ESI Table S1. Crystal data of urea/methylated urea compounds found in Cambridge Structural Database.

CODE	Me	UREA	COORD	WATER	SP. GR.	SOLV., ANION	Me…O$_{min}$	Me…O$_{max}$	Me…O$_{av}$	Me…O$_{diff}$	ANG2	ANG3	ANG4	ANG5	ANG AVE	Calc, Density	Me…Me Dist
BOPWEI	Mn(III)	-	HEXA	-	R-3c	ClO_4^-	1,985	1,985	1,985	0,000	132,96	132,96	132,96	132,96	132,96	1,780	**7,021**
WITQAR	Mn(II)	-	HEXA	-	$P2_1/c$	I^-	2,172	2,194	2,183	0,022	133,78	133,30	133,78	137,30	134,54	2,050	**7,793**
HEBMEG	Mn(II)	-	PENTA	H_2O	P-1	$ZnCl_4^{2-}$	2,15	2,203	2,177	0,053	132,40	136,30	136,55	134,99	135,06	1,716	**7,029**
KADROA	Mn(II)	monoMe	HEXA	-	P-1	Cl^-	2,158	2,182	2,170	0,024	127,35	127,35	126,06	126,06	126,71	1,465	**7,105**
ZZZWCO01	Mn(II)	monoMe	HEXA	-	R-3c	SO_4^{2-}	2,17	2,172	2,171	0,002	127,73	127,70	127,71	127,73	127,72	1,366	**9,336**
YIXMUQ	Mn(II)	monoMe	HEXA	-	R-3c	SO_4^{2-}	2,135	2,138	2,137	0,003	128,08	128,05	128,06	128,07	128,07	1,381	**9,305**
BAVZON	Mn(II)	N,N-diMe	HEXA	-	$P2_1/c$	NO_3^-	2,141	2,189	2,165	0,048	128,12	127,09	128,12	123,96	126,82	1,372	**8,842**
BAVZON	Mn(II)	N,N-diMe	DI	$4H_2O$	$P2_1/c$	NO_3^-	2,093	2,093	2,093	0,000	144,84	144,84	144,84	144,84	144,84	1,372	**8,842**
AKITET	Mn(II)	N,N'-diMe	HEXA	-	P-1	ClO_4^-	2,16	2,174	2,167	0,014	131,54	129,91	131,54	128,11	130,27	1,401	**8,043**
JANXEB	Mn(II)	N,N'-diEt	HEXA	-	P-1	$MnBr_4^{2-}$	2,164	2,289	2,227	0,125	143,28	125,57	143,28	154,02	141,54	1,390	**11,738**
MANJIU	Fe(III)	-	HEXA	-	$P6_1$	I_3^-	1,961	2,025	1,993	0,064	137,48	132,80	132,29	139,23	135,45	2,961	**6,976**
WITQEV	Fe(II)	-	HEXA	-	R-3	I^-	1,987	1,994	1,991	0,007	136,34	136,37	136,16	136,18	136,26	1,780	**6,966**
own data	Fe(III)	-	HEXA	-	C2	NO_3^-	1,96	2,039	2,000	0,079	130,15	136,25	137,41	141,05	136,22	1,658	**6,740**
own data	Fe(III)	N,N-diMe	TETRA	$2H_2O$	P-1	NO_3^-	1,96	2,009	1,985	0,049	131,75	133,74	136,53	141,35	135,84	1,513	**9,421**
own data	Fe(III)	N,N-diMe	HEXA	-	R-3	NO_3^-	1,989	1,992	1,991	0,003	131,85	131,85	134,53	134,53	133,19	1,337	**6,750**
own data	Fe(III)	N,N'-diMe	HEXA	-	R-3	NO_3^-	2,005	2,005	2,005	0,000	133,63	133,63	133,63	133,63	133,63	1,229	**10,275**
BENVIZ	Fe(III)	N,N'-diMe	HEXA	-	C2/c	ClO_4^-	1,989	2,023	2,006	0,034	130,00	138,62	131,53	131,53	132,92	1,429	**10,038**
EURFEC	Fe(II)	N,N'-diEt	HEXA	-	P-1	ClO_4^-	2,104	2,105	2,105	0,001	127,70	112,45	127,70	129,54	124,34	1,284	**9,142**
FOWQOX	Co(II)	-	HEXA	-	C2	urea, I_3^-	2,02	2,167	2,094	0,147	135,05	128,58	135,05	122,57	130,31	2,434	**9,128**
URCONT	Co(II)	-	HEXA	-	P-1	urea, NO_3^-	2,069	2,082	2,076	0,013	131,82	127,26	131,82	131,96	130,71	1,527	**7,350**
RUBLEG	Co(II)	-	HEXA	-	$P2_1/c$	urea, I^-	2,091	2,11	2,101	0,019	133,61	130,28	133,61	131,08	132,15	1,775	**7,268**

URCOSM01	Co(II)	-	HEXA	-	$Pbc2_1$	H_2O, SO_4^{2-}	2,085	2,162	2,124	0,077	131,89	132,26	126,61	135,66	131,61	1,612	**7,569**
WITLIU	Co(II)	-	HEXA	-	P-1	I_8^{2-}	2,075	2,107	2,091	0,032	132,28	133,61	131,33	133,37	132,65	2,856	**6,188**
COLLAQ	Co(II)	-	HEXA	-	$P2_1/c$	urea, Br^-	2,078	2,098	2,088	0,020	131,68	130,27	131,68	132,70	131,58	1,650	**7,193**
EPAMEO	Co(II)	-	PENTA	H_2O	P-1	$ZnCl_4^{2-}$	2,082	2,131	2,107	0,049	133,25	135,55	131,68	134,91	133,85	1,766	**7,572**
ACOURN01	Co(II)	-	TETRA	$2H_2O$	$P2_1/n$	NO_3^-	2,087	2,09	2,089	0,003	139,54	139,54	136,11	136,11	137,82	1,731	**6,466**
FADGEX	Co(II)	-	TETRA	$2H_2O$	$P2_1$	I^-	2,054	2,13	2,092	0,076	135,68	134,81	137,58	136,80	136,22	2,177	**7,290**
ATURCO	Co(II)	-	DI	$4H_2O$	P-1	NO_3^-	2,06	2,06	2,060	0,000	130,21	130,21	130,21	130,21	130,21	1,879	**5,110**
FADGAT	Co(II)	-	DI	$4H_2O$	$Pca2_1$	CoI_4^{2-}	2,048	2,12	2,084	0,072	132,49	132,49	134,85	134,85	133,67	2,780	**5,151**
MURCOA	Co(II)	monoMe	HEXA	-	R-3c	SO_4^{2-}	2,097	2,097	2,097	0,000	127,84	127,84	127,84	127,84	127,84	1,413	**9,254**
MURCOB	Co(II)	monoMe	HEXA	-	R-3c	$S_2O_3^{2-}$	2,099	2,099	2,099	0,000	127,39	127,39	127,39	127,39	127,39	1,422	**9,260**
ZZZEUO01	Co(II)	monoMe	HEXA	-	P-1	NO_3^-	2,089	2,108	2,099	0,019	126,68	127,19	126,92	126,92	126,93	1,464	**7,036**
QAZZEZ	Co(II)	monoMe	HEXA	-	R-3c	SO_4^{2-}	2,095	2,098	2,097	0,003	127,87	127,88	127,86	127,90	127,88	1,409	**9,258**
ZIJWEU	Co(II)	N,N-diMe	HEXA	-	$P2_1/c$	NO_3^-	2,076	2,13	2,103	0,054	129,94	126,80	129,94	126,37	128,26	1,407	**10,027**
ZIJWEU	Co(II)	N,N-diMe	DI	$4H_2O$	$P2_1/c$	NO_3^-	2,03	2,03	2,030	0,000	139,66	139,66	139,66	139,66	139,66	1,407	**10,027**
LUTRIB	Co(II)	N,N'-diMe	HEXA	-	P-1	ClO_4^-	2,099	2,112	2,106	0,013	130,92	130,28	130,92	128,68	130,20	1,413	**10,710**
LUTROH	Co(II)	N,N'-diMe	HEXA	-	P-1	BF_4^-	2,091	2,098	2,095	0,007	131,13	130,13	131,13	128,46	130,21	1,401	**10,670**
LUTRUN	Co(II)	N,N'-diMe	HEXA	-	P-1	NO_3^-	2,089	2,106	2,098	0,017	131,02	131,73	131,02	126,07	129,96	1,382	**7,858**
HAHKEJ	Co(II)	N,N'-diEt	HEXA	-	P-1	ClO_4^-	2,09	2,1	2,095	0,010	129,85	129,85	129,37	129,37	129,61	1,298	**9,052**
HAHKAF	Co(II)	N,N'-diEt	HEXA	-	$P2_1/c$	BF_4^-	2,088	2,113	2,101	0,025	132,51	132,51	127,66	127,66	130,08	1,243	**9,495**
FOWQIR	Ni(II)	-	HEXA	-	C2	urea, I_3^-	2,04	2,084	2,062	0,044	118,78	124,46	118,78	123,71	121,43	2,444	**9,107**
ADUFEK	Ni(II)	-	HEXA	-	$P2_1/c$	urea, Cl^-	2,05	2,068	2,059	0,018	131,96	131,24	131,96	131,52	131,67	1,508	**7,174**
XIMFOP	Ni(II)	-	TETRA	$2H_2O$	$P2_1/n$	NO_3^-	2,059	2,064	2,062	0,005	139,16	139,16	136,07	136,07	137,62	1,744	**6,458**
YIXNAX	Ni(II)	monoMe	HEXA	-	R-3c	SO_4^{2-}	2,091	2,093	2,092	0,002	128,24	128,22	128,25	128,21	128,23	1,404	**9,279**
QAZZEZ	Ni(II)	monoMe	HEXA	-	R-3c	SO_4^{2-}	2,095	2,098	2,097	0,003	127,87	127,88	127,86	127,90	127,88	1,409	**9,261**
YEWFAH	Ni(II)	N,N-diMe	HEXA	-	$P2_1/c$	NO_3^-	2,043	2,089	2,066	0,046	130,07	126,76	130,07	126,36	128,32	1,420	**10,001**
YEWFAH	Ni(II)	N,N-diMe	DI	$4H_2O$	$P2_1/c$	NO_3^-	2,028	2,028	2,028	0,000	137,65	137,65	137,65	137,65	137,65	1,420	**10,001**

