Supplementary Materials

Supramolecular diversity in metal–organic hybrids with $[VO_2(2,6\text{-pydc})]^-$ anion and piperazine and its derivatives

Mišel Hozjan and Franc Perdih*

Faculty of Chemistry and Chemical Technology, University of Ljubljana, Večna pot 113, SI-1000 Ljubljana, Slovenia

* Correspondence: franc.perdih@fkkt.uni-lj.si

Figures S1–**S10.** Crystal structures of compounds **1**·6H_2O–**10**·2H_2O.
Figure S11. Supramolecular packing in **1**·6H_2O.
Figure S12. Hydrogen-bonding in **2**·5H_2O.
Figure S13. Packing in **4**·H_2O.
Figure S14. Metavanadate chains in **8**.
Figures S15–**S19**. Supramolecular structure and graph set motifs in **9**·6H_2O.
Tables S1. Selected bond distances for compounds **1**·6H_2O–**6**·2,6-H_2pydc·2H_2O.
Table S2. Selected bond angles for compounds **1**·6H_2O–**6**·2,6-H_2pydc·2H_2O.
Tables S3. Structural parameter τ for the distortion of 5-coordinated geometry in $[VO_2(2,6\text{-pydc})]^-$ compounds **1**–**6** and in $[VO(2,6\text{-pydc})\text{-}(\mu\text{-}O)\text{-}VO(H_2O)(2,6\text{-pydc})]^-$ anion **7**.
Table S4–**S10**. Selected bond distances and angles for compounds **7**–**10**·2H_2O.
Tables S11. Comparison of bond angles between $[VO_2(2,6\text{-pydc})]^-$ and non-chelating pyridine-2,6-dicarboxylic acid in **6**·2,6-H_2pydc·2H_2O.
Tables S12–**S21.** Hydrogen bonding for **1**·6H_2O–**10**·2H_2O.
Table S22. Geometrical parameters (Å, °) for π···π stacking interactions in **s**tructures **5**·H_2O, **7** and **10**·2H_2O.
Figures S20–**S30**. ^{1}H NMR spectra.

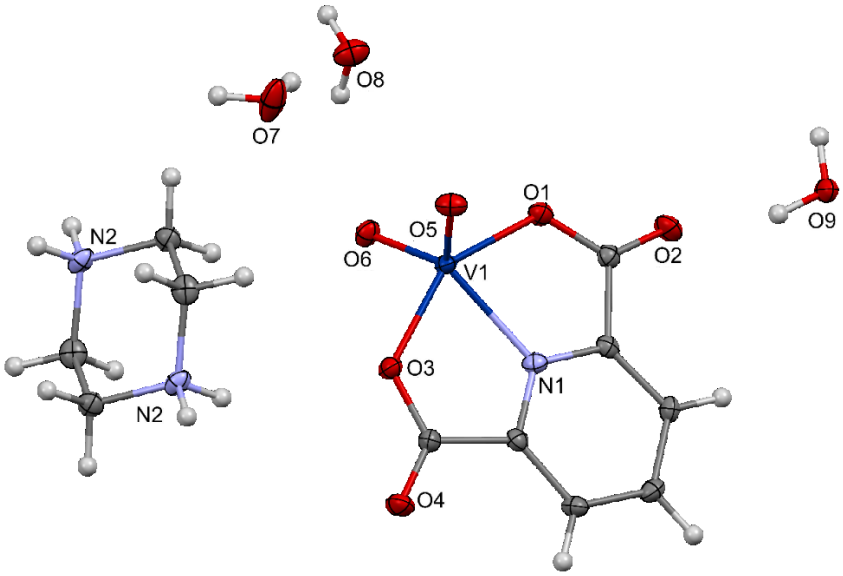


Figure S1. Crystal structure of **1**·6H_2O.

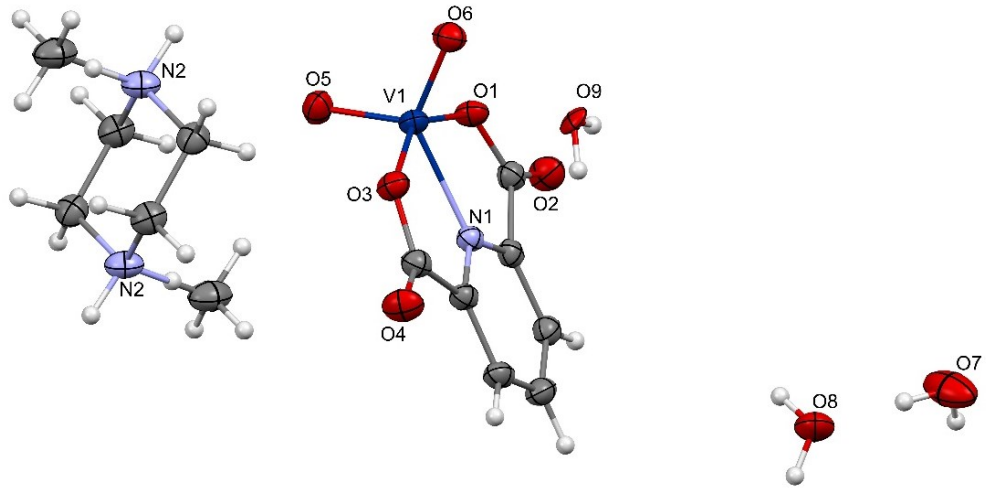


Figure S2. Crystal structure of **2**·5H_2O. Methylpiperazinium dication is shown disordered over two positions.

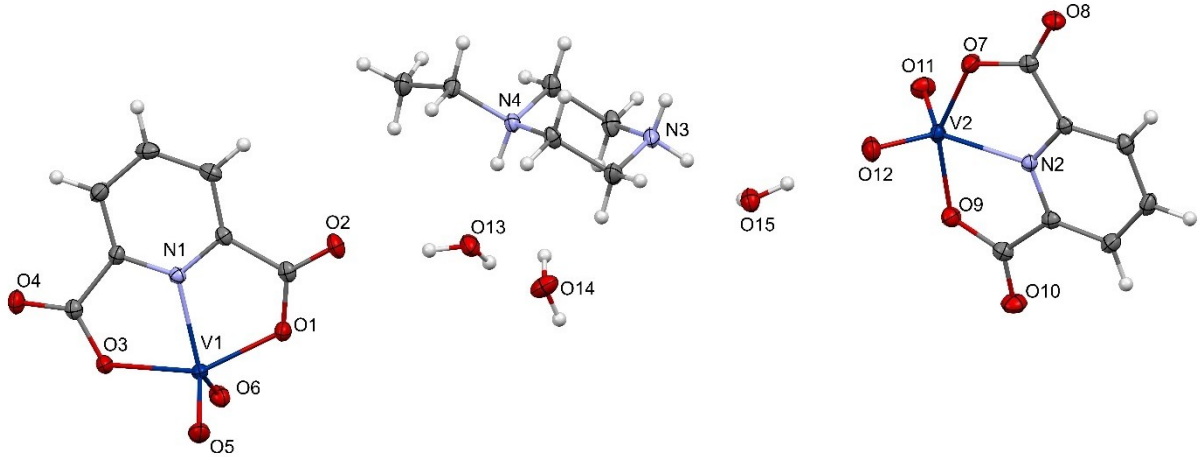


Figure S3. Asymmetric unit of **3**·3H_2O.

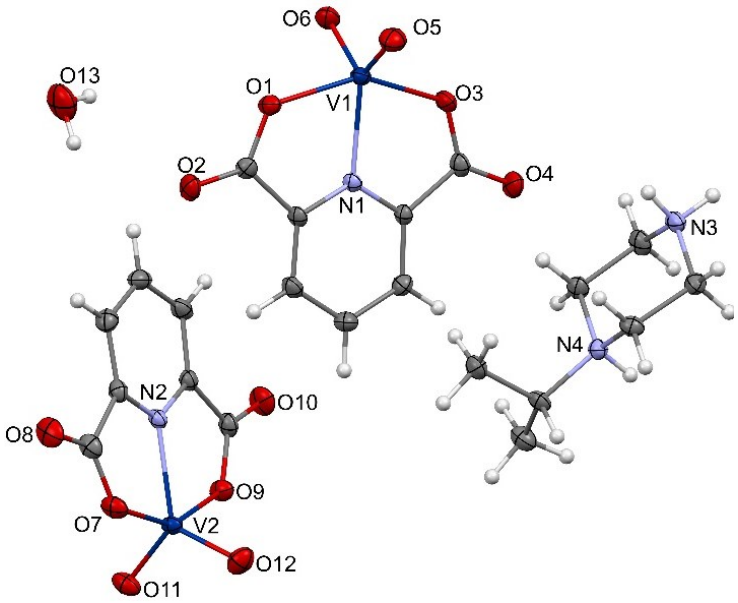


Figure S4. Asymmetric unit of **4**·H_2O.

