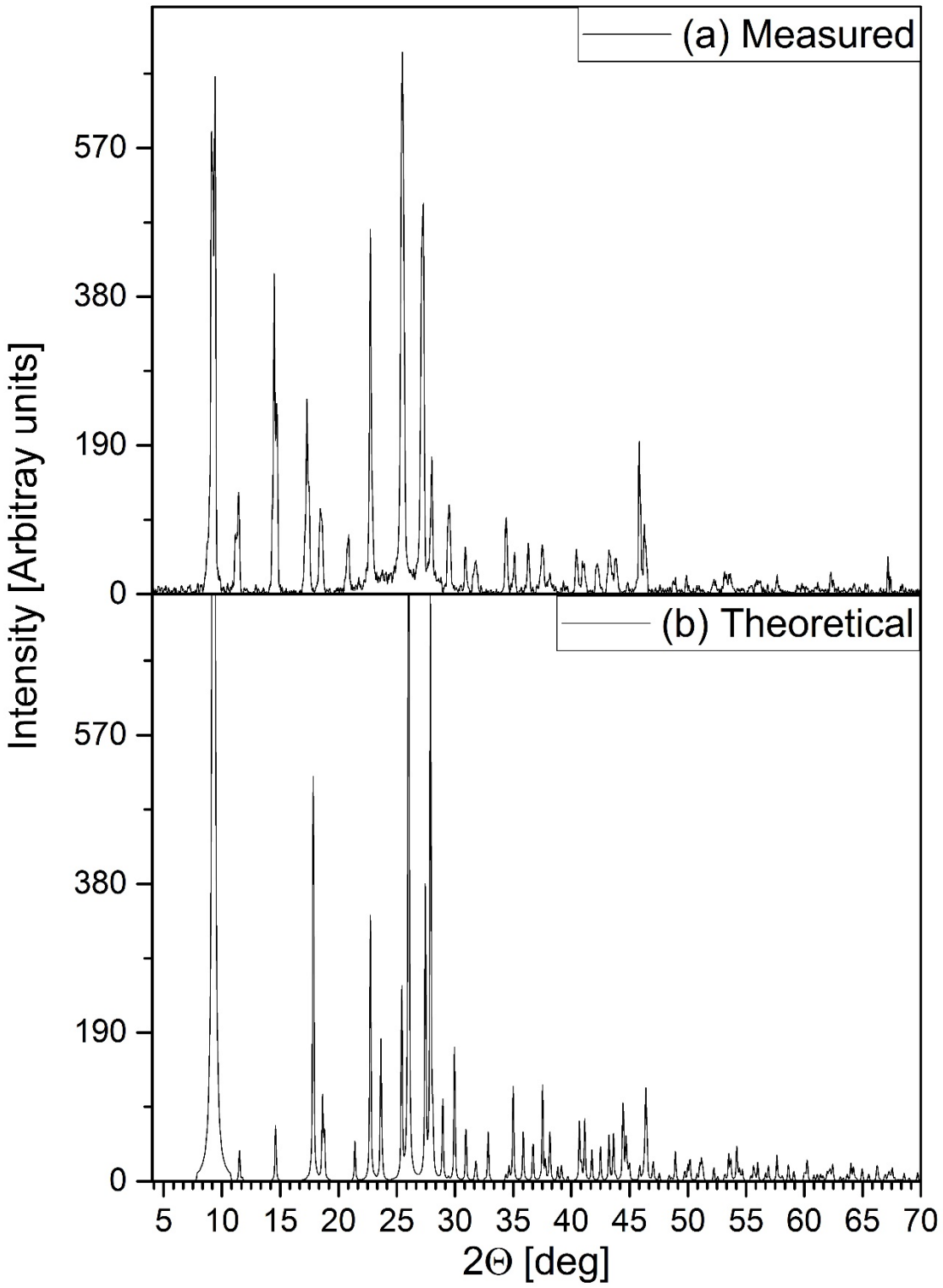
Nr	Donor	---	H....Acceptor	Symm. op.	D - H	H...A	D...A	D - H...A
1	N4	--H4	..O9	x,y,z	0.88	2.05	2.925(2)	170
2	N6	--H6	..O2	1-x+y,2-x,z	0.88	2.10	2.884(2)	149

ESI Table S9. 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 in compound **2.**

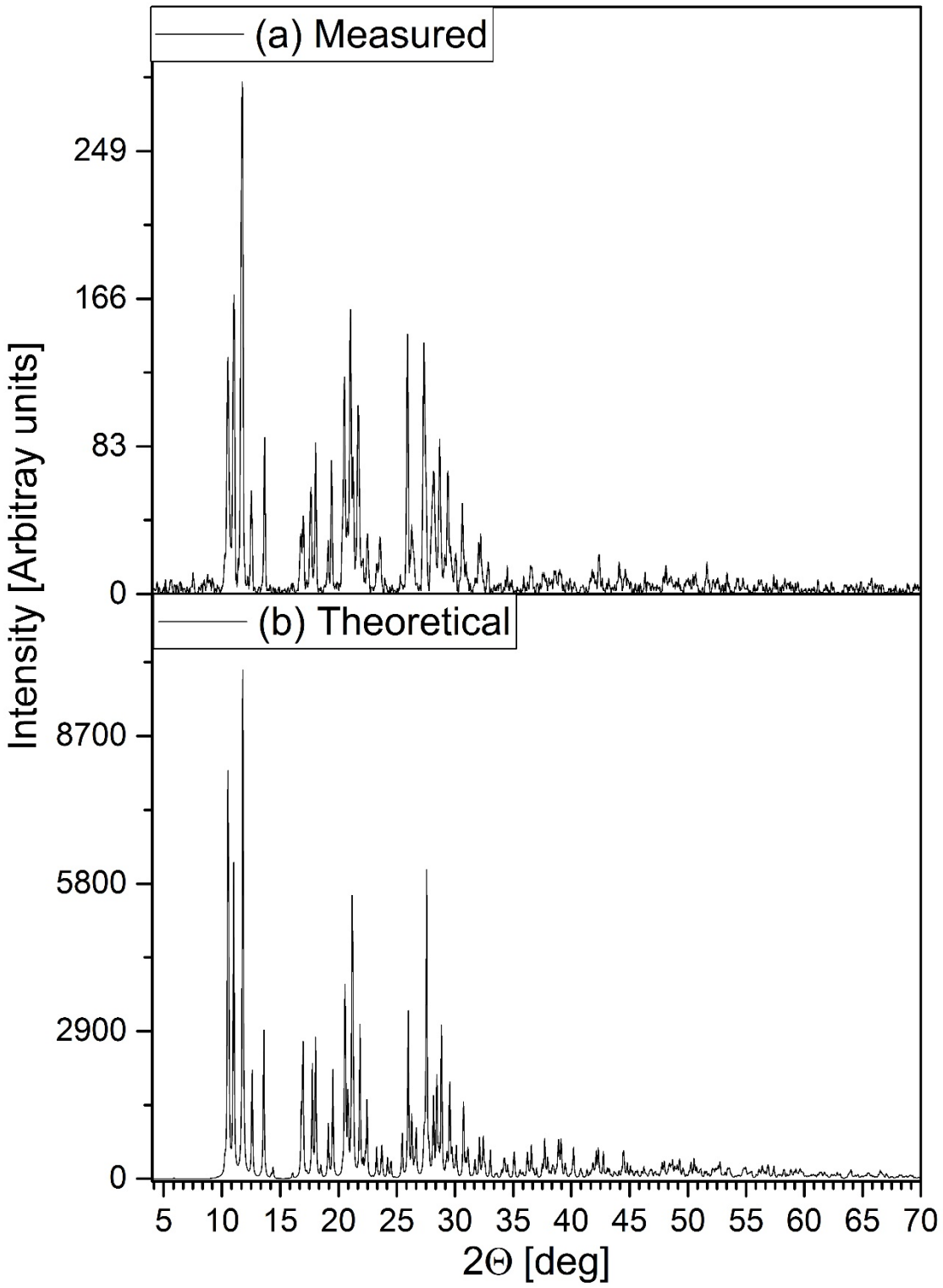
Nr	Donor --- H....Acceptor	Symm. op.	D - H	H...A	D...A	D - H...A
1	O1W --H1WA ..O8	1-x,1-y,1-z	0.85	1.82	2.663(3)	174
2	O1W --H1WB ..O6	1+x,y,z	0.85	1.83	2.672(3)	169
3	N2 --H2A ..O7	1-x,-y,1-z	0.86	2.17	2.916(4)	146
4	N2 --H2B ..O9	1-x,-y,1-z	0.86	2.07	2.912(4)	165
5	O2W --H2WA ..O11	x,y,z	0.85	2.5	3.190(4)	138
6	O2W --H2WA ..O13	x,y,z	0.85	1.79	2.611(4)	162
7	N3 --H3A ..O1	Intra	0.86	2.08	2.829(3)	145
8	N3 --H3B ..O10	x,y,z	0.86	2.19	2.987(4)	155
9	O2W --H2WB ..O5	x,y,z	0.85	1.84	2.680(4)	170
10	N6 --H6D ..O5	1-x,1-y,-z	0.86	2.24	2.970(4)	143
11	N6 --H6E ..O12	x,1+y,z	0.86	2.11	2.942(5)	164
12	N7 --H7A ..O3	Intra	0.86	2.09	2.828(3)	143
13	N7 --H7B ..O12	2-x,-y,-z	0.86	2.09	2.867(5)	151
14	C2 --H2C ..O1	Intra	0.98	2.28	2.724(4)	107
15	C3 --H3E ..O9	1-x,-y,1-z	0.98	2.58	3.217(4)	122
16	C5 --H5A ..O2	Intra	0.98	2.36	2.734(4)	102
17	C8 --H8A ..O2W	Intra	0.98	2.4	3.346(6)	161
18	C8 --H8A ..O3	Intra	0.98	2.34	2.706(4)	101
19	C8 --H8B ..O10	1-x,1-y,1-z	0.98	2.44	3.376(4)	161
20	C8 --H8C ..O6	1+x,y,z	0.98	2.53	3.352(6)	141
21	C11 --H11A ..O11	1-x,-y,-z	0.98	2.48	3.047(6)	117
22	C11 --H11C ..O4	Intra	0.98	2.35	2.699(4)	100
23	C12 --H12C ..O6	1-x,-y,-z	0.98	2.4	3.373(5)	171