AKITIX	Ni(II)	N,N'-diMe	HEXA	-	P-1	ClO_4^-	2,059	2,068	2,064	0,009	131,06	130,69	131,06	129,04	130,46	1,434	**8,022**
HAHJOS	Ni(II)	N,N'-diEt	HEXA	-	P-1	ClO_4^-	2,068	2,076	2,072	0,008	130,23	130,23	129,37	129,37	129,80	1,294	**9,063**
FAXKOE	Zn(II)	-	HEXA	-	$Pbc2_1$	H_2O, SO_4^{2-}	2,081	2,182	2,132	0,101	130,01	130,67	135,66	127,30	130,91	1,635	**10,047**
UREAZN01	Zn(II)	-	HEXA	-	C2/c	NO_3^-	2,067	2,137	2,102	0,070	131,24	127,74	131,24	132,76	130,74	1,718	**7,406**
KESTUA	Zn(II)	-	TETRA	$2H_2O$	C2/c	$Zn(NCS)_4^{2-}$	2,052	2,17	2,111	0,118	133,13	133,13	127,88	127,88	130,50	1,790	**5,024**
KUJCAU	Zn(II)	-	TETRA	$2H_2O$	$P2_1/n$	NO_3^-	2,075	2,089	2,082	0,014	136,27	136,27	139,43	139,43	137,85	1,794	**6,424**
ZZZWCK01	Zn(II)	monoMe	HEXA	-	R-3c	SO_4^{2-}	2,082	2,082	2,082	0,000	128,06	128,06	128,06	128,06	128,06	1,432	**9,241**
ZIJWIY	Zn(II)	N,N-diMe	HEXA	-	$P2_1/c$	NO_3^-	2,065	2,13	2,098	0,065	126,77	129,70	126,77	127,15	127,60	1,422	**10,030**
ZIJWIY	Zn(II)	N,N-diMe	DI	$4H_2O$	$P2_1/c$	NO_3^-	2,051	2,051	2,051	0,000	139,19	139,19	139,19	139,19	139,19	1,422	**10,030**
AKITUJ	Zn(II)	N,N'-diMe	HEXA	-	P-1	ClO_4^-	2,089	2,104	2,097	0,015	128,65	130,22	128,65	131,09	129,65	1,442	**8,024**
HAHJUY	Zn(II)	N,N'-diEt	HEXA	-	P-1	ClO_4^-	2,108	2,112	2,110	0,004	129,49	129,49	128,65	129,58	129,30	1,294	**9,092**

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**

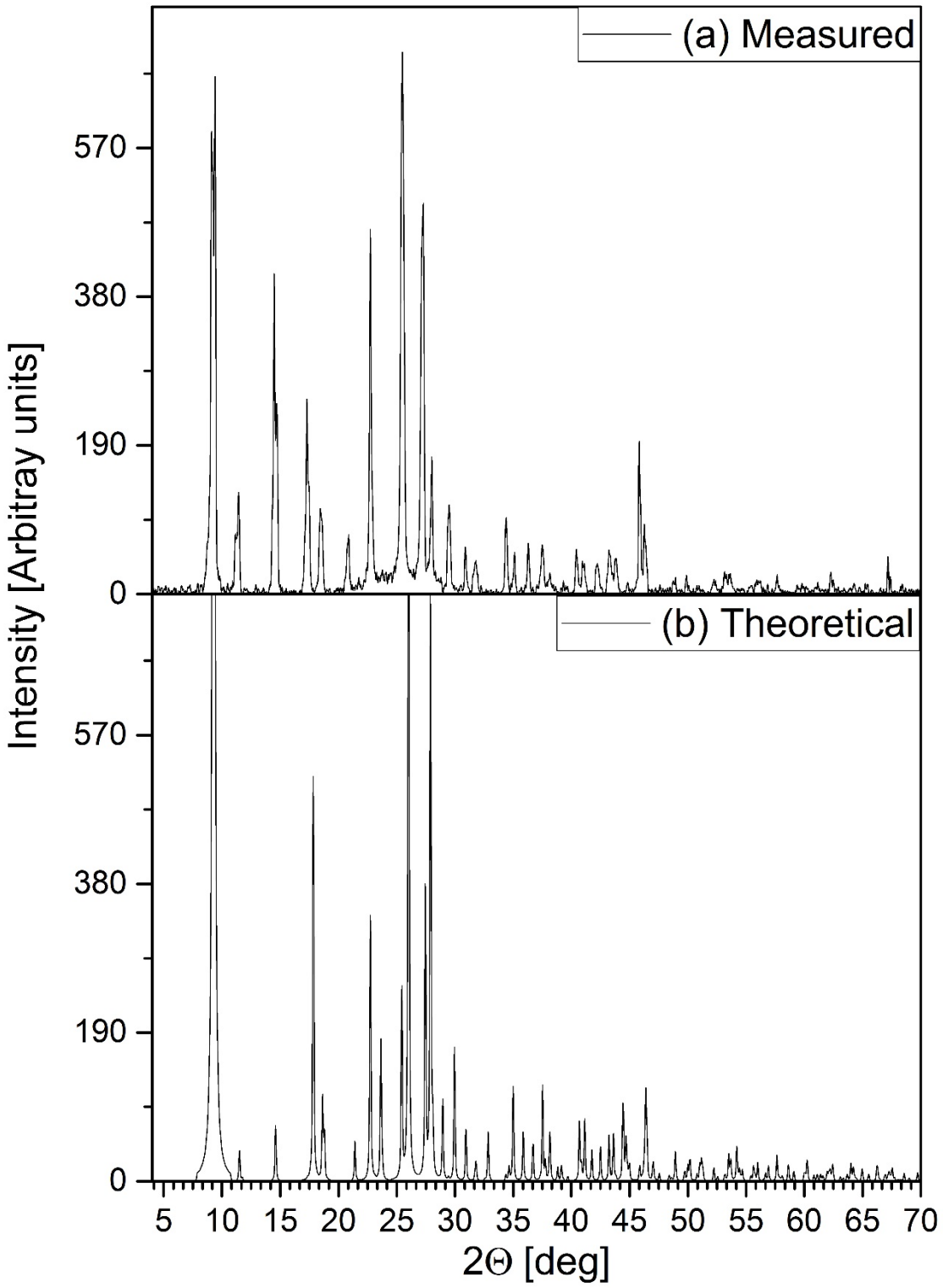
Nr	Donor	---	H....Acceptor	Symm. op.	D - H	H...A	D...A	D - H...A
1	N4	--H4	..O9	x,y,z	0.88	2.05	2.925(2)	170
2	N6	--H6	..O2	1-x+y,2-x,z	0.88	2.10	2.884(2)	149