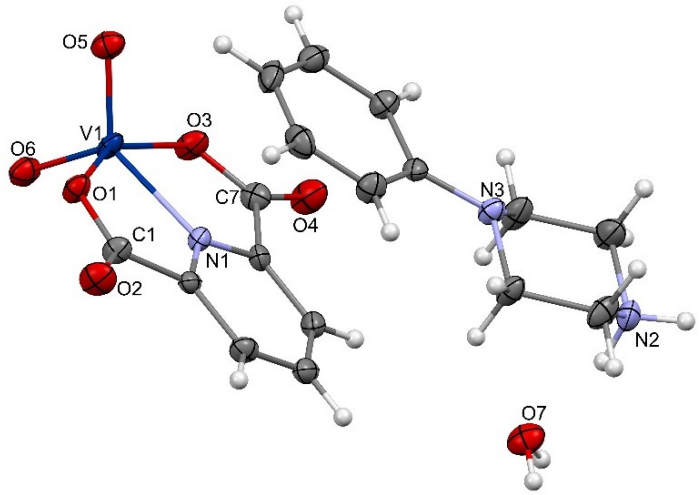


Figure S5. Asymmetric unit of **5**·H_2O.

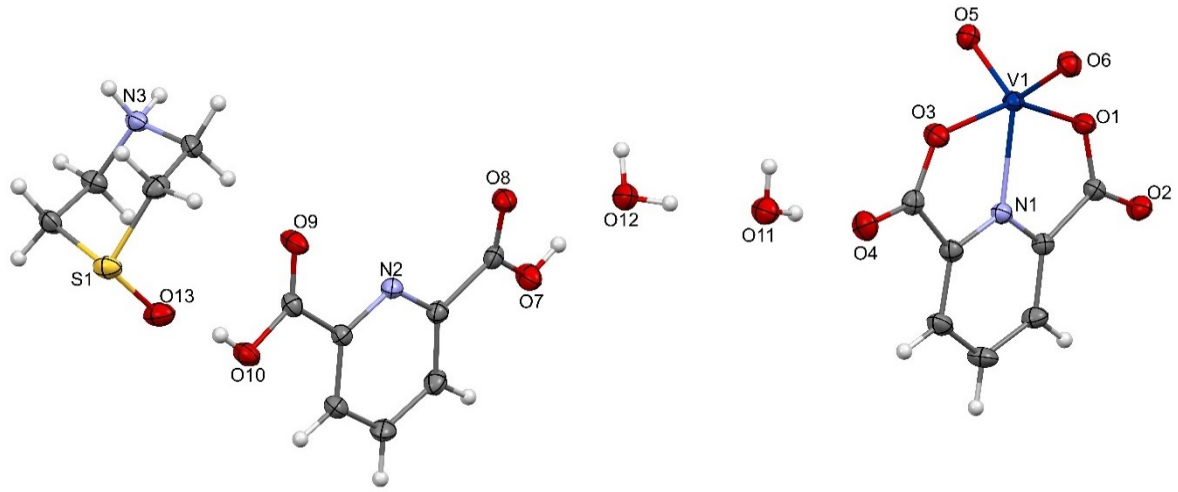


Figure S6. Asymmetric unit of **6**·2,6-H_2pydc·2H_2O.

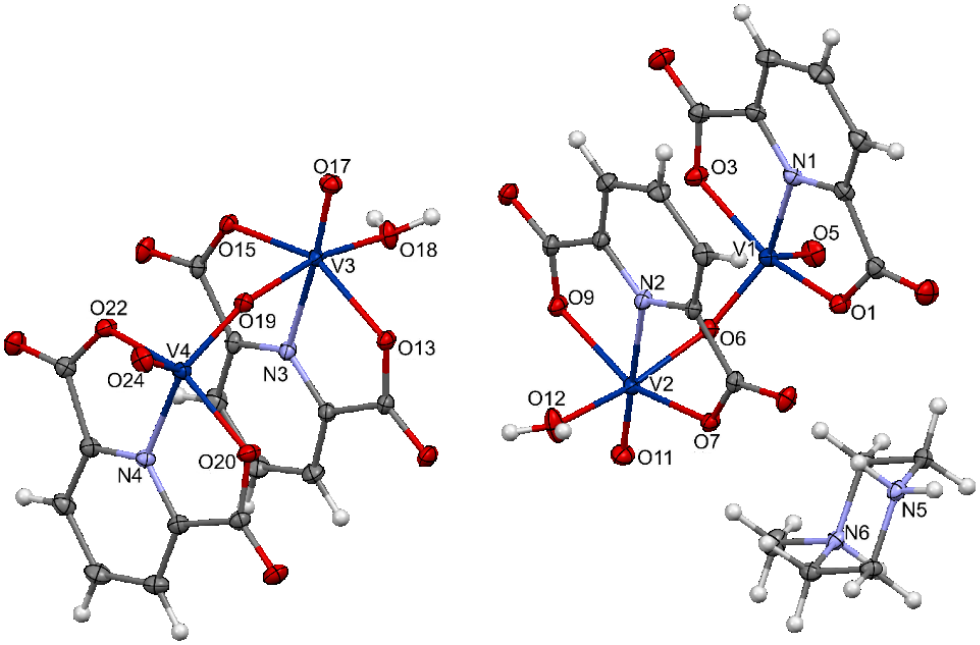
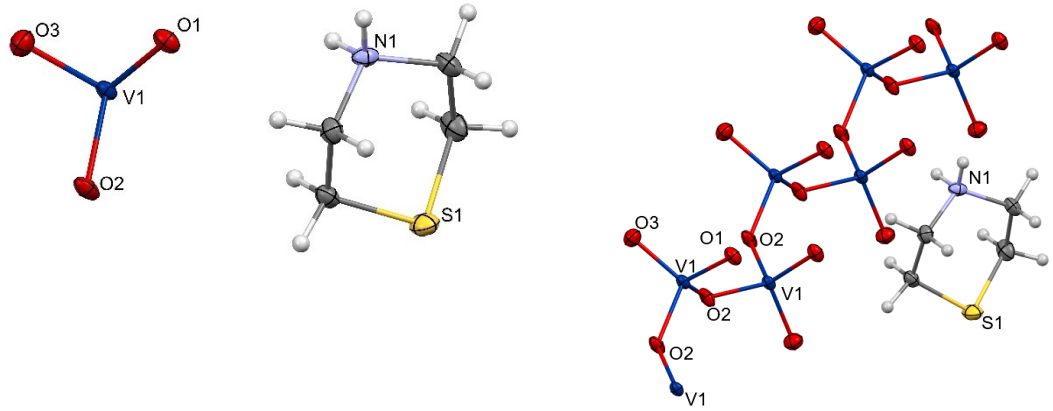


Figure S7. Asymmetric unit of **7**.



(a) **(b)**

Figure S8. Crystal structure of **8**. (**a**) asymmetric unit, (**b**) vanadate polymer expanded.

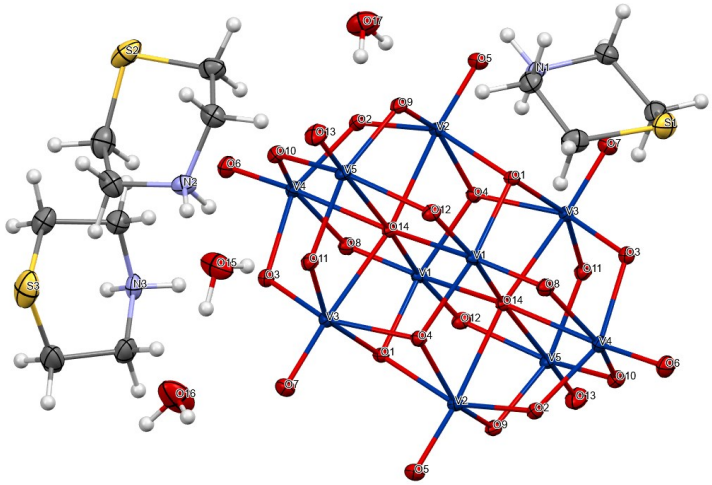


Figure S9. Crystal structure of **9**·6H_2O.

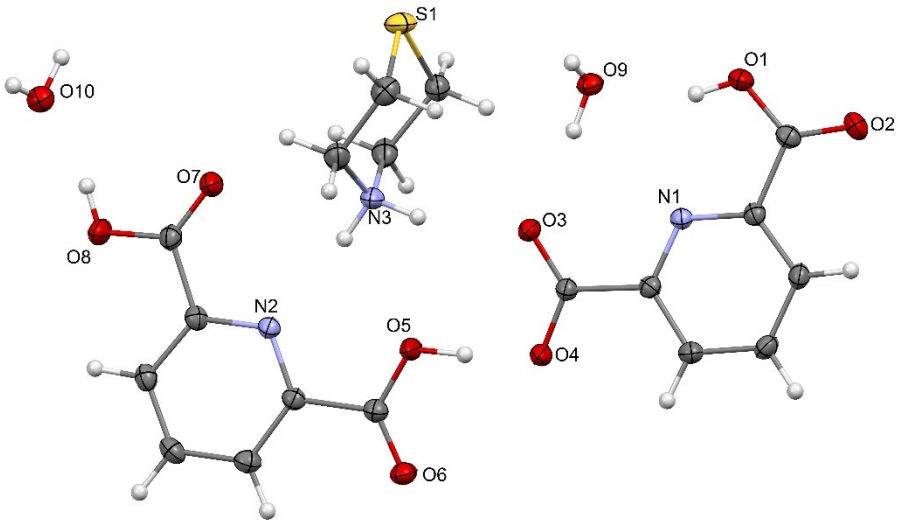


Figure S10. Asymmetric unit of **10**·2H_2O.