ESI Table S10. 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 in compound **3**

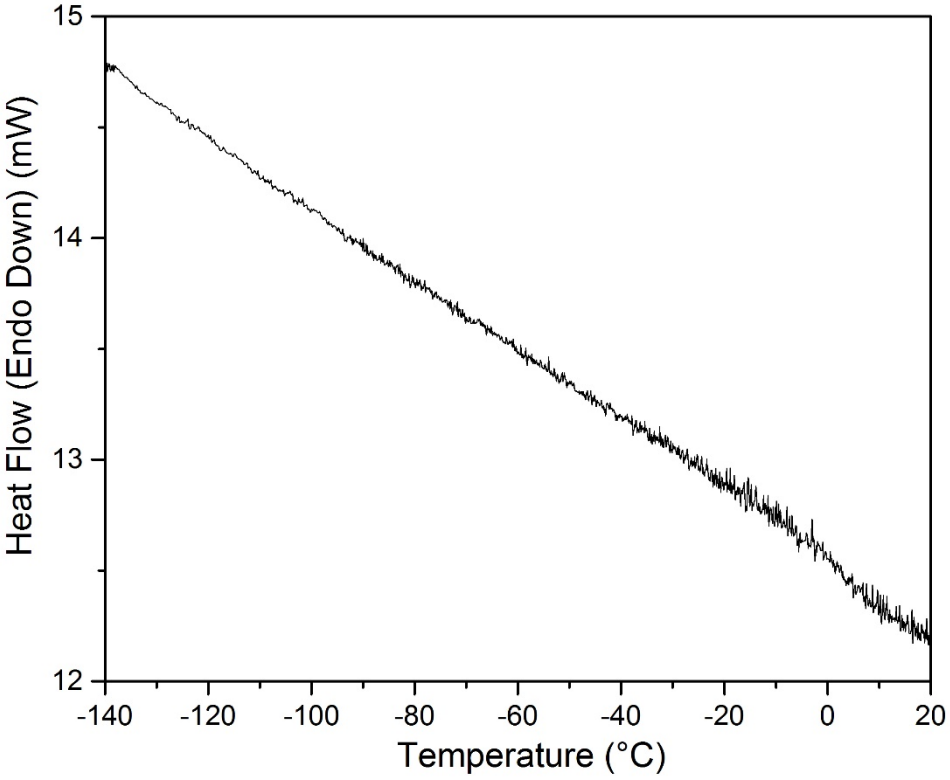
Nr	Donor	---	H....	Acceptor	Symm. op.	D - H	H...A	D...A	D - H...A
1	N4	--H4A		..O2	1-y,1+x-y,z	0.88	2.16	2.916(3)	144
2	N4	--H4B		..O18	x,y,z	0.88	2.05	2.850(3)	152
3	N10	--H10A		..O8	-x+y,1-x,z	0.88	2.12	2.893(2)	145
4	N10	--H10B		..O16	1/3+x-y,-1/3+x,2/3-z	0.88	2.10	2.954(2)	164
5	O18	--H18A		..O17	x,y,z	0.87	1.94	2.800(3)	169
6	O18	--H18B		..O15	5/3-y,4/3+x-y,1/3+z	0.87	2.27	3.108(3)	161
7	O18	--H18B		..O17	5/3-y,4/3+x-y,1/3+z	0.87	2.36	3.099(3)	142
8	C6	--H6A		..O2	Intra	0.98	2.24	2.689(4)	107
9	C6	--H6C		..O15	4/3-x,5/3-y,2/3-z	0.98	2.41	3.213(3)	139
10	C7	--H7B		..O15	1+x-y,x,1-z	0.98	2.55	3.509(4)	166
11	C13	--H13C		..O8	Intra	0.98	2.29	2.720(3)	106



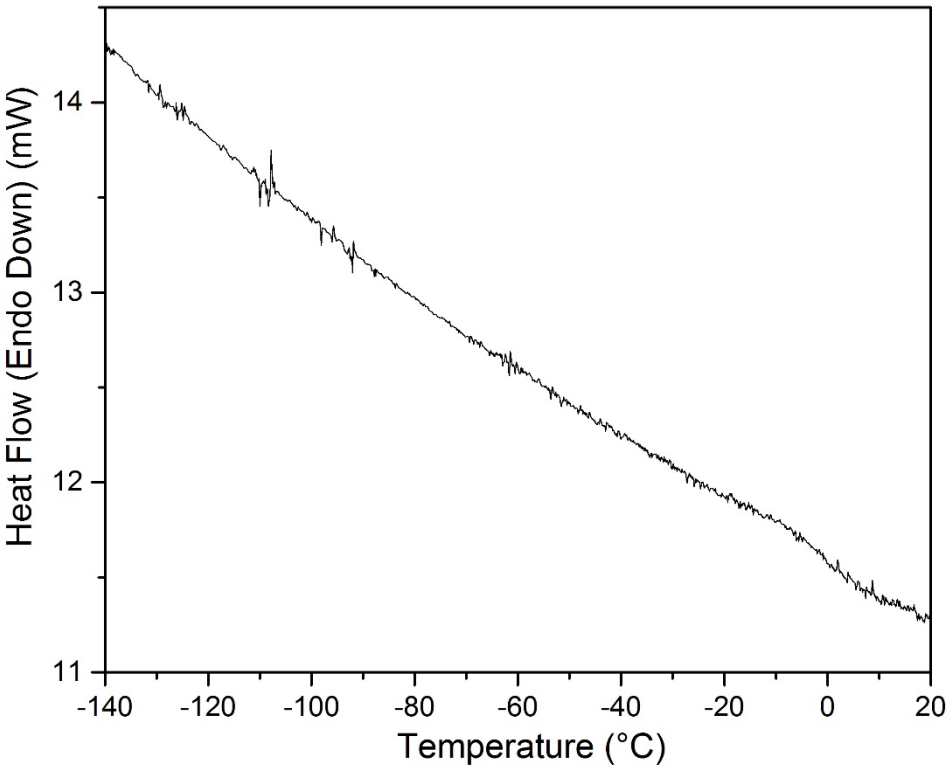
ESI Figure S1. The calculated and the experimental powder X-ray diffraction of compound **1.**