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.**

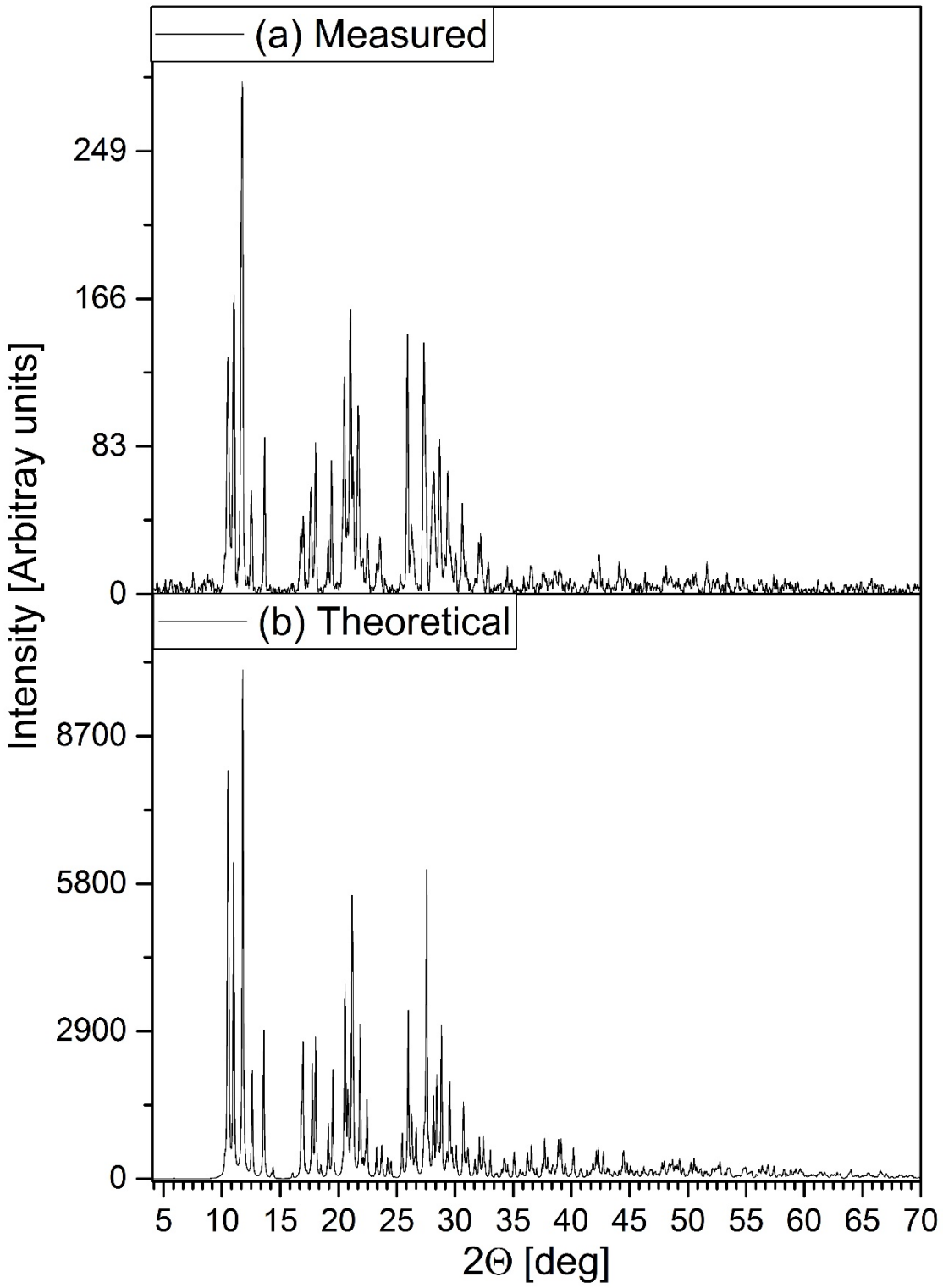
Nr	Donor --- H....Acceptor	Symm. op.	D - H	H...A	D...A	D - H...A
1	O1W --H1WA ..O8	1-x,1-y,1-z	0.85	1.82	2.663(3)	174
2	O1W --H1WB ..O6	1+x,y,z	0.85	1.83	2.672(3)	169
3	N2 --H2A ..O7	1-x,-y,1-z	0.86	2.17	2.916(4)	146
4	N2 --H2B ..O9	1-x,-y,1-z	0.86	2.07	2.912(4)	165
5	O2W --H2WA ..O11	x,y,z	0.85	2.5	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**

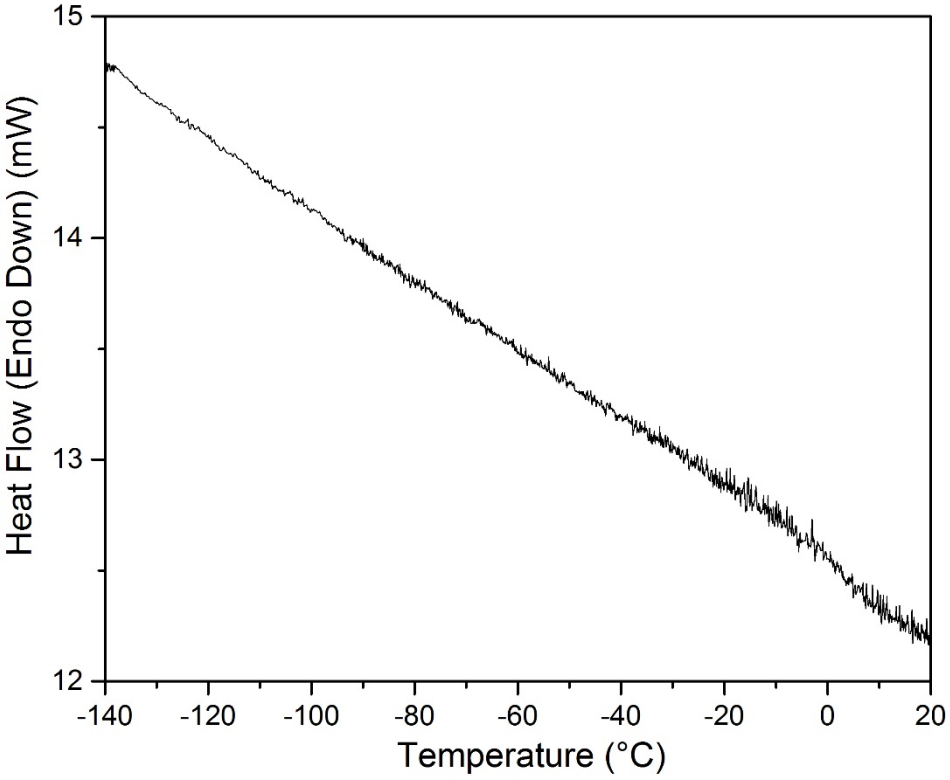
Nr	Donor	---	H....	Acceptor	Symm. op.	D - H	H...A	D...A	D - H...A
1	N4	--H4A		..O2	1-y,1+x-y,z	0.88	2.16	2.916(3)	144
2	N4	--H4B		..O18	x,y,z	0.88	2.05	2.850(3)	152
3	N10	--H10A		..O8	-x+y,1-x,z	0.88	2.12	2.893(2)	145
4	N10	--H10B		..O16	1/3+x-y,-1/3+x,2/3-z	0.88	2.10	2.954(2)	164
5	O18	--H18A		..O17	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