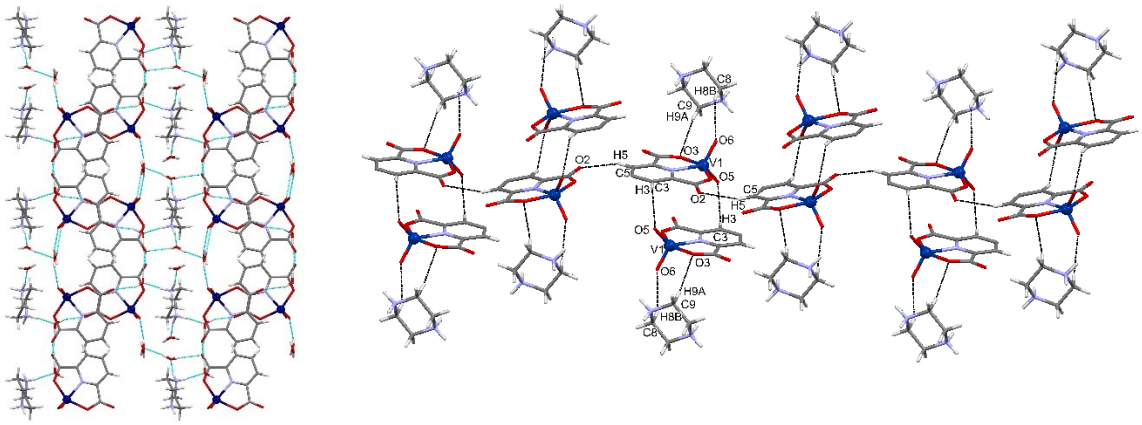


Figure S11. Supramolecular packing in **1**·6H_2O. (a) View along *c*-axis (b) Stabilization by C–H···O interactions.

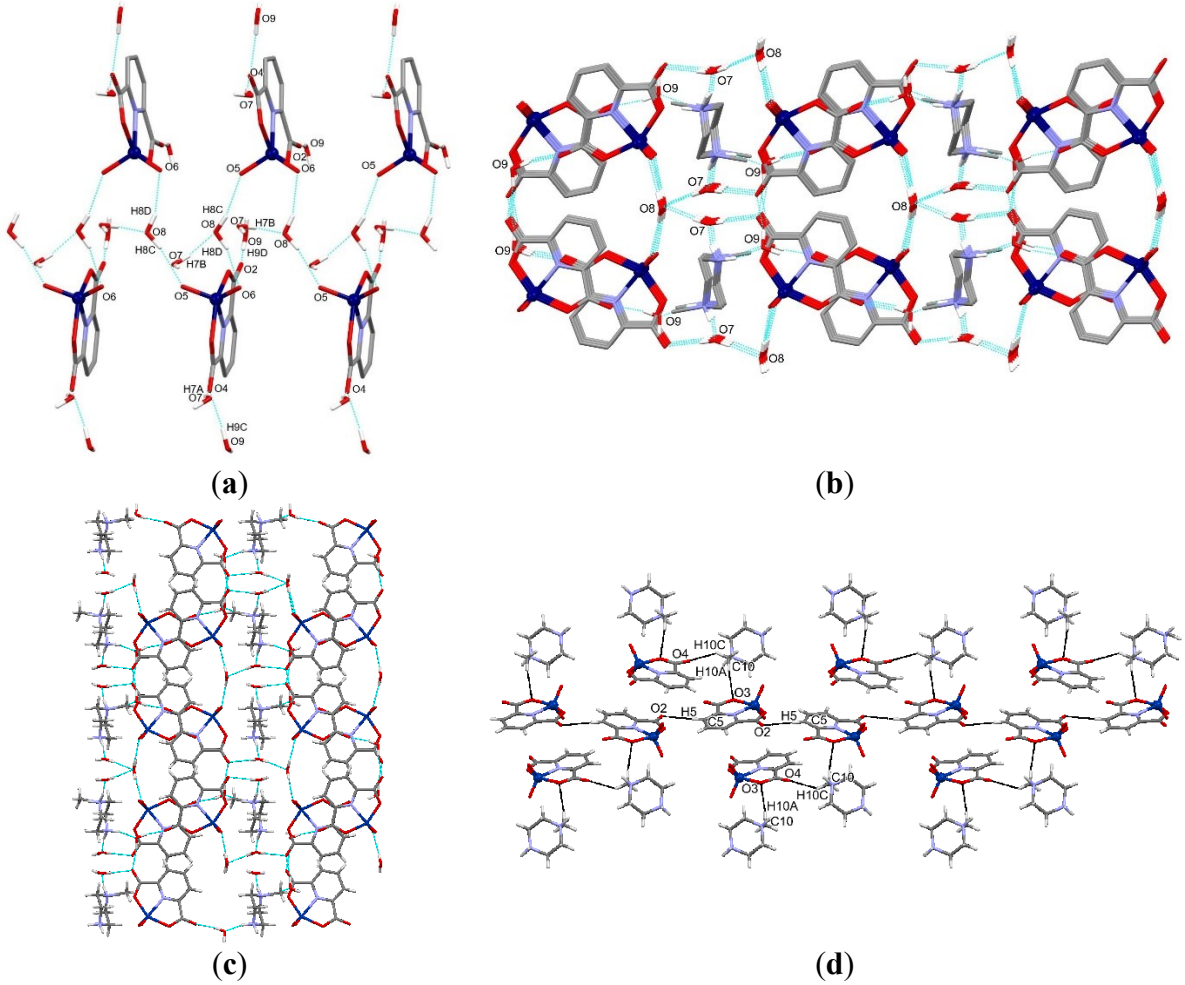
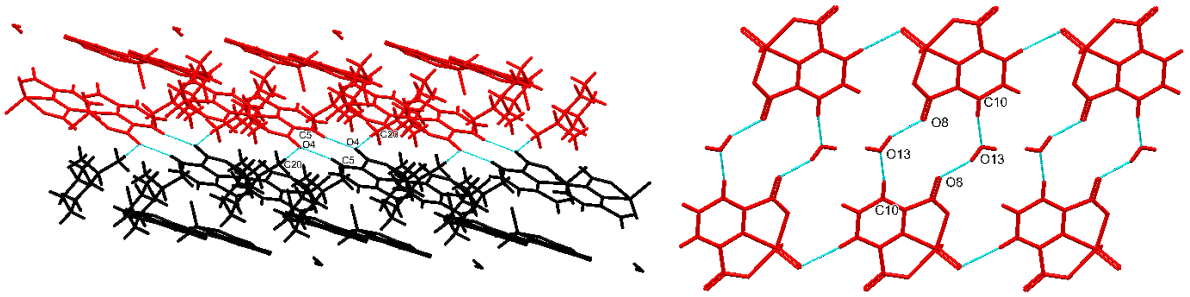
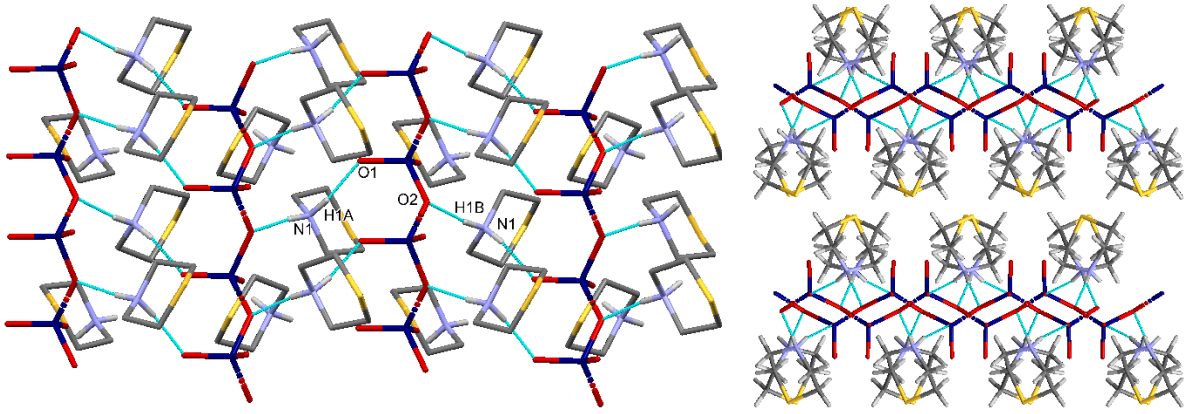


Figure S12. Hydrogen-bonding in **2**·5H_2O (a) between complex anions and adjacent water molecules along *c*-axis and (b) top view along *c*-axis with a channel of water molecules. (c) Top view along *c*-axis with a channel of water molecules. (d) Supramolecular structure is stabilized also by C–H···O interactions. Disorder on methylpiperazinium cation and H-atoms not involved in hydrogen-bonding motif shown have been omitted for clarity.



(**a**) (**b**)

Figure S13. Packing in **4**·H_2O. (a) C5–H5···O4, and C20–H20B···O4 interactions along the *c*-axis and (b) C10–H10···O13 interactions between water and anions. H-atoms not involved in hydrogen-bonding motif shown have been omitted for clarity.



(**a**) (**b**)

Figure S14. Metavanadate chains in **8** connecting to each other through hydrogen-bonded cations forming 2D layers. (a) View of hydrogen bonds between VO_3^- chains and thiomorpholine units along the *c*-axis. (b) Top-down view along the *b*-axis of the hydrogen bond network. H-atoms not involved in hydrogen-bonding motif shown have been omitted for clarity.