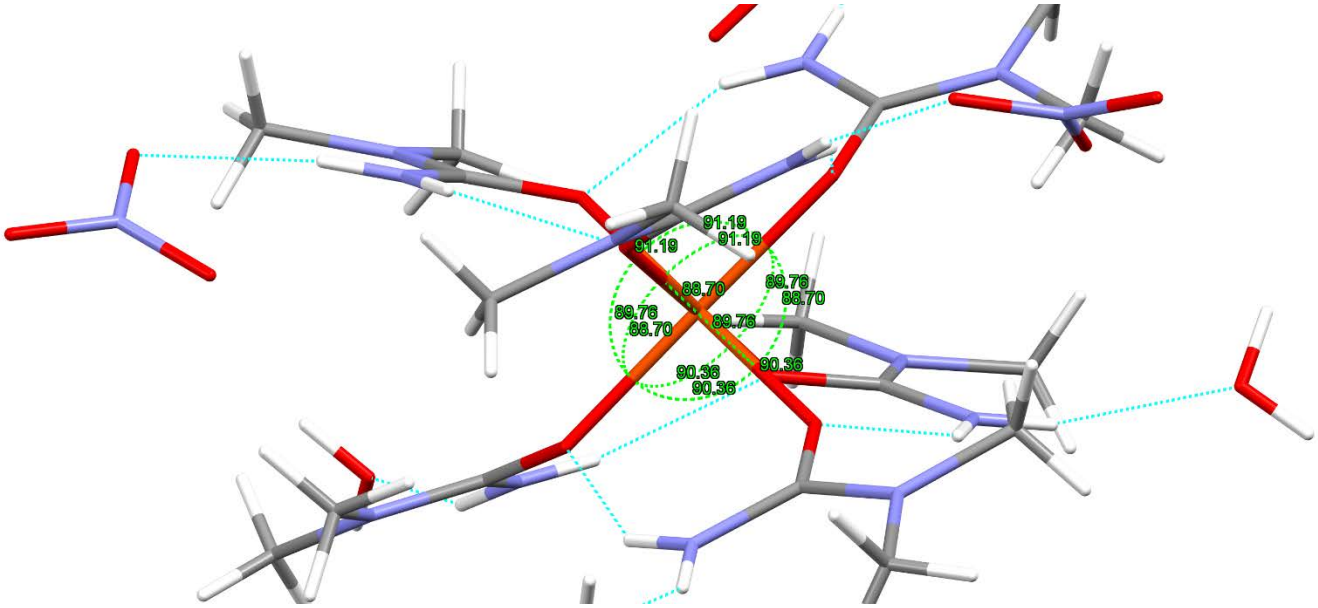
ESI Figure S2. The calculated and the experimental powder X-ray diffraction of compound **2.**



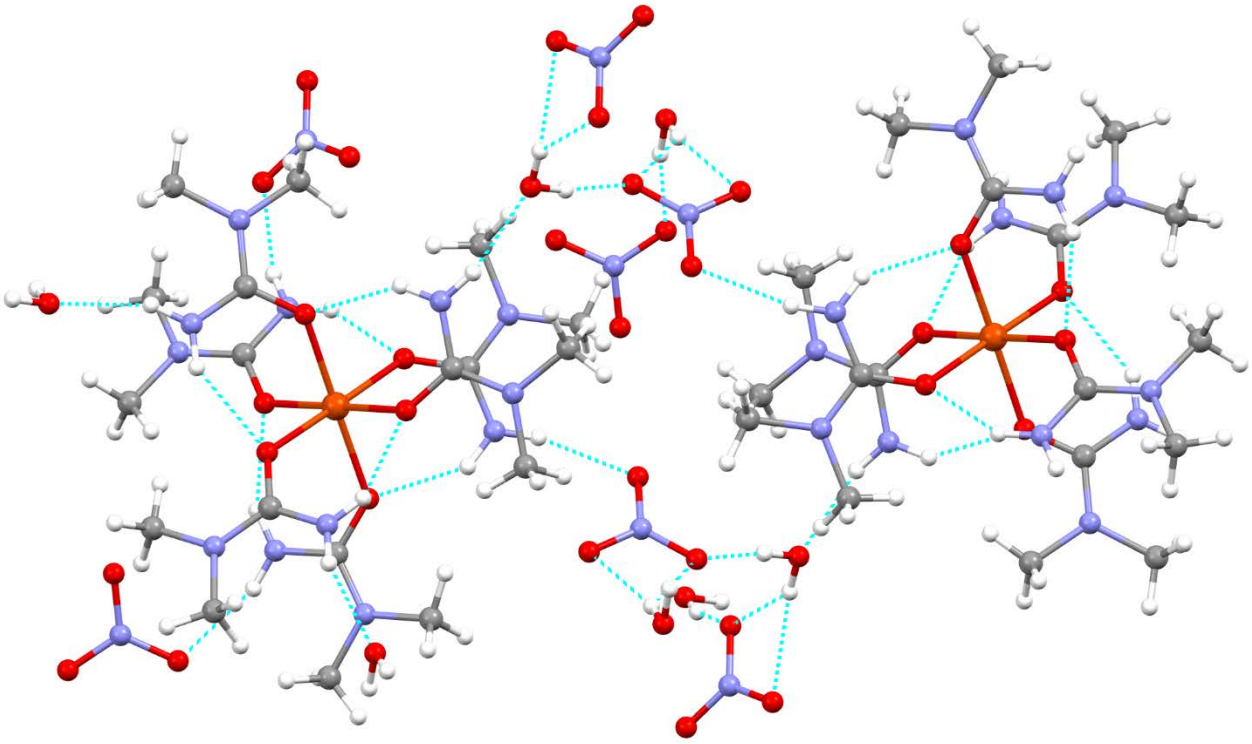
ESI Figure S3. The low-temperature DSC of compound **1.**