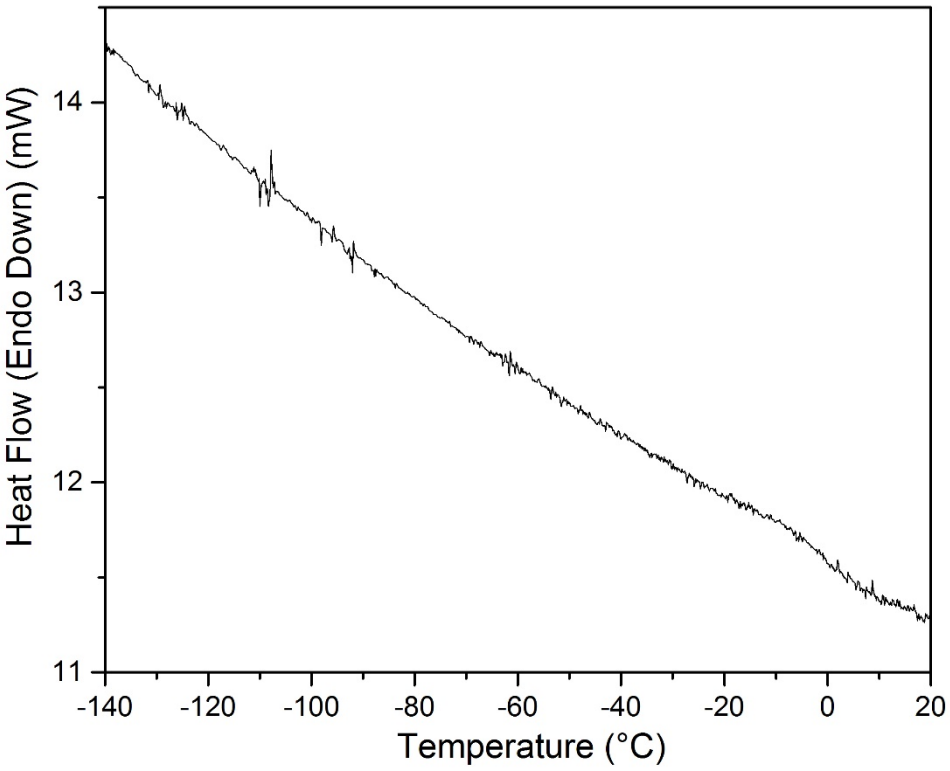
ESI Figure S1. The calculated and the experimental powder X-ray diffraction of compound **1.**



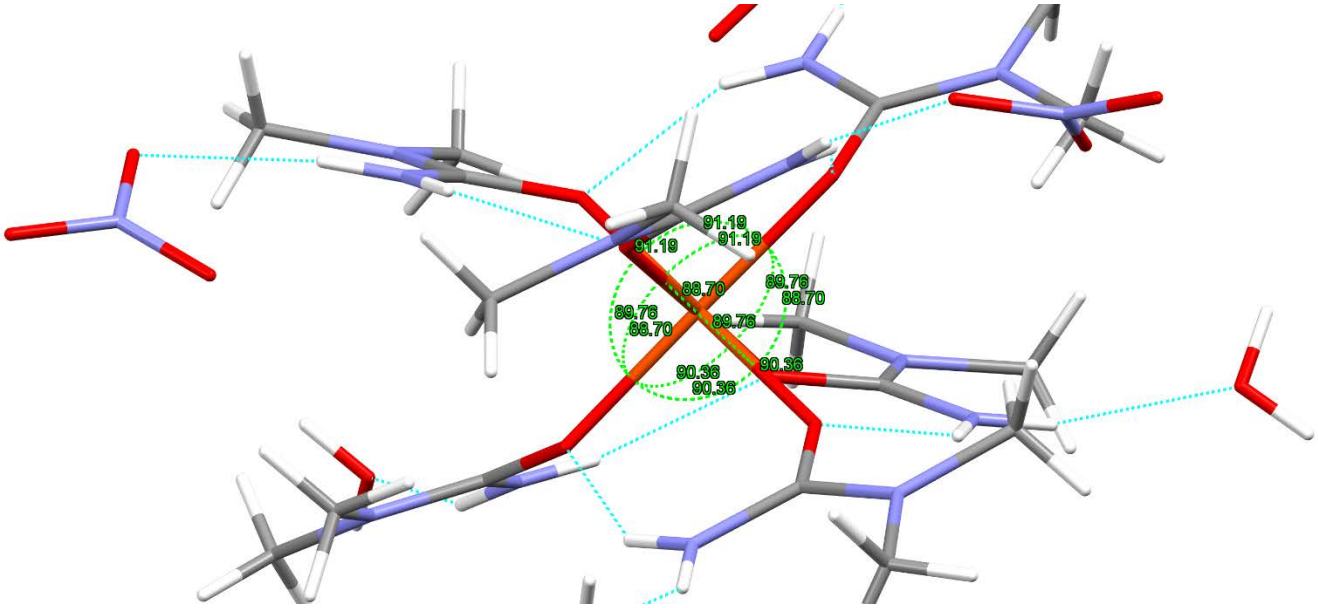
ESI Figure S2. The calculated and the experimental powder X-ray diffraction of compound **2.**



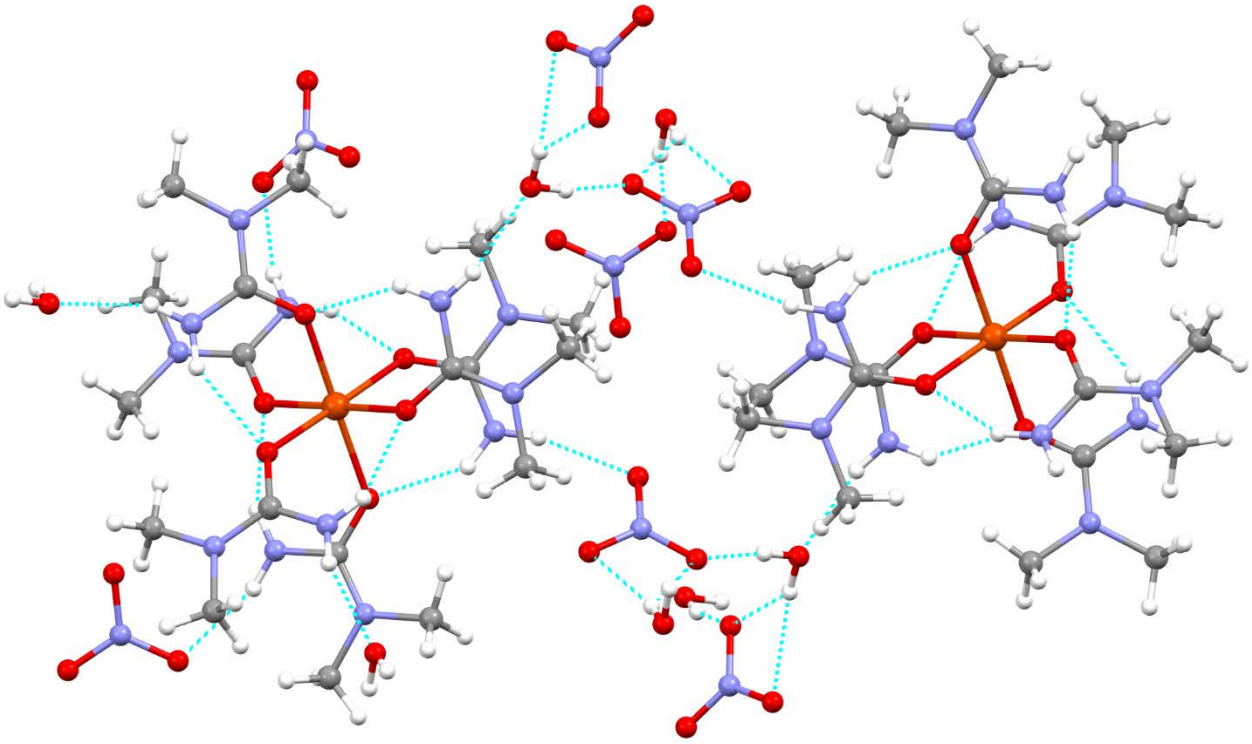
ESI Figure S3. The low-temperature DSC of compound **1.**