Supramolecular structure and graph set motifs in 9·6H_2O

The hydrogen bonds present in the structure are listed in Table S13. The thiomorpholinium ($Htmor^+$) cations exhibit diverse hydrogen bonding interactions. Two cations form hydrogen bonds with two decavanadate anions through their NH_2^+ hydrogen atoms. The third cation forms a hydrogen bond with a water molecule through one of NH_2^+ hydrogen atoms and a trifurcated hydrogen bond through the second NH_2^+ hydrogen atom with three different oxido atoms of decavanadate. This third cation also participates in a hydrogen bond as an acceptor through its thio functional group, interacting with one water molecule. A notably short hydrogen bond between one thiomorpholine cation and an oxygen atom of the decavanadate cluster $d_{N3\cdots O3}$ = 2.680(2) Å suggests a very strong interaction. Each decavanadate anion forms hydrogen bonds with nine thiomorpholinium cations and eight water molecules. This extensive

network of hydrogen bonds, including C–H···O interactions between the cations and the decavanadate cluster enables the formation of 3D supramolecular structure (Figures S12–S16).

In **9**·6H_2O, the hydrogen-bonding network exhibits six distinct repeating ring graph set motifs. These motifs are presented individually in the next four figures, except for those with a four-ring motif, which are shown together in a single figure. In the figures, decavanadate anion oxygens are colored black, vanadium atoms are gray, water molecules are blue, and the three different asymmetric cations are colored red, green, and purple, respectively.

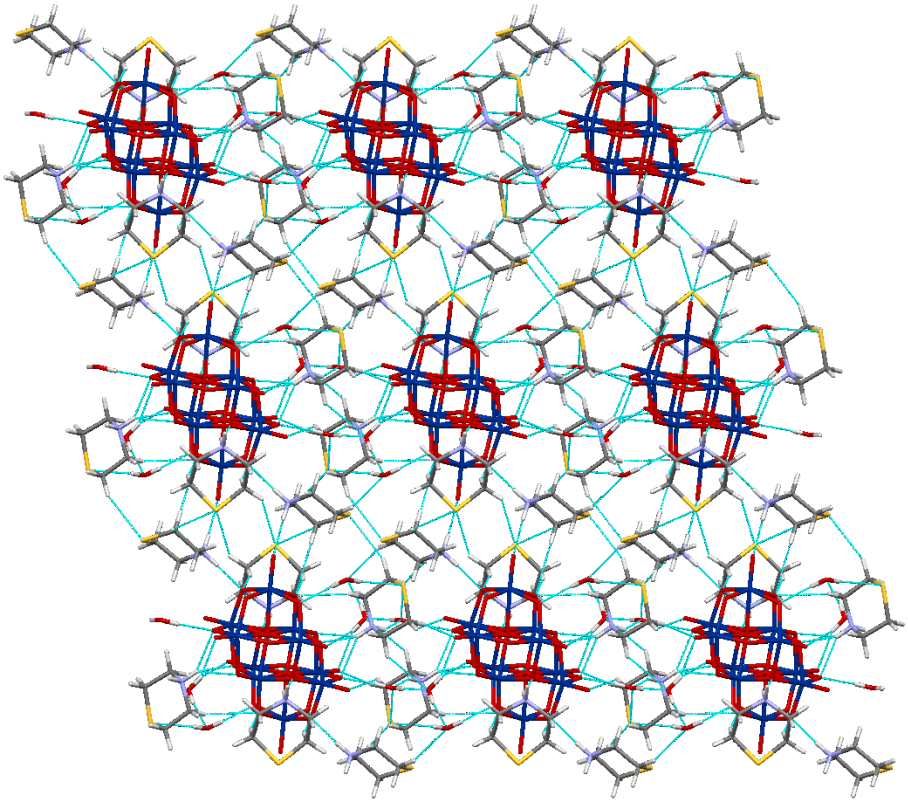


Figure S15. A 3-dimensional framework generated due to hydrogen bonding interactions between cation, decavanadate anion and water molecules in **9**·6H_2O along the *b*-axis.

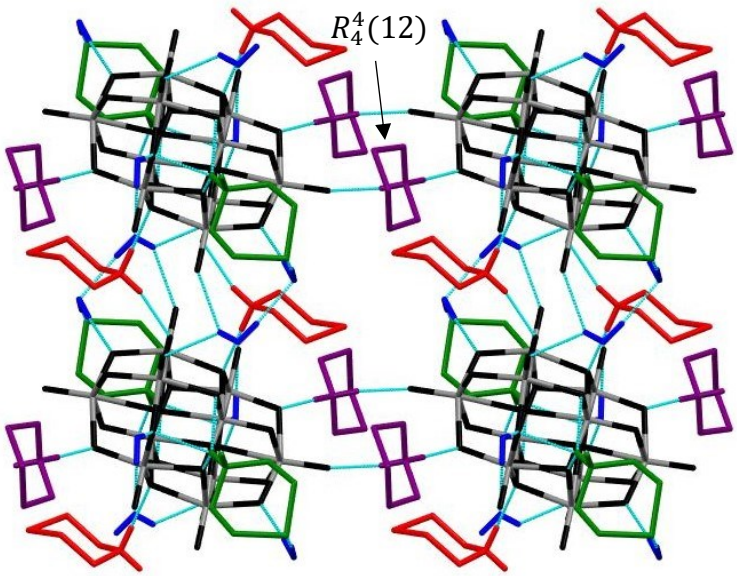


Figure S16. Graph set motif $R_4^4(12)$ in **9**·6H$_2$O along the *b*-axis.

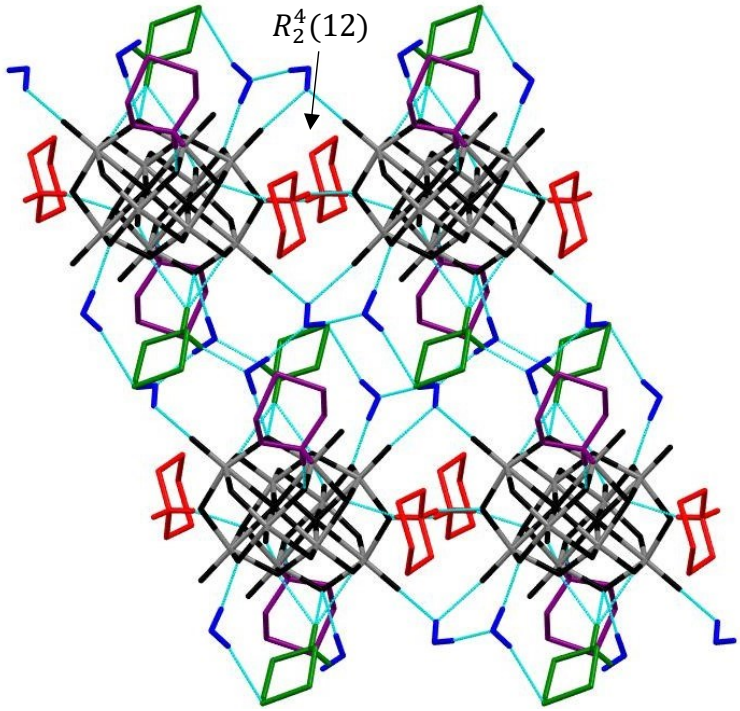


Figure S17. Graph set motif $R_2^4(12)$ in **9**·6H$_2$O along the *c*-axis.

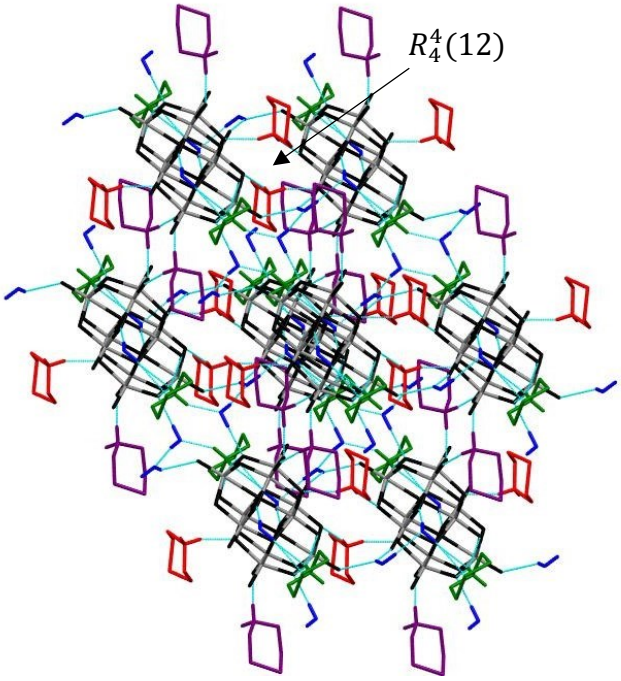


Figure S18. Graph set motif $R_4^4(12)$ in **9**·6H$_2$O along a custom axis.