ESI Figure S4. The low-temperature DSC of compound **2.**



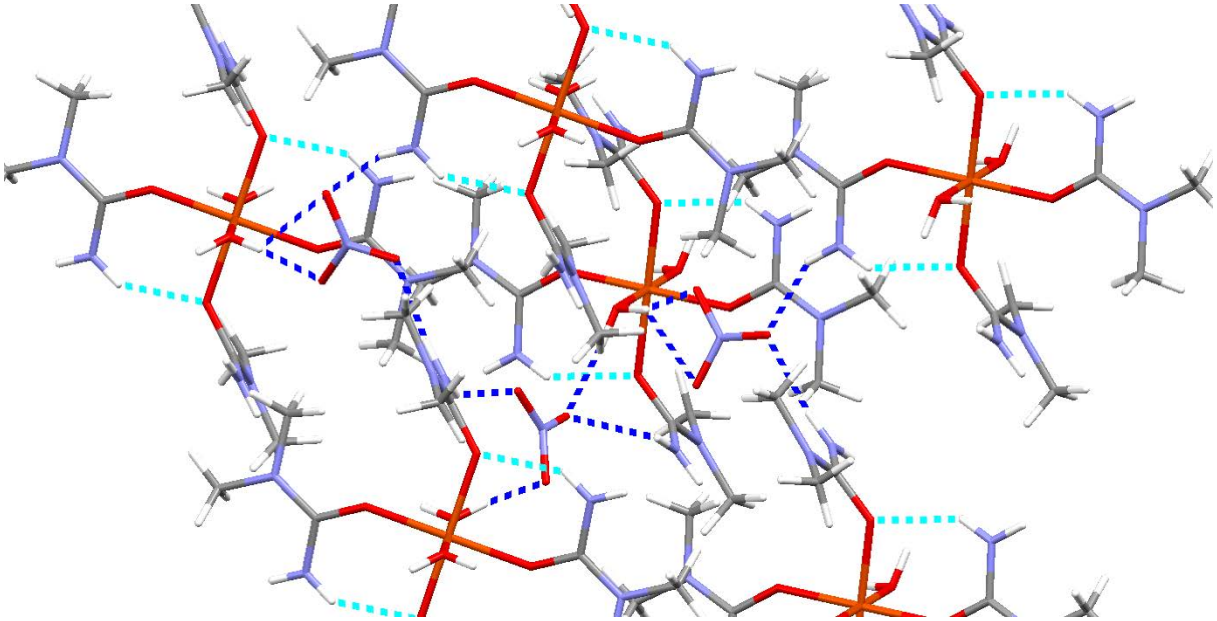
ESI Figure S5. Coordination geometry of compound **3.**



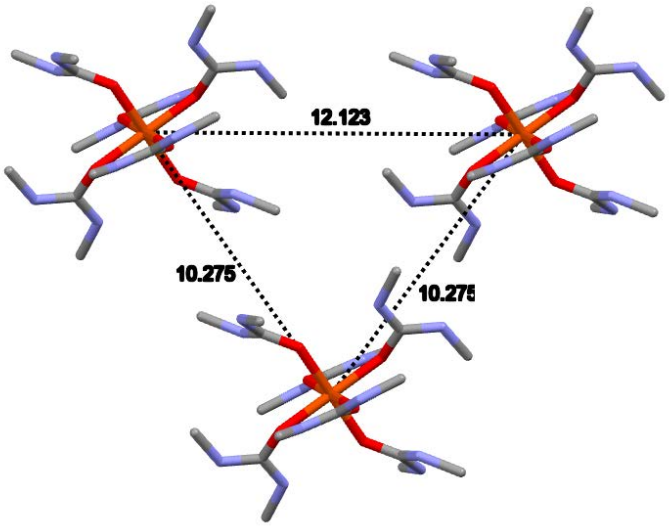
ESI Figure S6. Intra- and intermolecular hydrogen bonding system in compound **3.**

ESI Table S11. Torsion angles [°] of nitrate ions in compound **2**.

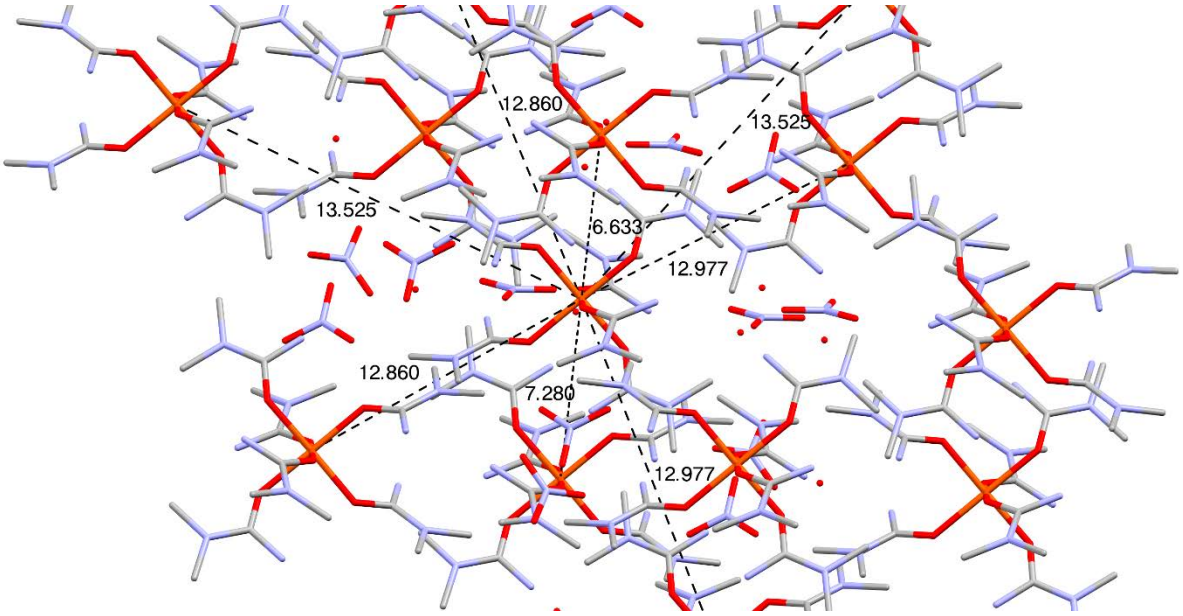
O(12)-N(11)-O(13)	119.8(3)
O(11)-N(11)-O(12)	122.5(4)
O(11)-N(11)-O(13)	117.8(3)
O(6)-N(9)-O(7)	120.6(3)
O(7)-N(9)-O(5)	119.8(3)
O(5)-N(9)-O(6)	119.6(3)
O(9)-N(10)-O(10)	119.9(3)
O(10)-N(10)-O(8)	120.4(3)
O(8)-N(10)-O(9)	119.7(3)



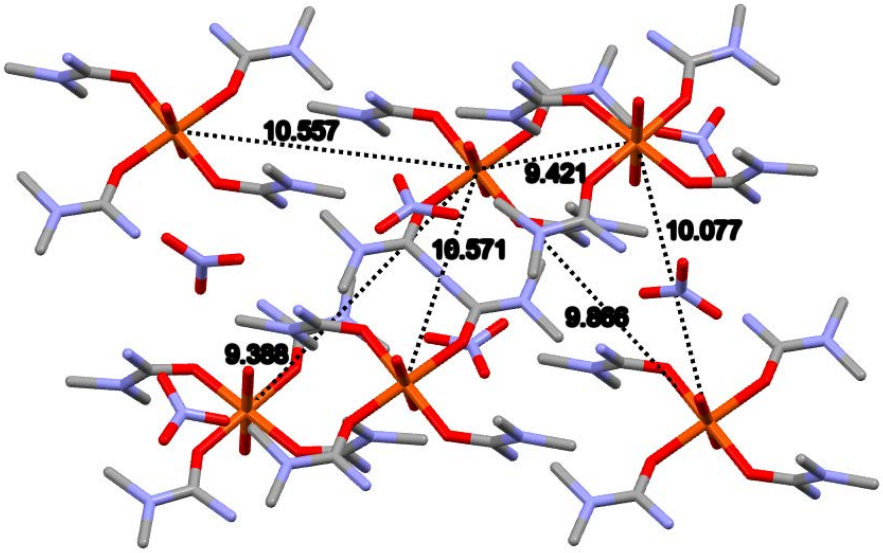
ESI Figure S7. Intra- and intermolecular hydrogen bonding system in compound **2.**