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



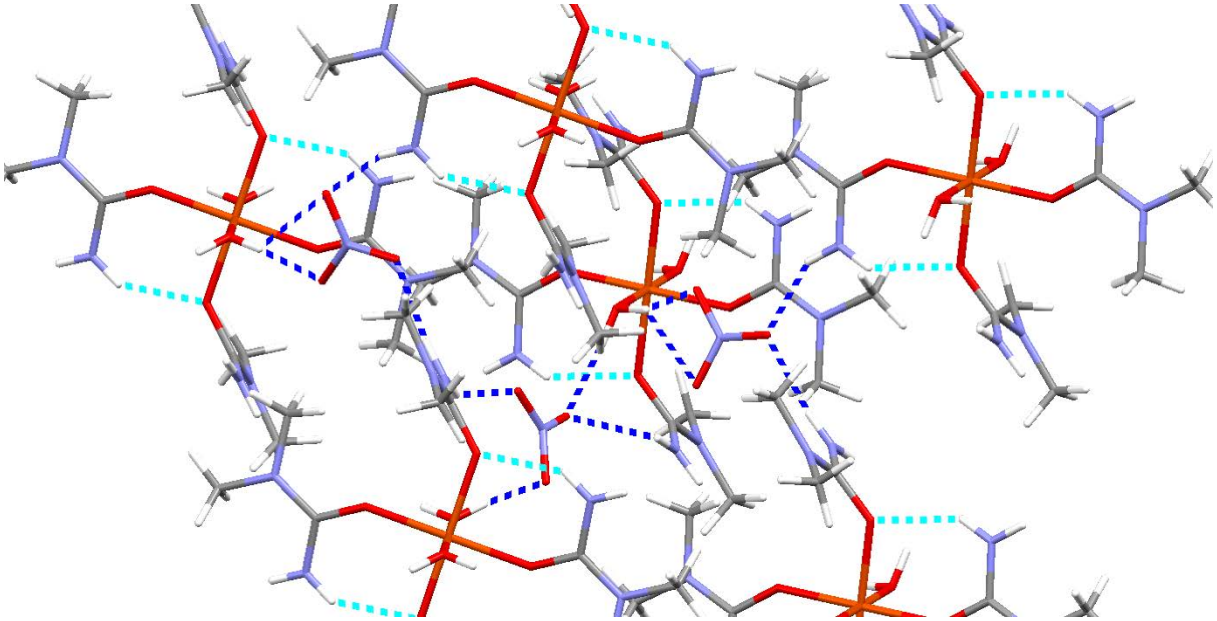
ESI Figure S5. Coordination geometry of compound **3.**



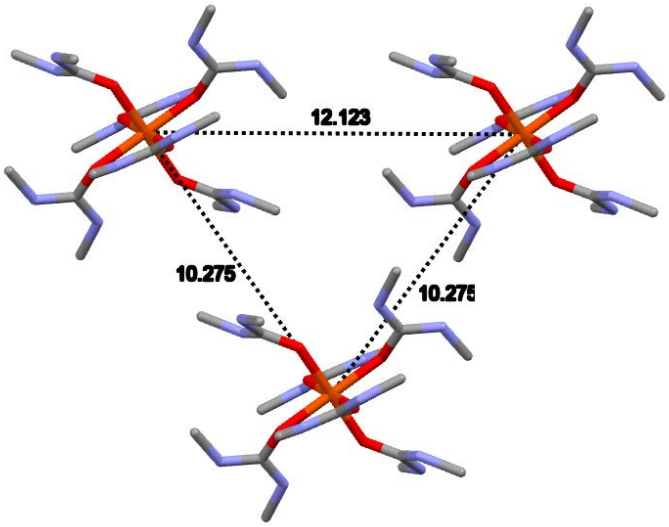
ESI Figure S6. Intra- and intermolecular hydrogen bonding system in compound **3.**

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

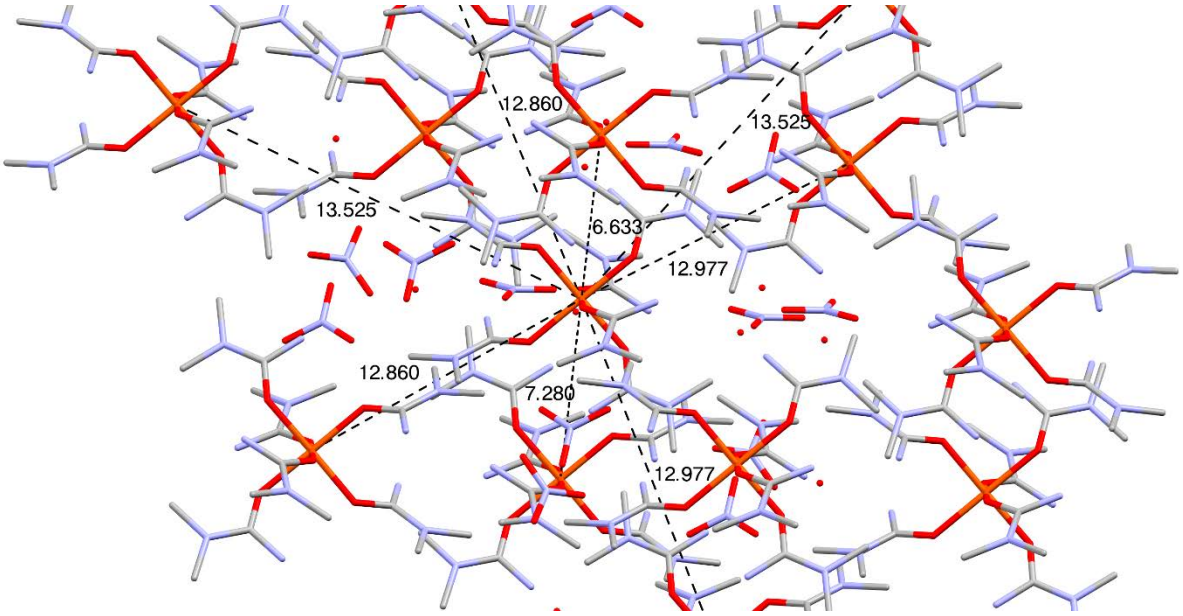
O(12)-N(11)-O(13)	119.8(3)
O(11)-N(11)-O(12)	122.5(4)
O(11)-N(11)-O(13)	117.8(3)
O(6)-N(9)-O(7)	120.6(3)
O(7)-N(9)-O(5)	119.8(3)
O(5)-N(9)-O(6)	119.6(3)
O(9)-N(10)-O(10)	119.9(3)
O(10)-N(10)-O(8)	120.4(3)
O(8)-N(10)-O(9)	119.7(3)



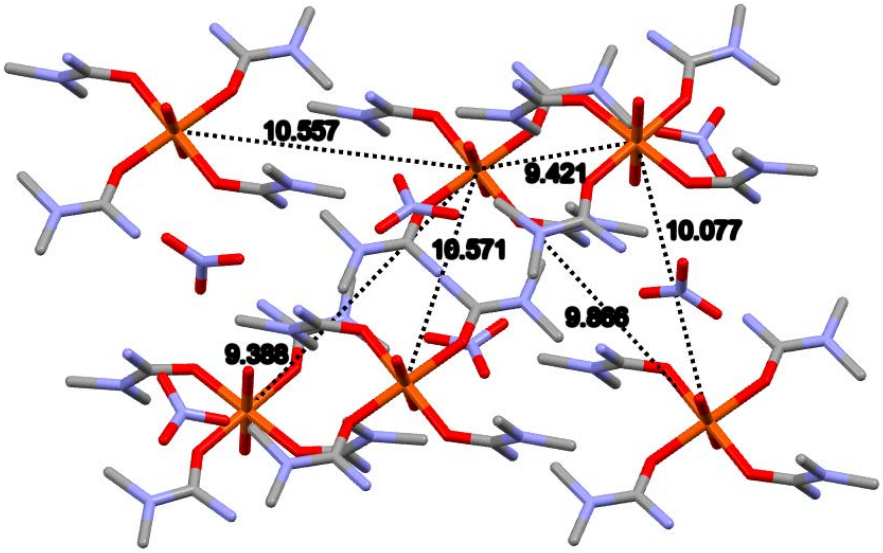
ESI Figure S7. Intra- and intermolecular hydrogen bonding system in compound **2.**