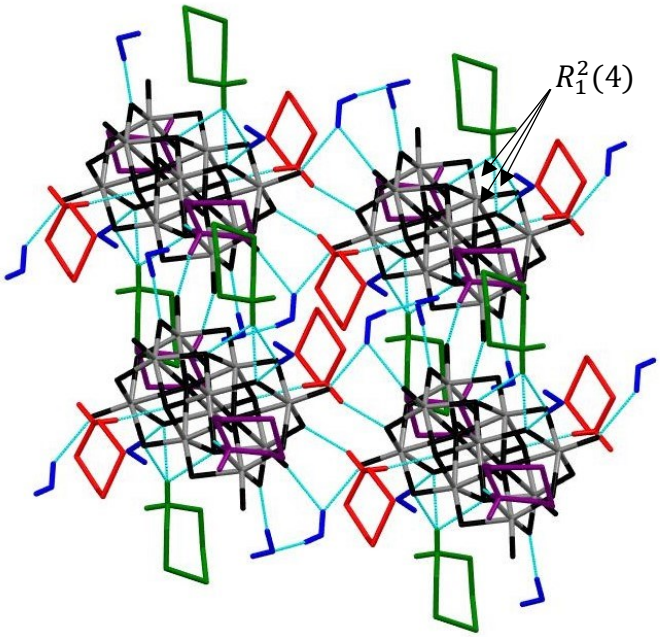


Figure S19. A graph set motif in **9**·6H$_2$O arising from a trifurcated NH fragmet, forming three four-membered hydrogen-bonded rings, $R_1^2(4)$, around the periphery of the seven-membered ring geometric figure.

Table S1. Selected bond distances for compounds **1**·6H_2O–**6**·2,6-H_2pydc·2H_2O.

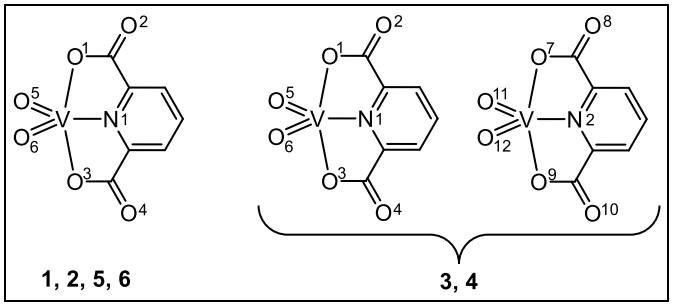
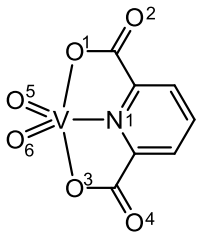
Distance	**1**·6H_2O [Å]	**2**·5H_2O [Å]	**3**·3H_2O [Å]	**4**·H_2O [Å]	**5**·H_2O [Å]	**6**·2,6-H_2pydc·2H_2O [Å]
V1–O1	1.992(4)	1.9819(18)	1.9931(11)	2.0308(14)	1.991(3)	1.9881(14)
V1–O3	1.998(4)	1.9919(18)	1.9898(11)	1.9883(14)	1.993(3)	1.9974(14)
V1–O5	1.610(4)	1.6198(18)	1.6115(11)	1.6176(15)	1.628(3)	1.6267(14)
V1–O6	1.615(4)	1.6232(18)	1.6365(12)	1.6232(14)	1.616(3)	1.6162(14)
V1–N1	2.098(4)	2.094(2)	2.0879(12)	2.0875(16)	2.096(3)	2.0928(16)
V2–O7			2.0009(11)	1.9704(14)		
V2–O9			1.9869(11)	2.0166(14)		
V2–O11			1.6241(11)	1.6200(14)		
V2–O12			1.6207(12)	1.6218(14)		
V2–N2			2.0775(12)	2.0811(16)		
O1–C1	1.295(6)	1.303(3)	1.2974(18)	1.305(2)	1.324(5)	1.304(2)
O2–C1	1.223(7)	1.212(3)	1.2216(18)	1.220(2)	1.205(5)	1.211(2)
O3–C7	1.292(6)	1.302(3)	1.3045(19)	1.299(2)	1.297(5)	1.298(2)
O4–C7	1.224(7)	1.220(3)	1.2176(18)	1.223(2)	1.222(5)	1.213(2)
O7–C8			1.2970(18)	1.295(3)		
O8–C8			1.2195(18)	1.221(2)		
O9–C14			1.2996(19)	1.302(2)		
O10–C14			1.2213(19)	1.213(2)		

Table S2. Selected bond angles for compounds **1**·6H_2O–**6**·2,6-H_2pydc·2H_2O.

Angle		**1**·6H_2O [°]	**2**·5H_2O [°]	**5**·H_2O [°]	**6**·2,6-H_2pydc·2H_2O [°]
O1–V1–O3		148.60(15)	148.64(7)	149.51(12)	148.95(6)
O1–V1–O5		99.85(19)	100.29(9)	98.51(14)	98.00(7)
O3–V1–O5		100.17(18)	99.44(9)	99.21(14)	99.16(7)
O5–V1–O6		109.7(2)	109.61(10)	108.98(15)	109.10(7)
N1–V1–O1		74.38(16)	74.61(7)	74.67(14)	74.74(6)
N1–V1–O3		74.77(16)	74.46(8)	74.98(14)	74.21(6)
N1–V1–O5		119.33(19)	119.87(9)	131.25(14)	124.81(7)

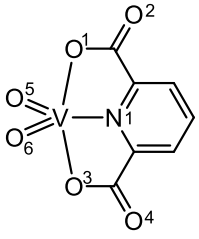
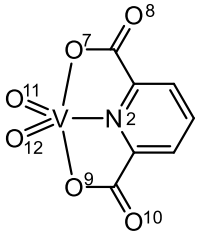
Angle		**3**·3H_2O [°]	**4**·H_2O [°]
O1–V1–O3		149.21(5)	149.34(6)
O1–V1–O5		99.18(5)	96.63(7)
O1–V1–O6		100.05(5)	95.26(7)
O3–V1–O5		97.34(5)	101.56(7)
O3–V1–O6		98.87(5)	101.54(7)
O5–V1–O6		108.98(6)	109.51(8)
N1–V1–O1		74.55(5)	74.09(6)
N1–V1–O3		74.78(5)	75.26(6)
N1–V1–O5		127.76(6)	126.10(7)
N1–V1–O6		123.24(5)	124.01(7)
O7–V2–O9		149.75(5)	149.98(6)
O7–V2–O11		97.56(5)	100.42(7)
O7–V2–O12		97.90(5)	103.07(7)
O9–V2–O11		98.92(5)	97.10(7)
O9–V2–O12		99.89(6)	93.86(7)
O11–V2–O12		110.34(6)	109.09(8)
N2–V2–O7		74.57(5)	75.79(6)
N2–V2–O9		75.18(5)	74.21(6)
N2–V2–O11		124.34(6)	128.30(7)
N2–V2–O12		125.28(6)	122.13(7)

Table S3. Structural parameter τ for the distortion of 5-coordinated geometry in $[VO_2(2,6\text{-pydc})]^-$ compounds **1**–**6** and in $[VO(2,6\text{-pydc})\text{-}(\mu\text{-}O)\text{-}VO(H_2O)(2,6\text{-pydc})]^-$ anion **7**.

Compound	τ
1·6H_2O	0.29
2·5H_2O	0.30
3·3H_2O	0.41, 0.36
4·H_2O	0.39, 0.36
5·H_2O	0.30
6·2,6-H_2pydc·2H_2O	0.38
7	0.25, 0.21

Table S4. Selected bond distances for compound **7**.

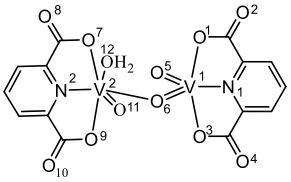
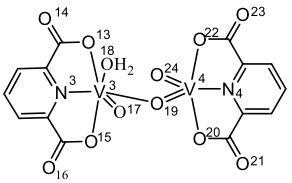
Distance	[Å]			[Å]
V1–O1	1.9521(13)		V3–O13	2.0240(13)
V1–O3	1.9779(13)		V3–O15	2.0447(13)
V1–O5	1.5889(14)		V3–O17	1.6076(13)
V1–O6	1.6783(13)		V3–O18	2.0343(14)
V1–N1	2.0892(15)		V3–O19	1.9949(13)
V2–O6	1.9913(13)		V3–N3	2.1516(15)
V2–O7	2.0192(13)		V4–O19	1.6707(13)
V2–O9	2.0227(13)		V4–O20	1.9609(13)
V2–O11	1.6026(13)		V4–O22	1.9678(13)
V2–O12	2.0484(15)		V4–O24	1.5963(13)
V2–N2	2.1412(15)		V4–N4	2.0760(15)

Table S5. Selected bond angles for compound **7**.