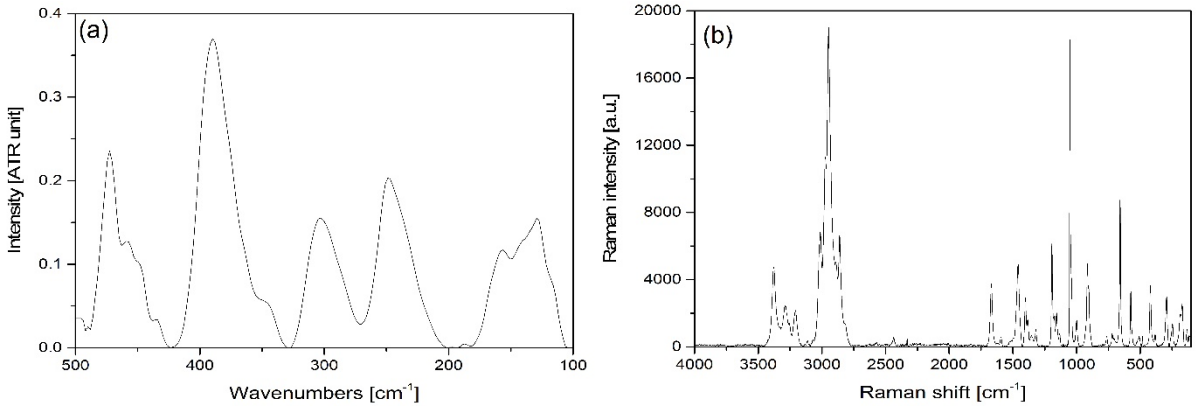
ESI Figure S8. The Fe-Fe distances in compound **1.**



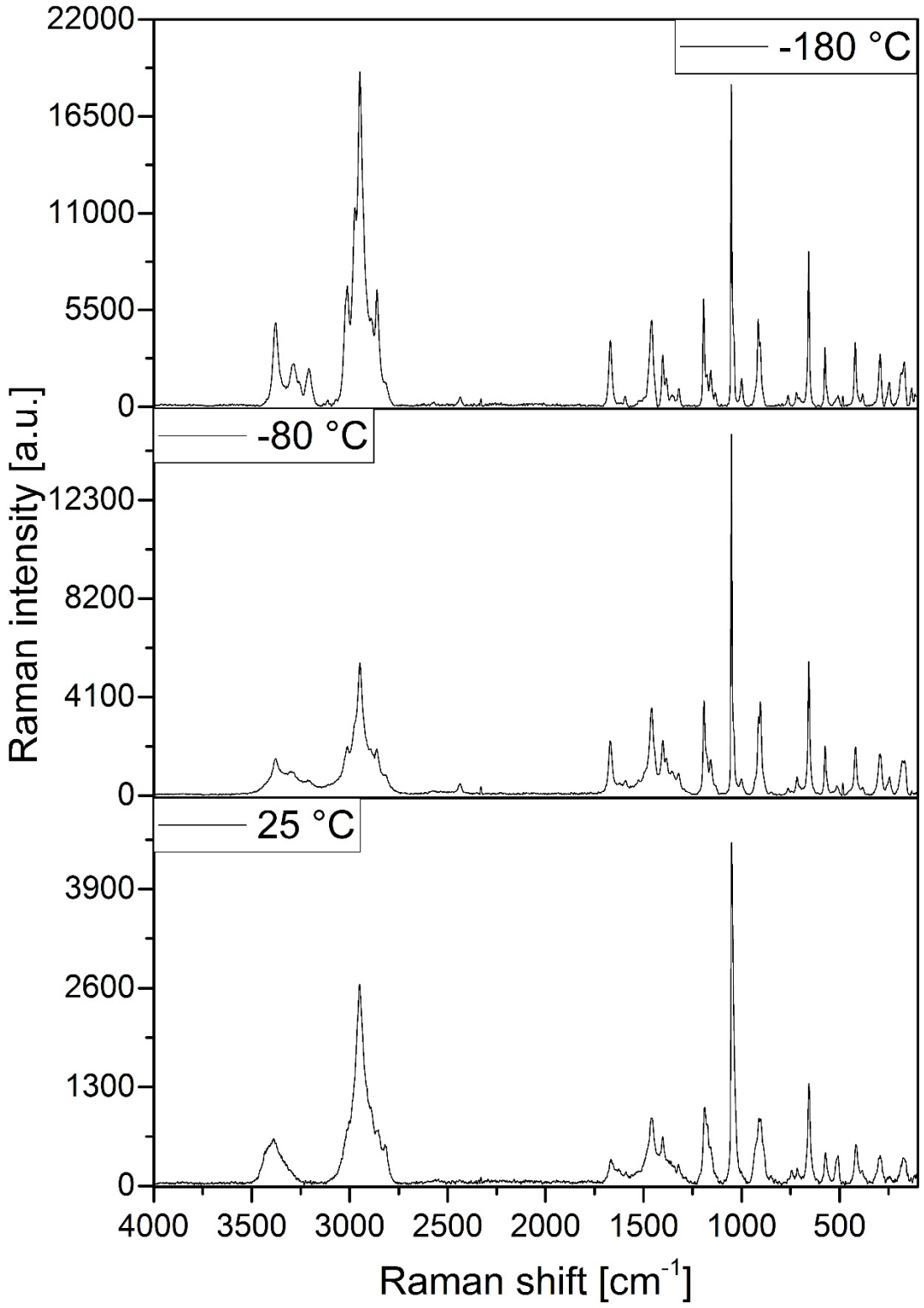
ESI Figure S9. The Fe-Fe distances in compound **3.**



ESI Figure S10. The Fe-Fe distances in compound 2.



ESI Figure S11. (a) Far-range and (b) analytical rang IR spectra of compound **1** at room temperature.

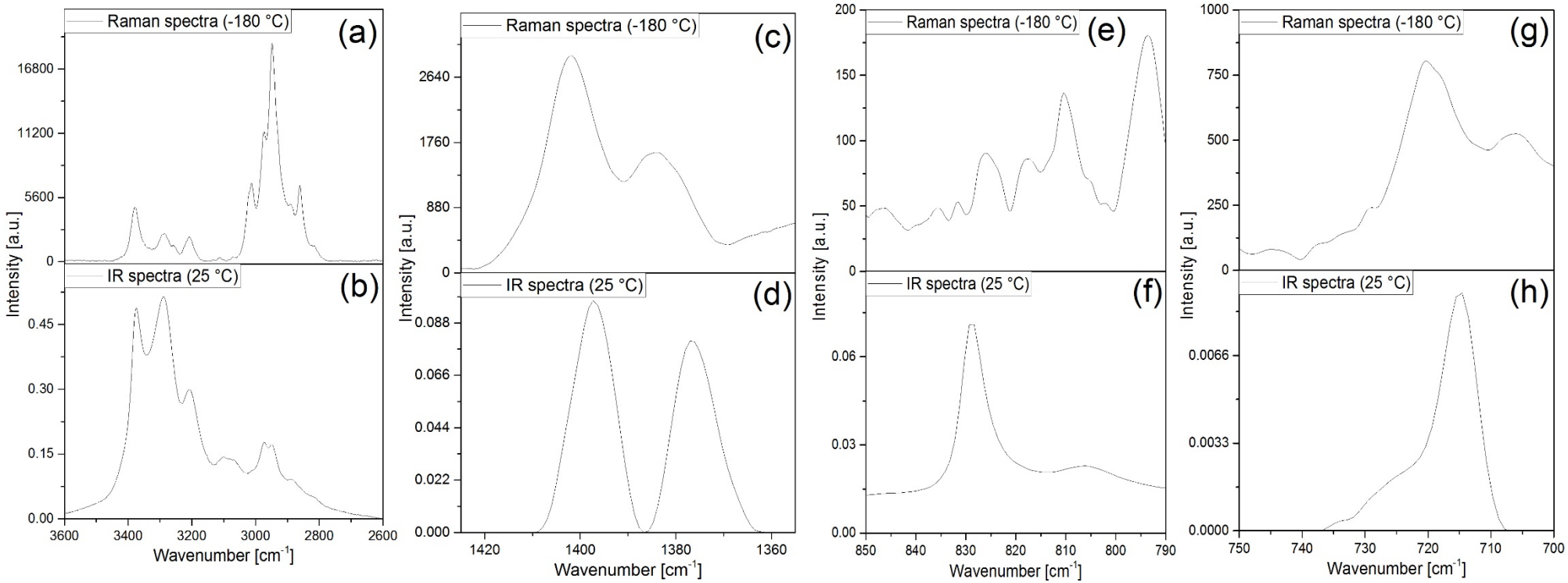


ESI Figure S12. Raman spectra of compound **1** at different temperature.