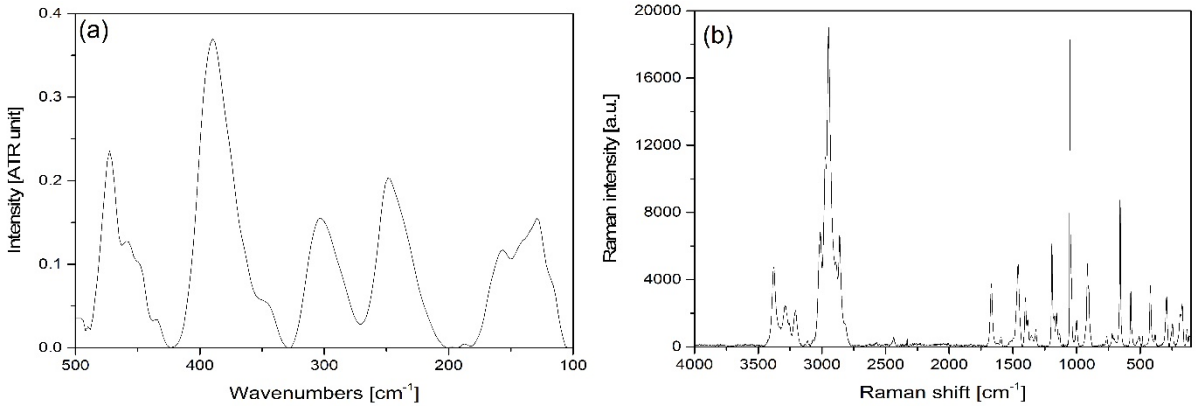
ESI Figure S8. The Fe-Fe distances in compound **1.**



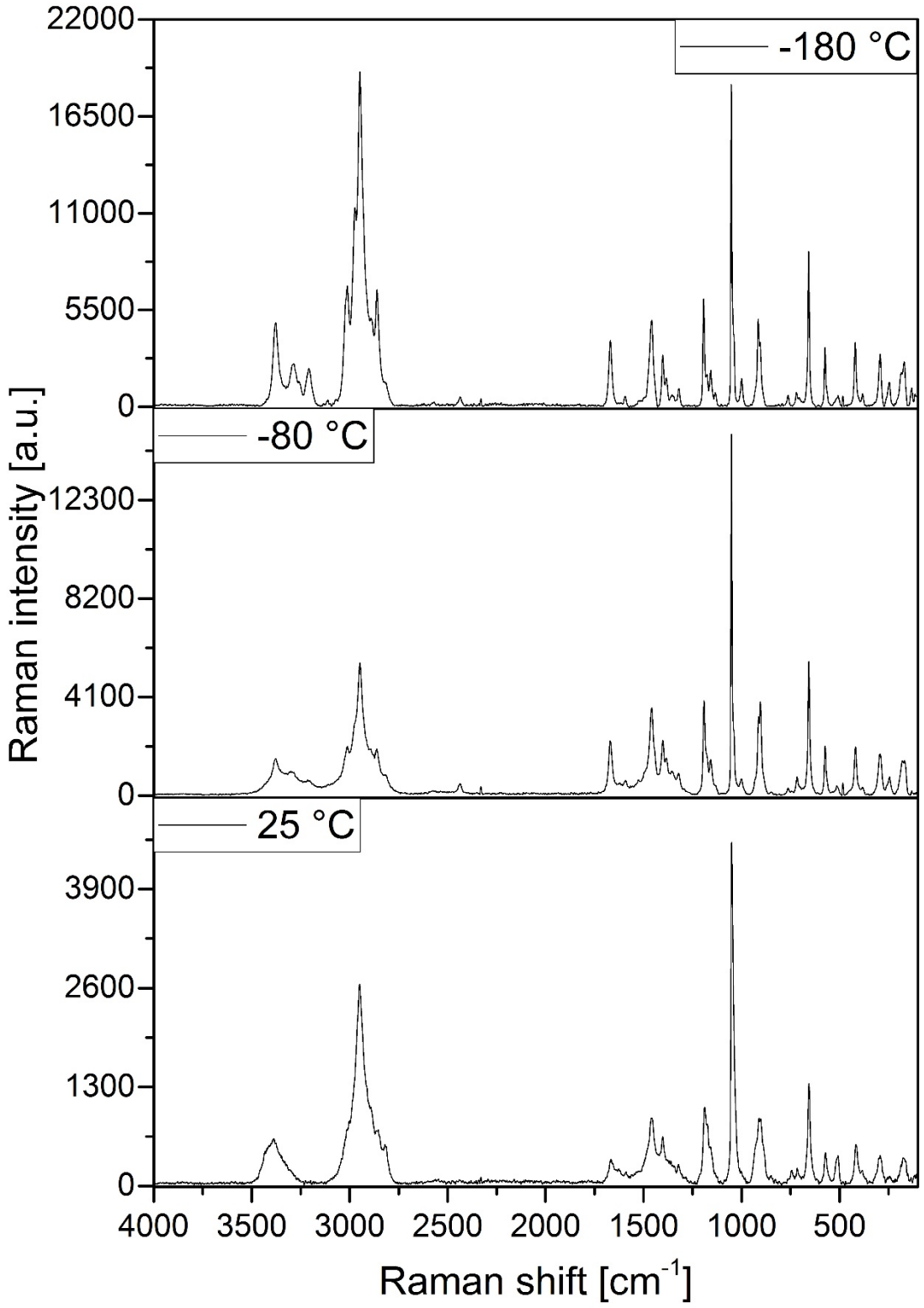
ESI Figure S9. The Fe-Fe distances in compound **3.**



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.

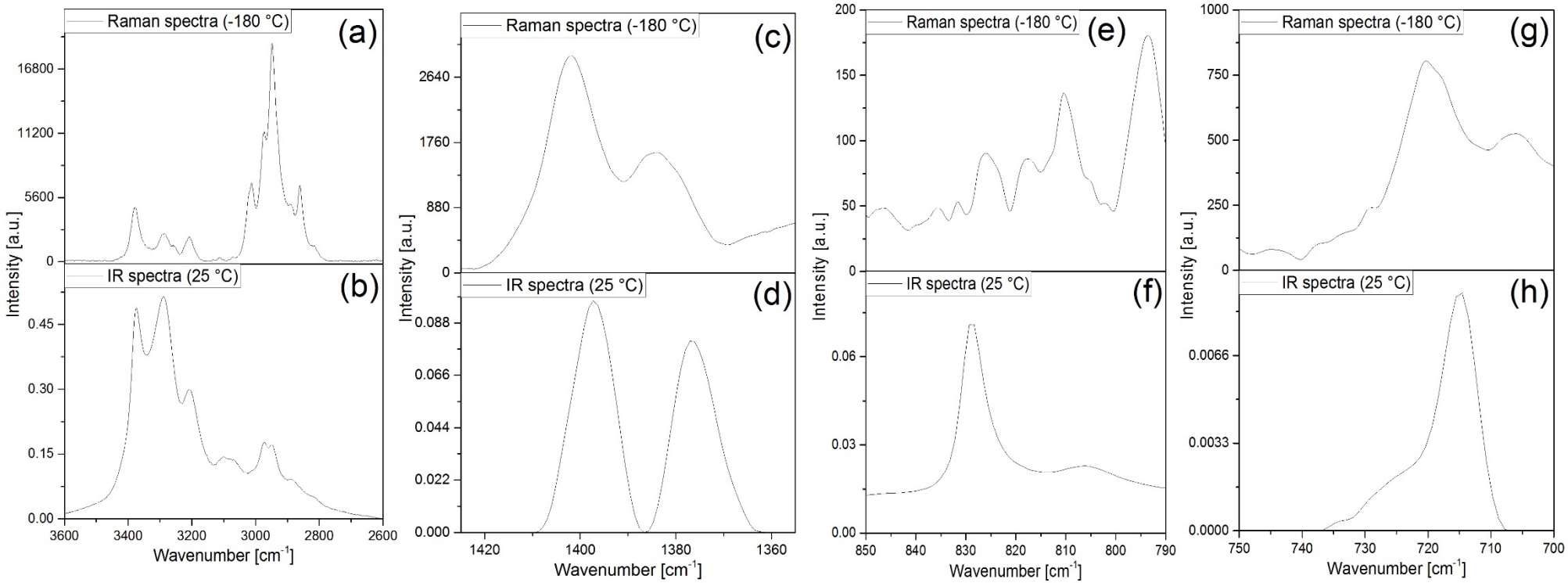


ESI Figure S12. Raman spectra of compound **1** at different temperature.