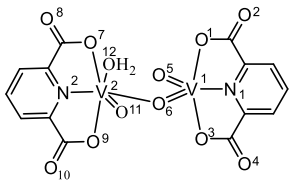
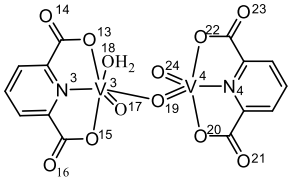
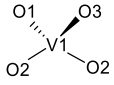
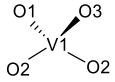
Angle	[°]		Angle	[°]
O1–V1–O3	148.15(6)		O13–V3–O15	147.89(5)
O1–V1–N1	74.69(6)		O13–V3–O18	85.98(6)
O3–V1–N1	74.68(6)		O13–V3–N3	74.44(5)
O5–V1–O1	101.78(7)		O15–V3–N3	73.48(5)
O5–V1–O3	99.50(7)		O17–V3–O13	111.24(6)
O5–V1–O6	107.98(7)		O17–V3–O15	100.86(6)
O5–V1–N1	116.60(7)		O17–V3–O18	96.53(6)
O6–V1–O1	97.62(6)		O17–V3–O19	95.94(6)
O6–V1–O3	98.01(6)		O17–V3–N3	174.27(7)
O6–V1–N1	135.42(6)		O18–V3–O15	91.27(5)
O6–V2–O7	88.94(5)		O18–V3–N3	82.88(6)
O6–V2–O9	87.92(5)		O19–V3–O13	86.73(5)
O6–V2–O12	166.75(6)		O19–V3–O15	89.31(5)
O6–V2–N2	84.18(5)		O19–V3–O18	167.17(6)
O7–V2–O9	148.81(5)		O19–V3–N3	85.00(5)
O7–V2–O12	87.23(6)		O19–V4–O20	99.51(6)
O7–V2–N2	74.20(5)		O19–V4–O22	95.86(6)
O9–V2–O12	88.80(6)		O19–V4–N4	134.01(6)
O9–V2–N2	74.61(6)		O20–V4–O22	149.15(6)
O11–V2–O6	98.77(7)		O20–V4–N4	75.14(6)
O11–V2–O7	102.56(6)		O22–V4–N4	74.92(6)
O11–V2–O9	108.59(6)		O24–V4–O19	108.54(7)
O11–V2–O12	94.44(7)		O24–V4–O20	100.30(7)
O11–V2–N2	175.65(7)		O24–V4–O22	99.91(7)
O12–V2–N2	82.58(6)		O24–V4–N4	117.40(7)

Table S6. Selected bond distances for compound **8**.

Distance		[Å]
V1–O1		1.6479(15)
V1–O2		1.8140(15)
V1–O2^{i}		1.8220(15)
V1–O3		1.6263(15)

Symmetry code:(i) ½ + *x*, *y*, ½ – *z*

Table S7. Selected bond angles for compound **8**.

Angle		[°]
O1–V1–O2		110.12(7)
O1–V1–O2^{i}		111.84(7)
O2–V1–O2^{i}		108.03(5)
O3–V1–O1		108.68(8)
O3–V1–O2^{i}		110.47(8)
O3–V1–O2		107.62(8)

Symmetry code: (i) ½ + *x*, *y*, ½ – *z*

Table S8. Selected bond distances for compound **9**·6H_2O [Å].

Distance	[Å]		[Å]
V1–O1	1.9284(12)	V3–O7	1.6061(13)
V1–O4	1.9122(12)	V3–O11	1.8364(12)
V1–O8	1.6753(12)	V3–O14^{i}	2.2300(12)
V1–O12	1.7035(12)	V4–O2	1.8618(13)
V1–O14	2.0533(12)	V4–O3	1.8947(13)
V1–O14^{i}	2.1770(11)	V4–O6	1.6168(13)
V2–O1	2.0132(12)	V4–O8^{i}	2.0918(12)
V2–O2	1.8205(12)	V4–O10	1.7834(13)
V2–O4^{i}	1.9812(12)	V4–O14^{i}	2.2968(11)
V2–O5	1.6046(13)	V5–O9	1.8600(13)
V2–O9	1.8378(12)	V5–O10	1.8622(12)
V2–O14^{i}	2.2422(12)	V5–O11	1.8782(13)
V3–O1^{i}	1.9856(12)	V5–O12	2.0033(12)
V3–O3	1.8177(12)	V5–O13	1.5997(13)
V3–O4	2.0126(12)	V5–O14^{i}	2.3209(12)

Symmetry code: (i) $1 - x$, $1 - y$, $1 - z$

Table S9. Selected bond angles for compound **9**·6H_2O [°].

Angle	[°]		[°]		[°]
O1–V1–O14	81.70(5)	O1–V2–O14^{i}	76.20(5)	O1^{i}–V3–O4	76.53(5)
O1–V1–O14^{i}	79.50(5)	O2–V2–O1	155.69(5)	O1^{i}–V3–O141	76.12(5)
O4–V1–O1	155.68(5)	O2–V2–O4^{i}	90.77(5)	O3–V3–O1^{i}	91.57(5)
O4–V1–O14^{i}	79.75(5)	O2–V2–O9	94.88(6)	O3–V3–O4	155.90(5)
O4–V1–O14	81.86(5)	O2–V2–O14^{i}	80.61(5)	O3–V3–O11	95.13(6)
O8–V1–O1	98.37(6)	O4^{i}–V2–O1	76.61(5)	O3–V3–O14^{i}	80.44(5)
O8–V1–O4	99.14(6)	O4^{i}–V2–O14^{i}	75.72(5)	O4–V3–O14^{i}	76.41(5)
O8–V1–O12	106.31(6)	O5–V2–O1	99.28(6)	O7–V3–O1^{i}	100.24(6)
O8–V1–O14^{i}	167.49(5)	O5–V2–O2	103.44(6)	O7–V3–O3	101.71(6)
O8–V1–O14	89.04(5)	O5–V2–O4^{i}	100.42(6)	O7–V3–O4	101.01(6)
O12–V1–O1	94.99(6)	O5–V2–O9	102.49(6)	O7–V3–O11	102.62(6)
O12–V1–O4	96.13(6)	O5–V2–O14^{i}	174.56(6)	O7–V3–O14^{i}	175.89(6)
O12–V1–O14^{i}	86.18(5)	O9–V2–O1	88.50(5)	O11–V3–O1^{i}	154.30(5)
O12–V1–O14	164.62(5)	O9–V2–O4^{i}	154.38(5)	O11–V3–O4	87.68(5)
O14–V1–O14^{i}	78.46(5)	O9–V2–O14^{i}	80.59(5)	O11–V3–O14^{i}	80.57(5)
O2–V4–O3	153.78(5)	O9–V5–O10	89.65(6)		
O2–V4–O8^{i}	82.50(5)	O9–V5–O11	155.03(5)		
O2–V4–O14^{i}	78.32(5)	O9–V5–O12	85.74(5)		
O3–V4–O8^{i}	81.76(5)	O9–V5–O14^{i}	78.04(5)		
O3–V4–O14^{i}	77.16(5)	O10–V5–O11	90.27(6)		
O6–V4–O2	102.83(6)	O10–V5–O12	156.21(5)		
O6–V4–O3	100.52(6)	O10–V5–O14^{i}	80.23(5)		
O6–V4–O8^{i}	100.28(6)	O11–V5–O12	84.34(5)		
O6–V4–O10	103.74(6)	O11–V5–O14^{i}	77.34(5)		

O6–V4–O14^{i}	173.47(6)	O12–V5–O14^{i}	75.98(4)
O8^{i}–V4–O14^{i}	73.41(4)	O13–V5–O9	102.17(6)
O10–V4–O2	93.99(6)	O13–V5–O10	103.13(6)
O10–V4–O3	91.89(6)	O13–V5–O11	102.16(6)
O10–V4–O8^{i}	155.89(5)	O13–V5–O12	100.66(6)
O10–V4–O14^{i}	82.51(5)	O13–V5–O14^{i}	176.62(6)

Symmetry code: (i) $1-x, 1-y, 1-z$

Table S10. Selected bond distances for compound **10**·2H$_2$O.

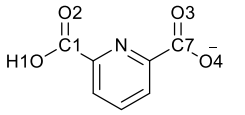
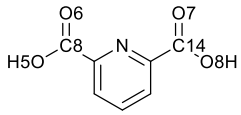
Distance		[Å]
C1–O1		1.316(2)
C1–O2		1.2157(19)
C7–O3		1.2436(19)
C7–O4		1.2702(19)
C8–O5		1.290(2)
C8–O6		1.220(2)
C14–O7		1.205(2)
C14–O8		1.317(2)

Table S11. Comparison of bond angles between [VO$_2$(2,6-pydc)]$^-$ and non-chelating pyridine-2,6-dicarboxylic acid in **6**·2,6-H$_2$pydc·2H$_2$O.

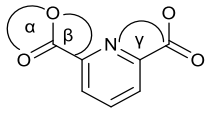
	Angle	α [°]	β [°]	γ [°]
	[VO$_2$(2,6-pydc)]$^-$	126.36(18)	111.97(16)	111.37(16)
		125.77(19)	112.73(16)	110.51(16)
	pyridine-2,6-dicarboxylic acid	124.76(18)	112.76(16)	114.42(16)
		123.92(18)	112.82(16)	114.66(16)

Table S12. Hydrogen bonds for **1**·6H$_2$O [Å and °]

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)	Symmetry transformation for acceptors
N2–H2A···O7	0.91(2)	1.83(3)	2.725(6)	167(6)	$1+x, y, z$
N2–H2B···O9	0.911(14)	1.88(3)	2.733(6)	155(6)	x, y, z
O7–H7A···O4	0.86(2)	2.04(5)	2.814(6)	149(9)	$-x, -y, 1-z$
O7–H7B···O8	0.87(2)	1.94(3)	2.794(7)	168(9)	x, y, z
O8–H8C···O5	0.86(2)	2.10(4)	2.930(6)	160(8)	$x, \frac{1}{2}-y, -\frac{1}{2}+z$
O8–H8D···O6	0.87(2)	2.21(6)	2.872(6)	133(7)	x, y, z
O9–H9C···O4	0.86(2)	1.90(2)	2.752(5)	171(7)	$1-x, \frac{1}{2}+y, 3/2-z$
O9–H9D···O2	0.86(2)	1.93(3)	2.744(5)	158(7)	x, y, z
C3–H3···O6	0.95	2.54	3.134(6)	120.9	$1-x, -y, 1-z$
C5–H5···O2	0.95	2.44	3.315(7)	153.4	$1-x, -\frac{1}{2}+y, 3/2-z$
C8–H8B···O5	0.99	2.54	3.296(7)	133.0	$1+x, y, z$
C8–H8B···O6	0.99	2.51	3.130(7)	120.2	$1+x, y, 1+z$
C9–H9A···O3	0.99	2.48	3.382(6)	150.6	$1+x, y, z$