ESI Table S12. Assignment of vibrational modes of compound **1**.

Raman [cm^{-1}] 123 K - 532 nm	IR [cm^{-1}] 298 K	Assignment [C1,AA31]
3370 (s), 3286 (m) 3258 (sh), 3208 (m), 3111 (vw)	3374(s), 3289(s), 3208(m), 3111(m), 3071(sh)	ν_s, ν_{as} (NH)
3012(s), 2973 (s), 2948(vs), 2890 (sh), 2861 (s), 2813 (sh)	2972(m), 2949(m), 2886(sh), 2812(sh)	ν_s, ν_{as} (CH)
1669 (m)	-------	ν(CN)
1616 (sh), 1593 (vw)	1621(s), 1595(vs)	δ(NH) + ν(CO)
1520 (sh), 1497 (sh),	1493(w)	*???*
1458 (m)	1454(sh)	$\delta_s(CH_3)$
1425 (vw)	1440(w)	$\delta_{as}(CH_3)$
1402 (m), 1384 (w),	1396(m), 1374(s)	ν_3(NO)
1354 (w), 1344 (sh) 1319 (w)	1336(s), 1280(sh)	δ(NH), ν(CN) , ν(C'N), ν(C-O)
1193 (s), 1157 (w), 1134 (w)	1185(w), 1169(m), 1151(m)	δ(NH)
1176 (w)	1126(sh)	$\delta_r(CH_3)$
1052 (vs), 1038 (sh), 1000(w)	1099(sh), 1064(sh), 1047(m), 1037(sh)	ν_1(NO), ν(CN)
915 (m), 906 (m)	901(m)	$\delta_r(CH_3)_o$
793 (vw), 762 (vw)	829(w), 762(w)	ν_2(NO)
720 (vw)	729(w), 716(w)	ν_4(NO)
706 (sh)	700, 689(w)	π(NH)
657 (s)	653(w)	δ(NCN)
574 (m), 564 (sh)	566(m)	π(NH)
528 (sh), 514 (sh) 508 (vw) 483 (vw)	522, 473, 458, 451, 435, 389, 346, 303, 248, 187, 157, 141, 129,	δ(NCN)
420 (m), 383 (vw)		Fe-O
293 (m), 246 (w), 184 (w), 170 (w), 131 (vw),115 (w)		Lattice modes

*our measurements; intensity: v – very, s – strong, m – medium, w – weak,

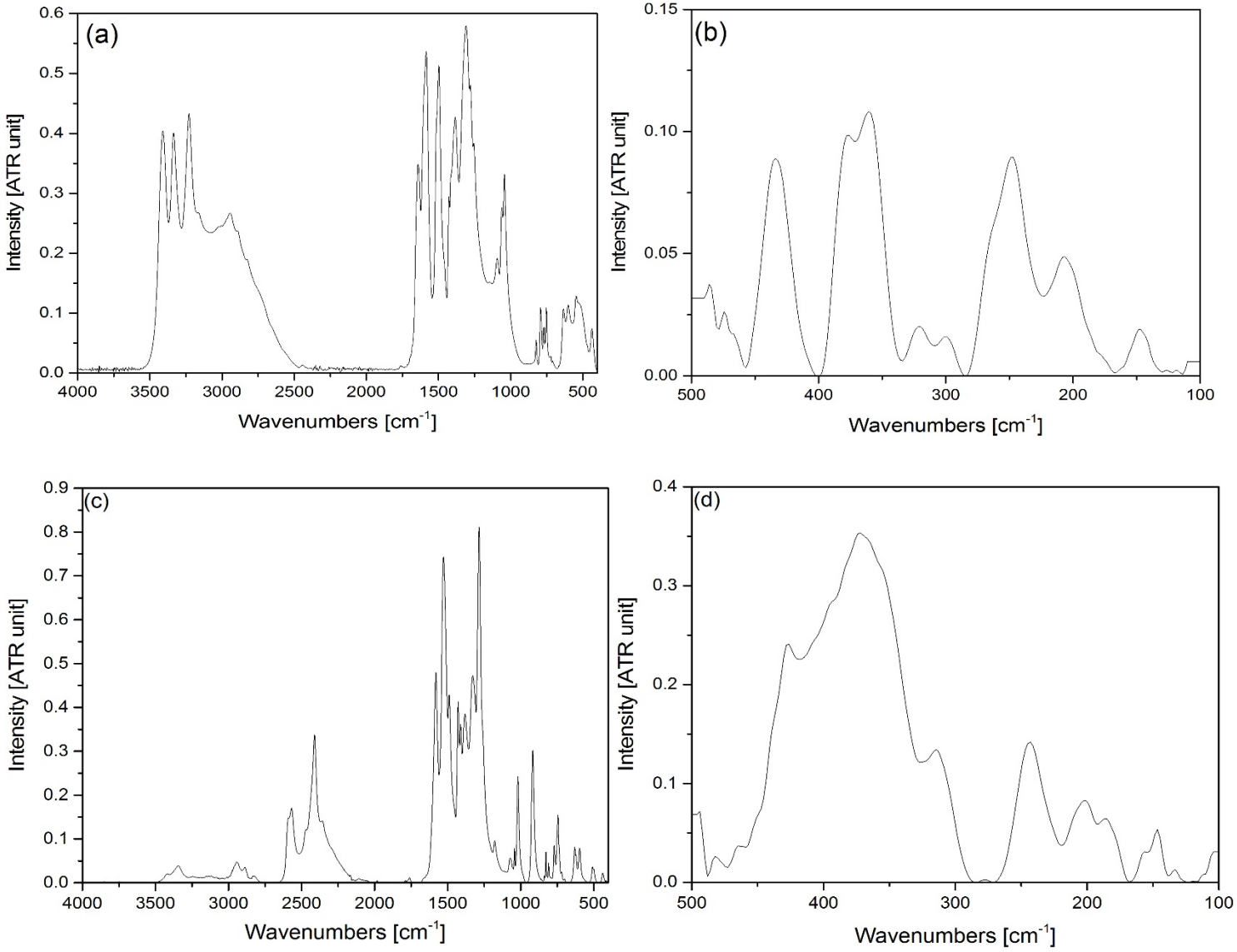


ESI Figure S13. Raman and IR spectra of compound **1** in different wavenumber regions.