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,

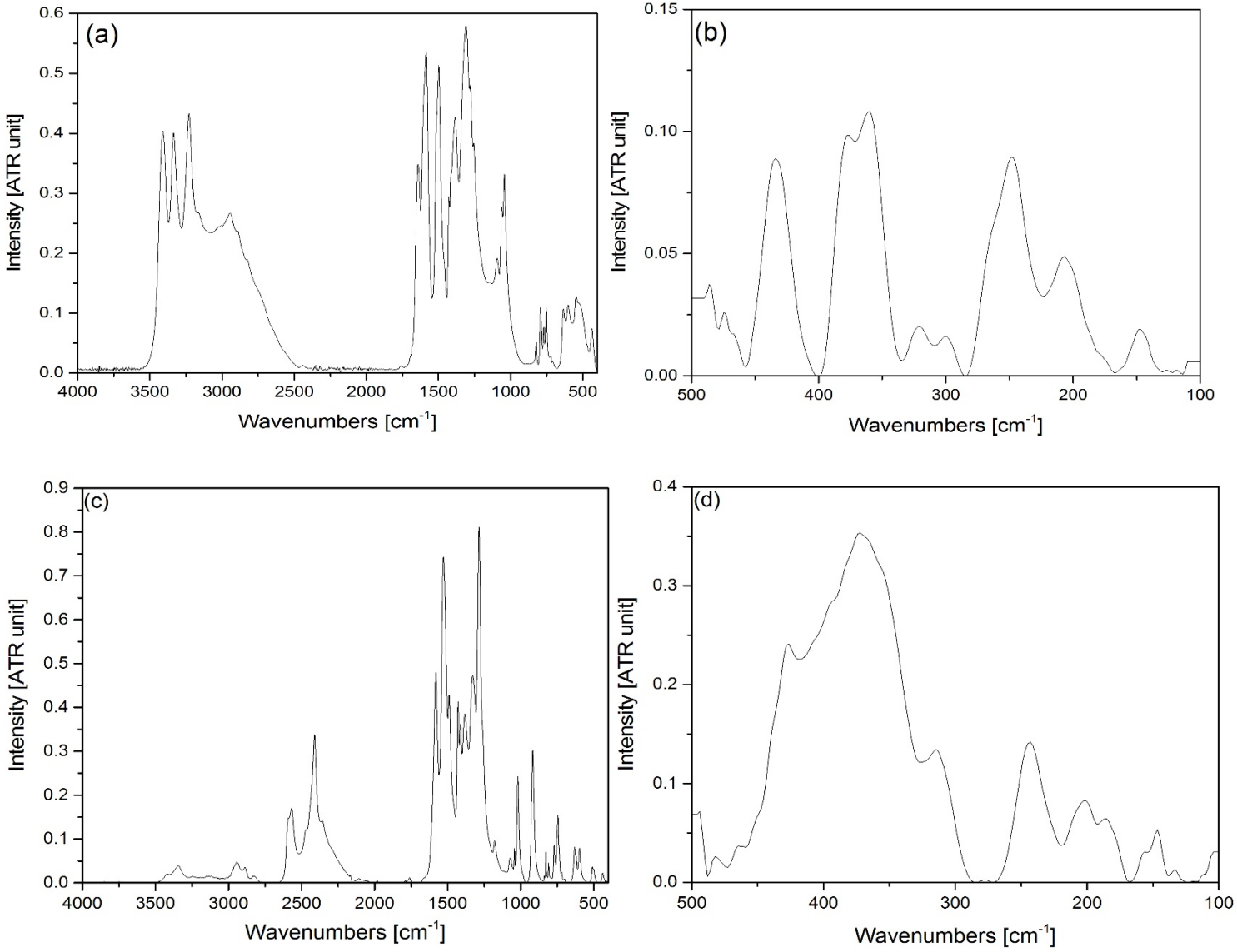


ESI Figure S13. Raman and IR spectra of compound **1** in different wavenumber regions.

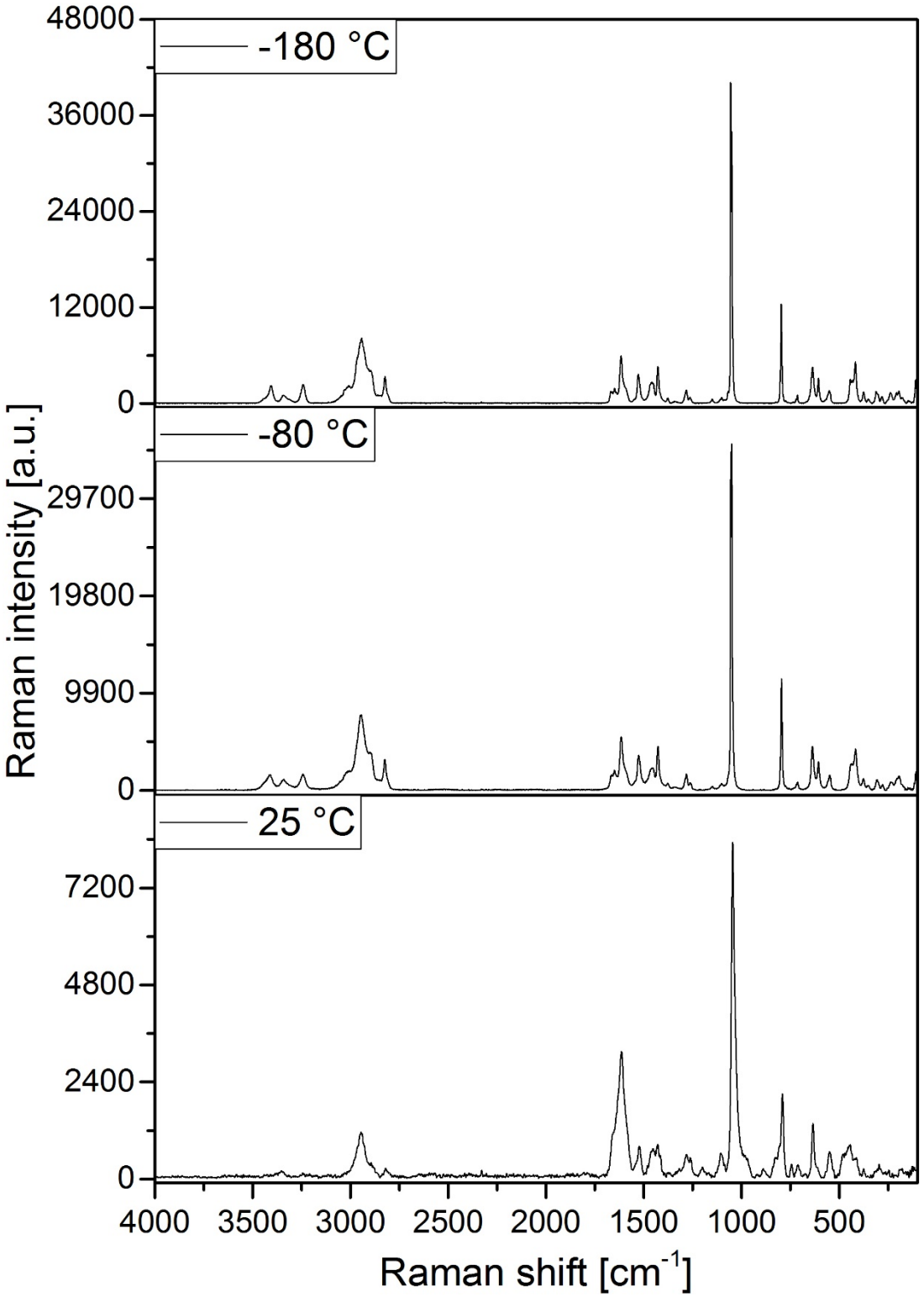
ESI Table S13. Assignment of vibrational modes of compound **2**.