Table S13. Hydrogen bonds for **2**·5H_2O [Å and °]

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)	Symmetry transformation for acceptors
N2–H2A···O7	0.980(18)	1.722(19)	2.695(3)	171(3)	*x*, *y*, *z*
N2–H2B···O9	0.957(2)	1.675(3)	2.609(4)	164.32(18)	*x*, *y*, *z*
O7–H7A···O4	0.873(10)	1.964(17)	2.808(3)	162(4)	1 –*x*, 1 – *y*, –*z*
O7–H7B···O8	0.867(10)	1.940(14)	2.795(3)	169(5)	*x*, *y*, *z*
O8–H8C···O5	0.860(10)	2.086(14)	2.925(3)	165(4)	1 + *x*, ½ – *y*, –½ + *z*
O8–H8D···O6	0.862(10)	2.030(17)	2.850(3)	159(4)	1 + *x*, *y*, *z*
O9–H9C···O4	0.865(10)	1.934(18)	2.782(4)	167(6)	1 – *x*, –½ + *y*, ½ – *z*
O9–H9D···O2	0.863(10)	1.786(15)	2.639(4)	170(6)	*x*, *y*, *z*
C5–H5···O2	0.95	2.44	3.329(3)	155.2	1 – *x*, ½ + *y*, ½ – *z*
C8–H8A···O5	0.99	2.49	3.323(3)	141.5	1 + *x*, *y*, *z*
C9–H9A···O3	0.99	2.42	3.360(3)	157.7	1 – *x*, 1 – *y*, 1 – *z*
C10–H10A···O3	0.98	2.41	3.283(6)	148.4	1 –*x*, 1 – *y*, –*z*
C10–H10C···O4	0.98	2.31	3.129(6)	140.9	1 – *x*, –½ + *y*, ½ – *z*

Table S14. Hydrogen bonds for **3**·3H_2O [Å and °]

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)	Symmetry transformation for acceptors
N3–H3A···O6	0.906(9)	1.884(10)	2.7783(17)	168.7(18)	*x*, *y*, 1 + *z*
N3–H3B···O15	0.912(9)	1.810(10)	2.7036(18)	165.9(18)	*x*, *y*, *z*
N4–H4···O13	0.979(9)	1.780(11)	2.7129(17)	158.1(16)	*x*, *y*, *z*
O14–H14*A*···O8	0.854(10)	1.949(10)	2.7954(16)	171(2)	*x*, *y*, –1 + *z*
O14–H14*B*···O11	0.851(10)	2.028(14)	2.8171(17)	154(2)	1 – *x*, 1 – *y*, 1 – *z*
O15–H15*C*···O10	0.862(9)	1.958(11)	2.7926(17)	163(2)	2 – *x*, 1 – *y*, 1 – *z*
O15–H15*D*···O12	0.852(9)	1.943(10)	2.7937(16)	176(2)	*x*, *y*, *z*
O13–H13*A*···O14	0.855(10)	1.860(11)	2.7016(18)	168(2)	*x*, *y*, *z*
O13–H13*B*···O2	0.852(10)	1.938(10)	2.7799(16)	169(2)	*x*, *y*, *z*
C5–H5···O1	0.95	2.52	3.2324(19)	132.4	–1 + *x*, *y*, *z*
C15–H15A···O11	0.99	2.55	3.1840(19)	121.7	1 – *x*, 1 – *y*, 1 – *z*
C15–H15B···O10	0.99	2.40	3.278(2)	148.2	–1 + *x*, *y*, *z*
C16–H16B···O9	0.99	2.53	3.4836(19)	162.8	1 – *x*, 1 – *y*, 1 – *z*
C17–H17A···O4	0.99	2.41	3.0862(19)	125.1	1 + *x*, *y*, 1 + *z*
C18–H18A···O4	0.99	2.48	3.4181(19)	158.2	–*x*, –*y*, –*z*
C18–H18B···O3	0.99	2.37	3.3041(19)	157.8	*x*, *y*, *z*
C19–H19B···O5	0.99	2.53	3.2898(19)	133.6	*x*, *y*, *z*

Table S15. Hydrogen bonds for **4**·H_2O [Å and °]

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)	Symmetry transformation for acceptors
N3–H3A···O10	0.901(10)	2.103(17)	2.838(2)	138(2)	*x*, *y*, *z*
N3–H3A···O13	0.901(10)	2.49(2)	3.111(3)	126.7(19)	–1 + *x*, 1 + *y*, *z*
N3–H3B···O1	0.899(10)	1.915(11)	2.799(2)	168(2)	*x*, *y*, *z*
N4–H4···O9	0.905(9)	2.050(14)	2.863(2)	149(2)	–1 + *x*, *y*, *z*
N4–H4···O12	0.905(9)	2.438(16)	3.174(2)	138.6(18)	–1 + *x*, *y*, *z*
O13–H13*A*···O8	0.865(10)	1.936(17)	2.748(2)	156(3)	*x*, *y*, *z*
O13–H13*B*···O2	0.858(10)	2.45(3)	3.063(2)	129(3)	1 + *x*, –1 + *y*, *z*
C3–H3···O6	0.95	2.24	3.053(2)	142.4	1 + *x*, *y*, *z*
C5–H5···O4	0.95	2.39	3.331(2)	170.0	–*x*, 3 – *y*, 1 – *z*
C10–H10···O13	0.95	2.40	3.293(3)	157.4	2 – *x*, –*y*, –*z*
C12–H12B···O11	0.95	2.38	3.298(3)	162.9	–1 + *x*, *y*, *z*
C15–H15A···O6	0.99	2.51	3.496(2)	175.0	*x*, *y*, *z*
C16–H16B···O5	0.99	2.37	3.360(2)	177.7	*x*, *y*, *z*
C17–H17B···O12	0.99	2.42	3.218(3)	137.7	–1 + *x*, *y*, *z*
C18–H18A···O11	0.99	2.36	3.317(2)	163.4	–1 + *x*, *y*, *z*
C18–H18B···O8	0.99	2.27	3.062(2)	136.4	–1 + *x*, 1 + *y*, *z*
C19–H19···O2	1.00	2.56	3.291(2)	129.7	–1 + *x*, *y*, *z*
C20–H20B···O4	0.98	2.45	3.434(3)	178.2	–1 – *x*, 2 – *y*, 1 – *z*

Table S16. Hydrogen bonds for **5**·H_2O [Å and °]

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)	Symmetry transformation for acceptors
N2–H2A···O7	0.916(12)	1.870(18)	2.766(5)	166(4)	*x*, *y*, *z*
N2–H2B···O1	0.911(12)	1.913(14)	2.820(5)	173(5)	–1 + *x*, –1 + *y*, –1 + *z*
O7–H7*A*···O5	0.867(12)	1.911(15)	2.771(4)	171(5)	*x*,–1+*y*, –1+*z*
O7–H7*B*···O4	0.868(12)	1.966(19)	2.815(5)	166(5)	*x*, *y*, –1 + *z*
C3–H3···O6	0.95	2.56	3.268(5)	131.3	*x*, *y*, –1 + *z*
C9–H9A···O2	0.99	2.38	3.191(6)	138.6	–1 + *x*, –1 + *y*, *z*
C10–H10B···O6	0.99	2.54	3.320(6)	135.8	–1 + *x*, *y*, –1 + *z*

Table S17. Hydrogen bonds for **6**·2,6-H_2pydc·2H_2O [Å and °]

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)	Symmetry transformation for acceptors
N3–H3A···O8	0.907(10)	2.016(14)	2.866(2)	156(2)	1 – *x*, 2 – *y*, 2 – *z*
N3–H3A···N2	0.907(10)	2.35(2)	2.967(2)	125.6(19)	1 – *x*, 2 – *y*, 2 – *z*
N3–H3B···O5	0.896(10)	2.344(19)	3.019(2)	132(2)	2 – *x*, 1 – *y*, 2 – *z*
N3–H3B···O9	0.896(10)	2.123(17)	2.885(2)	142(2)	1 – *x*, 2 – *y*, 2 – *z*
O7–H7···O12	0.838(17)	1.676(19)	2.497(2)	166(3)	*x*, *y*, *z*
O10–H10···O13	0.824(17)	1.768(18)	2.579(2)	168(3)	*x*, *y*, *z*
O11–H11A···O4	0.864(10)	1.916(11)	2.777(2)	174(3)	*x*, *y*, *z*
O11–H11B···O5	0.862(10)	1.946(13)	2.789(2)	166(3)	*x*, *y*, *z*
O12–H12A···O6	0.864(10)	2.141(14)	2.969(2)	160(3)	2 – *x*, –*y*, 2 – *z*