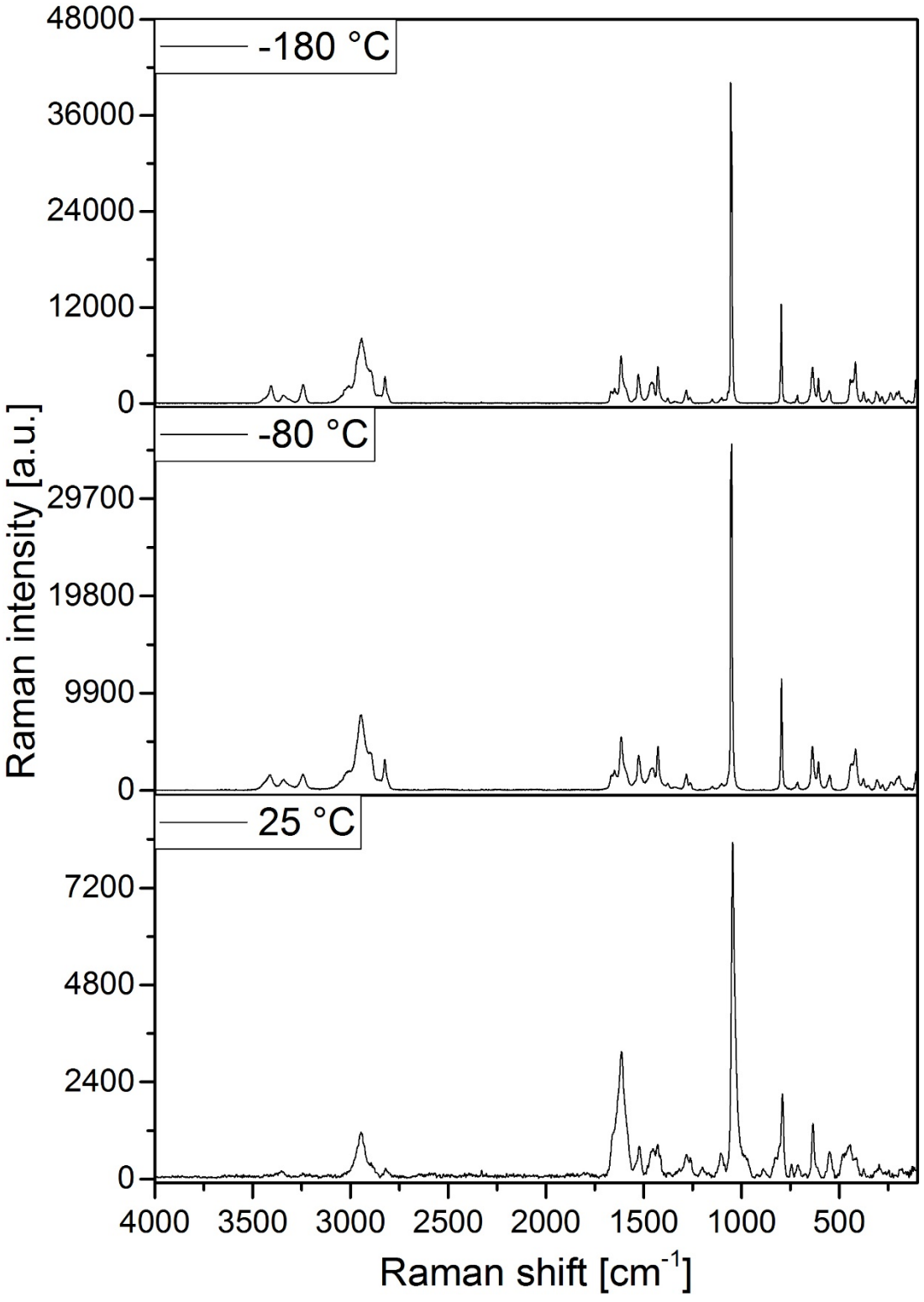
ESI Table S13. Assignment of vibrational modes of compound **2**.

Raman [cm^{-1}] 123 K - 532 nm	IR [cm^{-1}] 298 K	IR of the deuterated sample [cm^{-1}] 298 K	Assignment [45]
3442 (sh)	---------	3420(w)	ν_s, ν_{as}(OH)
3404 (m)	3410(s)		ν_s, ν_{as}(OH and NH)
3342 (w), 3310 (sh), 3243 (m)	3336(s), 3229(s) 3159(sh)	3342 (w)	ν_s, ν_{as} (NH)
3033 (sh), 3010 (m), 2942 (m), 2883 (sh), 2823 (m)	3026 (sh), 2946(s), 2888 (sh),	2944(w),2889(w), 2833(w)	ν_s, ν_{as} (CH)
		2590(sh), 2566(m), 2478(sh), 2411(m), 2359(m)	ν_s, ν_{as} (ND)
1667 (w),1648 (w), 1614 (m),1589 (sh)	1642 (s), 1604 (sh) 1585 (vs)	1581(s)	ν(CO) + ν(CN), δ(NH), δ(OH)
1527 (m)	1514 (sh), 1497 (vs)	1528(vs), 1488(s)	ν(CN) and $\delta(NH_2)$
1457 (m), 1450 (sh)	1457 (sh)	1164(sh)	$\delta_{as}(CH_3)$
1427 (m)	1427(m), 1415 (sh)	1428(s), 1412(m)	$\delta_s(CH_3)$
1376 (vw)	1384 (s), 1309 (vs)	1381(m), 1328(s)	ν_3(NO)
1288(sh), 1281 (w), 1263 (vw)	1279(sh) , 1255(sh)	1284(vs), 1258(sh)	δ(NH)+ ν_s(CN)
-------	-------	1178(w)	δ(OD), δ(ND)
1149 (vw)	1146(w)	1156(sh)	$\delta_r(CH_3)$
1101 (vw)	1093 (m)	-------	$\delta_r(NH_2)$
1071 (sh), 1055 (vs) 1050 (vs)	1062 (m), 1044(m) 1023(sh)	1072(w), 1043(w) 1019(m)	$\delta_r(CH_3)$, ν_1(NO), ν_s(CN) and $\delta(ND_2)$
-------	-------	917(m)	$\delta r(ND_2)$
821 (sh), 796 (s)	823 (w), 793(m)	837(vw), 827(w), 809(w), 790(vw)	ν_2(NO)
773 (vw)	770(w), 752(m)	771(w),750(sh), 745(w), 736(sh)	δ(NCO)
719 (sh), 713 (w)	722(sh), 707(sh)	719(vw), 700(vw)	$\pi(NH_2)$ and ν_4(NO)
636 (m), 606 (m)	634 (m), 601 (m)	630(w), 621(w), 596(w)	δ(CO)
551(w), 545(sh)	546 (m) 520(sh)	507(w), 497(w), 482(vw)	δ(NCN), $\pi(ND_2)$
443 (m),	469 (sh), 436 (sh),	464(vw), 427(w),	$\varrho_r(H_2O)$
428 (m), 417 (m) 374 (w), 351 (w) 311 (vw), 300 (sh), 282 (w), 238 (w), 216 (sh), 207 (w), 194 (w), 143 (vw),	419 (sh), 376 (w), 360 (w), 320 (vw), 265 (sh), 247 (w), 207(w), 175(w), 147(vw)	394(sh) 373(m), 315(w), 243(w), 202(w), 186(w), 157(sh), 147(vw), 133(vw),	ν(Fe-O), $\nu(Fe-OH_2)$, $\varrho_r(D_2O)$ and lattice modes

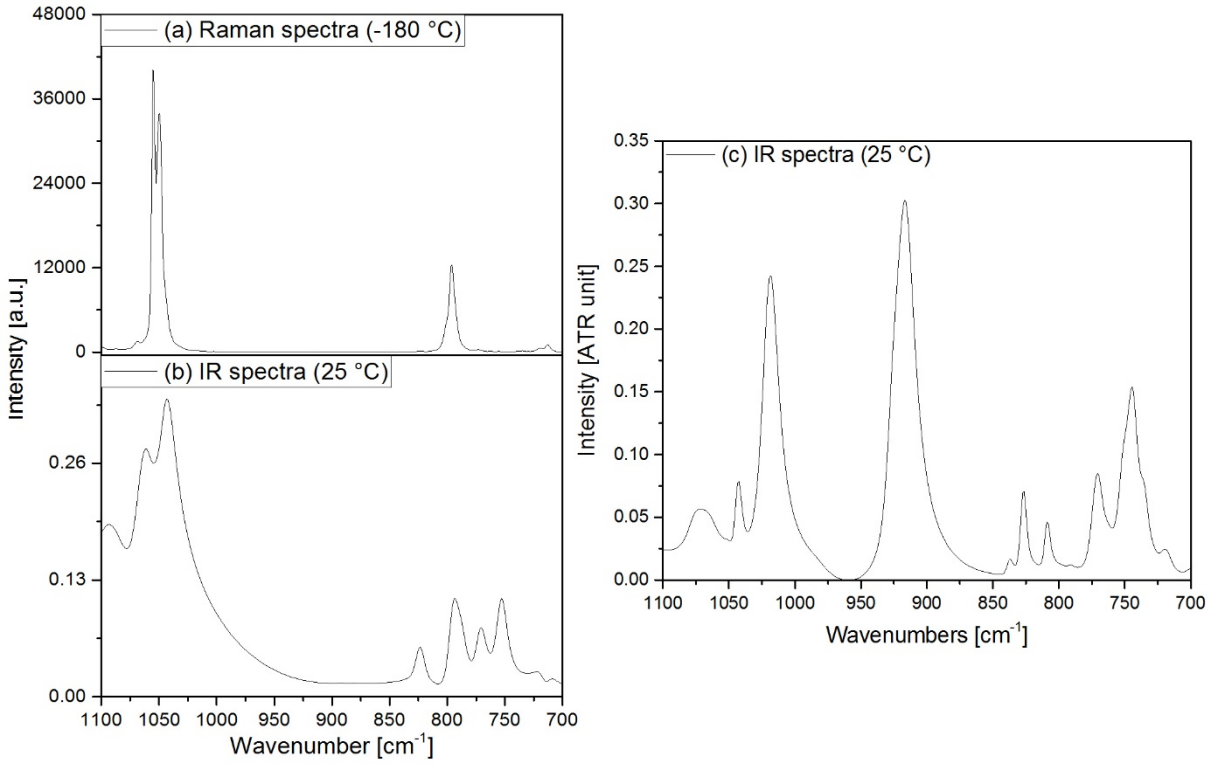
intensity: v – very, s – strong, m – medium, w – weak,