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

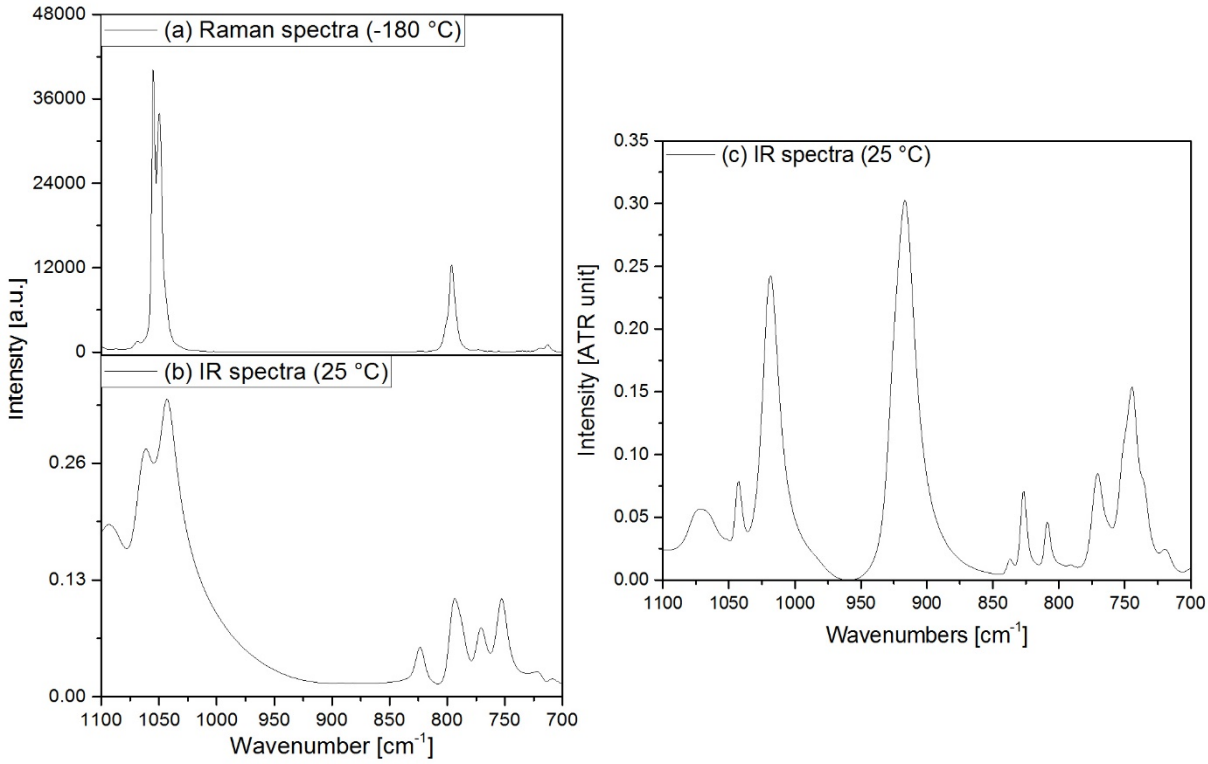
intensity: v – very, s – strong, m – medium, w – weak,



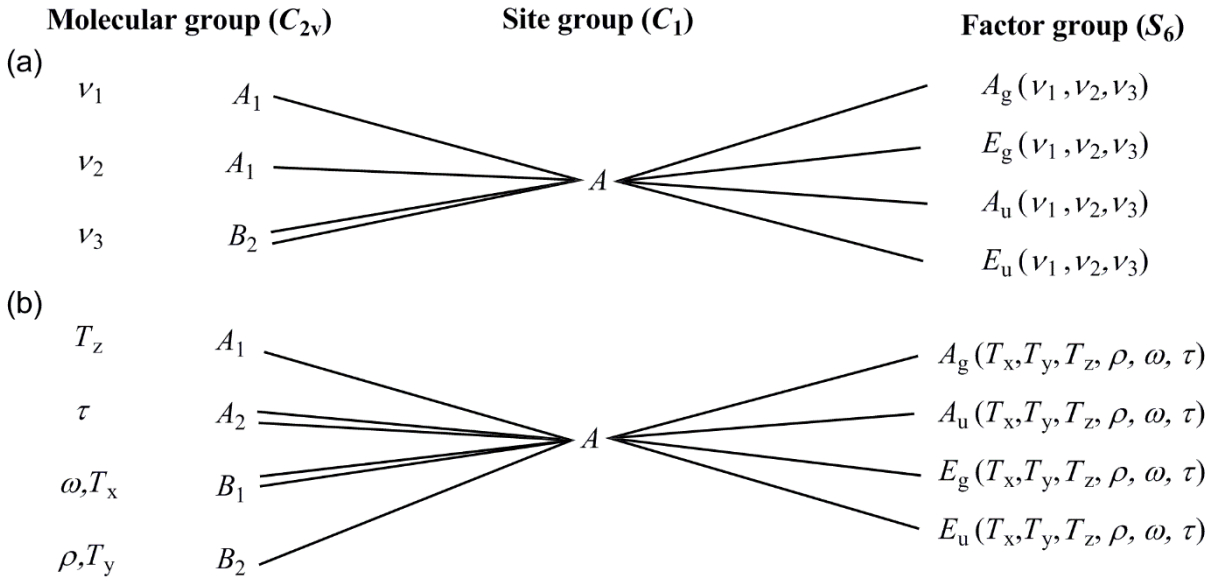
ESI Figure S14. (a) Close range and (b) Far-range IR spectra of compound **2** .(c) Close range and (d) Far-range IR spectra of compound **2-D**$_{12}$.



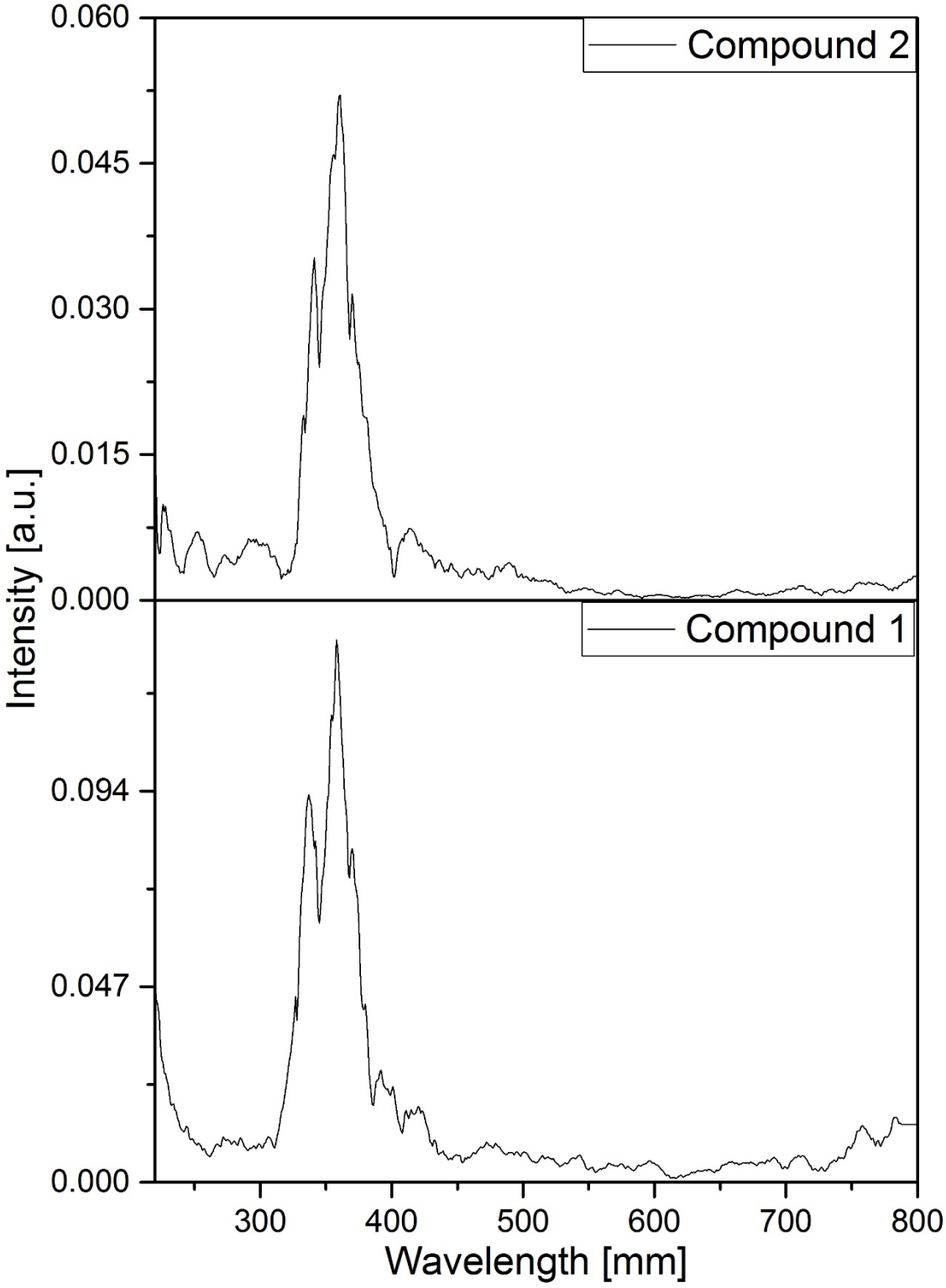
ESI Figure S15. Raman spectra of compound **2** at different temperature.



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**.