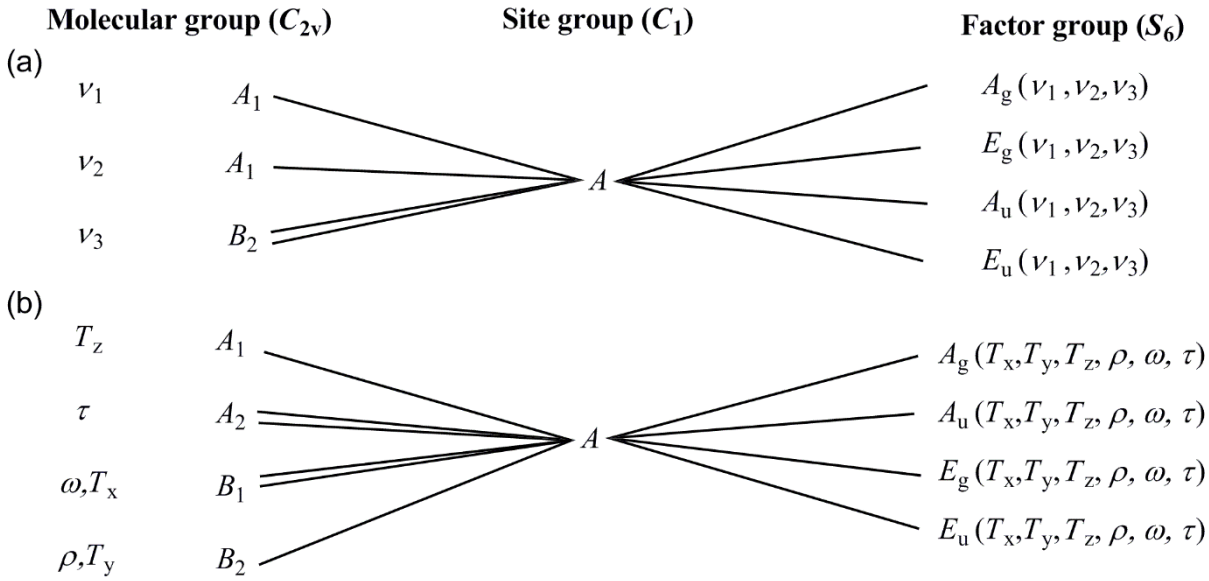
ESI Figure S14. (a) Close range and (b) Far-range IR spectra of compound **2** .(c) Close range and (d) Far-range IR spectra of compound **2-D**$_{12}$.



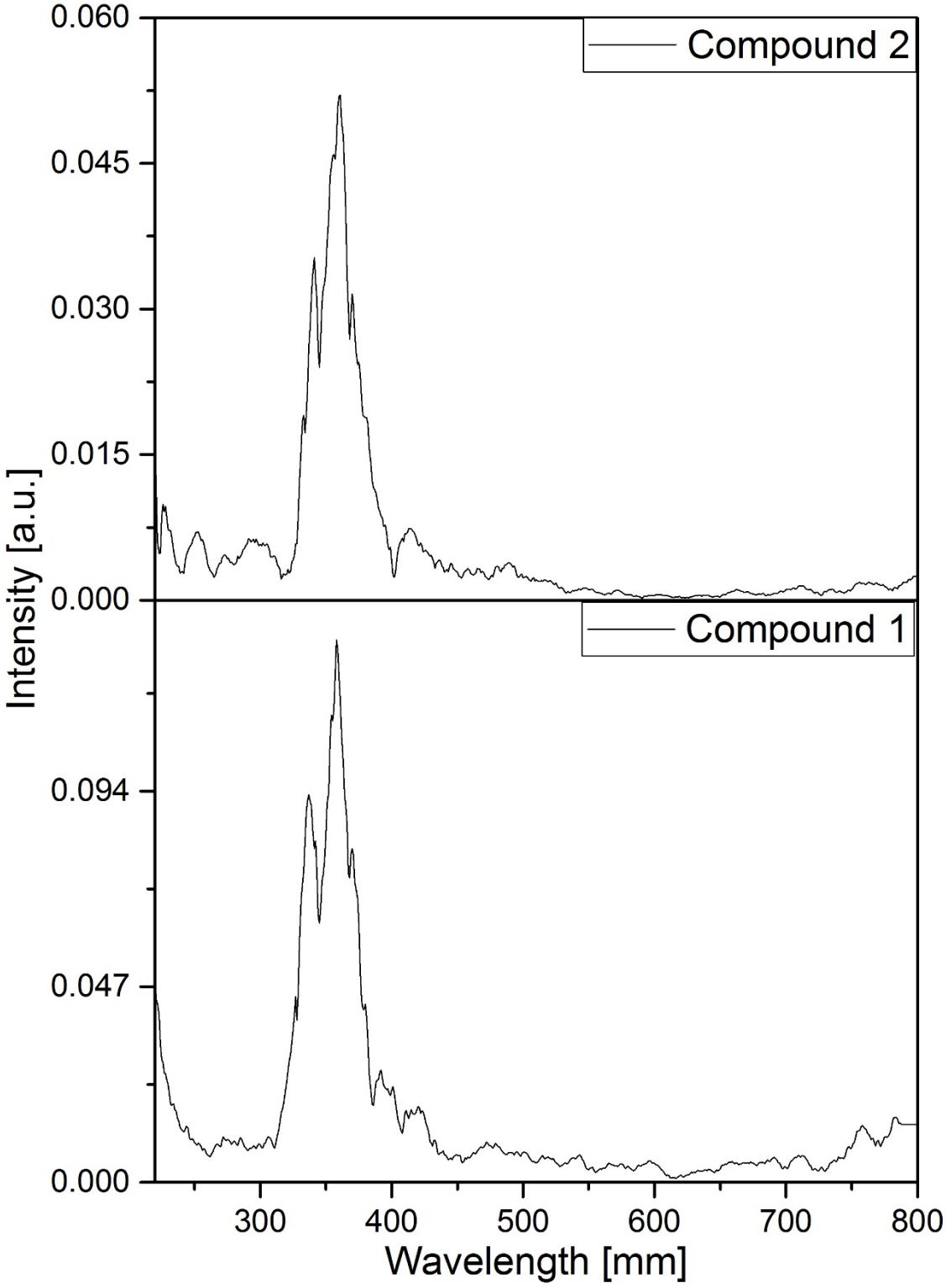
ESI Figure S15. Raman spectra of compound **2** at different temperature.



ESI Figure S16. Raman and IR spectra of compound **2** and **2-D$_{12}$** in 1100 and 700 cm^{-1} wavenumber region.



ESI Figure S17. (a) Internal and (b) external H_2O modes in compound **2**.



ESI Figure S18. UV-VIS spectra of compound **1** and compound **2**.