O12–H12B···O11	0.867(10)	1.834(10)	2.700(2)	177(3)	*x*, *y*, *z*
C3–H3···O7	0.95	2.47	3.399(2)	167.4	2 – *x*, –*y*, 1 – *z*
C4–H4···S1	0.95	2.85	3.597(2)	135.8	1 – *x*, 1 – *y*, 1 – *z*
C10–H10A···O2	0.95	2.40	3.254(2)	149.0	2 – *x*, –*y*, 1 – *z*
C15–H15A···O6	0.99	2.49	3.324(3)	141.8	1 – *x*, 1 – *y*, 2 – *z*
C16–H16B···O9	0.99	2.40	3.348(3)	161.2	*x*, *y*, *z*
C18–H18A···O2	0.99	2.40	3.152(2)	132.2	–1 + *x*, 2 + *y*, *z*
C18–H18A···O8	0.99	2.56	3.317(2)	133.3	*x*, 1 + *y*, *z*
C18–H18B···O8	0.99	2.53	3.319(3)	136.1	1 – *x*, 2 – *y*, 2 – *z*

Table S18. Hydrogen bonds for **7** [Å and °]

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)	Symmetry transformation for acceptors
O12–H12A···O14	0.834(17)	1.790(18)	2.603(2)	165(3)	*x*, *y*, *z*
O12–H12B···O21	0.849(17)	1.915(18)	2.743(2)	165(3)	1 – *x*, 1 – *y*, 1 – *z*
O18–H18A···O10	0.851(16)	1.786(17)	2.6179(19)	165(2)	*x*, *y*, *z*
O18–H18B···O4	0.836(16)	1.865(17)	2.6649(19)	160(2)	1 – *x*, 1 – *y*, 2 – *z*
N5–H5A···O16	0.898(10)	2.117(15)	2.924(2)	149(2)	–1 + *x*, –1 + *y*, *z*
N5–H5B···O8	0.909(10)	1.957(10)	2.864(2)	176(2)	*x*, *y*, *z*
N6–H6···O15	0.894(16)	2.009(17)	2.881(2)	165(2)	*x*, –1 + *y*, *z*
C3–H3···O6	0.95	2.58	3.321(2)	135.5	–1 + *x*, *y*, *z*
C10–H10···O11	0.95	2.13	3.077(2)	176.8	–1 + *x*, *y*, *z*
C12–H12···O4	0.95	2.31	3.212(2)	157.7	–*x*, 1 – *y*, 2 – *z*
C17–H17···O21	0.95	2.34	3.207(2)	150.8	2 – *x*, 1 – *y*, 1 – *z*
C19–H19···O17	0.95	2.32	3.191(2)	151.8	1 + *x*, *y*, *z*
C24–H24···O14	0.95	2.49	3.348(2)	151.0	2 – *x*, 1 – *y*, 1 – *z*
C26–H26···O24	0.95	2.46	3.300(2)	146.9	1 + *x*, *y*, *z*
C29–H29A···O24	0.99	2.41	3.120(2)	128.5	1 – *x*, 1 – *y*, 1 – *z*
C29–H29B···O19	0.99	2.39	3.264(2)	146.7	*x*, –1 + *y*, *z*
C30–H30A···O22	0.99	2.36	3.233(2)	146.4	*x*, –1 + *y*, *z*
C30–H30B···O7	0.99	2.46	3.338(2)	148.0	*x*, *y*, *z*
C31–H31A···O17	0.99	2.34	3.271(2)	156.5	*x*, –1 + *y*, *z*
C31–H31B···O2	0.99	2.44	3.320(2)	148.3	*x*, *y*, *z*
C32–H32A···O1	0.99	2.39	3.015(2)	120.3	*x*, *y*, *z*
C32–H32A···O7	0.99	2.54	3.395(2)	144.6	*x*, *y*, *z*
C32–H32B···O5	0.99	2.24	3.172(2)	155.9	1 – *x*, –*y*, 2 – *z*
C33–H33B···O2	0.98	2.49	3.250(2)	134.5	1 + *x*, *y*, *z*
C33–H33C···O11	0.98	2.30	3.274(3)	170.1	*x*, *y*, *z*

Table S19. Hydrogen bonds for **8** [Å and °]

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)	Symmetry transformation for acceptors
N1–H1A···O1	0.906(10)	1.895(12)	2.783(2)	166(2)	*x*, *y*, *z*
N1–H1B···O2	0.895(10)	1.999(10)	2.888(2)	172(2)	½ – *x*, ½ + *y*, *z*
C1–H1D···O3	0.99	2.48	3.461(3)	171.9	3/2 – *x*, ½ + *y*, *z*
C4–H4A···O1	0.99	2.48	3.274(3)	136.4	–1 + *x*, *y*, *z*
C4–H4A···O1	0.99	2.41	3.189(3)	135.0	–½ +*x*, *y*, ½ – *z*
C4–H4B···O3	0.99	2.41	3.140(3)	129.8	½ – *x*, ½ + *y*, *z*

Table S20. Hydrogen bonds for **9**·6H_2O [Å and °].

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)	Symmetry transformation for acceptors
N1–H1A···O9	0.897(16)	2.052(17)	2.913(2)	161(2)	–*x*, 1 – *y*, 1 – *z*
N1–H1B···O1	0.889(16)	1.923(17)	2.783(2)	162(2)	*x*, *y*, *z*
N2–H2C···O15	0.904(16)	1.894(18)	2.727(2)	152(2)	*x*, *y*, *z*
N2–H2D···O4	0.880(16)	2.31(2)	2.918(2)	126.4(19)	1 – *x*, –*y*, 1 – *z*
N2–H2D···O11	0.880(16)	2.207(18)	2.985(2)	147(2)	1 – *x*, –*y*, 1 – *z*
N2–H2D···O12	0.880(16)	2.42(2)	3.144(2)	140(2)	1 – *x*, –*y*, 1 – *z*
N3–H3C···O6	0.884(16)	1.899(16)	2.772(2)	169(2)	1 – *x*, 1 – *y*, –*z*
N3–H3D···O3	0.911(16)	1.770(16)	2.680(2)	176(2)	*x*, *y*, *z*
O15–H15*A*···O11	0.858(10)	1.871(10)	2.727(2)	176(3)	*x*, *y*, *z*
O15–H15*B*···O16	0.866(10)	1.862(11)	2.722(3)	172(3)	*x*, *y*, *z*
O16–H16*A*···O17	0.867(10)	1.955(11)	2.817(3)	173(3)	1 + *x*, –1 + *y*, *z*
O16–H16B···O5	0.862(10)	2.31(3)	2.993(2)	136(3)	1 + *x*,–1 + *y*, *z*
O16–H16B···O13	0.862(10)	2.39(3)	3.080(2)	137(3)	1 – *x*, –*y*, 1 – *z*
O17–H17A···S2	0.859(10)	2.536(13)	3.3725(17)	165(3)	*x*, 1 + *y*, *z*
O17–H17B···O2	0.857(10)	1.898(10)	2.752(2)	174(3)	*x*, *y*, *z*
C1–H1C···O10	0.99	2.48	3.275(2)	136.5	–*x*, 1 – *y*, 1 – *z*
C2–H2B···O3	0.99	2.51	3.470(2)	161.9	1 – *x*, 1 – *y*, 1 – *z*
C4–H4B···O2	0.99	2.46	3.261(2)	137.7	–*x*, 1 – *y*, 1 – *z*
C6–H6A···O13	0.99	2.27	3.251(2)	171.8	*x*, *y*, *z*
C6–H6A···O7	0.99	2.37	3.212(2)	141.9	–1 + *x*, *y*, *z*
C8–H8A···S3	0.99	2.79	3.713(2)	155.6	1 – *x*, –*y*, –*z*
C12–H12A···O17	0.99	2.46	3.385(3)	156.4	1 + *x*, –1 + *y*, *z*

Table S21. Hydrogen bonds for **10**·2H_2O [Å and °]

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)	Symmetry transformation for acceptors
N3–H3A···N2	0.900(9)	2.191(10)	3.0861(19)	173.0(19)	*x*, *y*, *z*
N3–H3B···O3	0.912(9)	2.070(11)	2.9594(19)	164.9(18)	*x*, *y*, *z*
O1–H1···O9	0.840(10)	1.885(13)	2.6801(17)	157(2)	*x*, *y*, *z*
O5–H4···O4	1.01(3)	1.44(3)	2.4482(17)	174(2)	*x*, *y*, *z*
O8–H8···O10	0.844(10)	1.747(11)	2.5796(17)	168(2)	*x*, *y*, *z*
O9–H9A···O2	0.840(15)	1.990(17)	2.8035(17)	163(2)	½ – *x*, ½ + *y*, 3/2 – *z*
O9–H9*B*···O3	0.871(15)	1.983(16)	2.8403(16)	168(2)	*x*, *y*, *z*
O10–H10*A*···O9	0.866(16)	1.875(16)	2.7382(18)	174(2)	3/2 – *x*, ½ + *y*, 3/2 – *z*
O10–H10*B*···O6	0.865(16)	2.078(17)	2.8947(17)	157(2)	½ + *x*, 3/2 – *y*, ½ + *z*
C5–H5···S1	0.95	2.86	3.5764(17)	133.4	–½ +*x*, 3/2 – *y*,–½ + *z*
C10–H10···O1	0.95	2.44	3.148(2)	131.5	½ + *x*, 3/2 – *y*, –½ + *z*
C15–H15A···O7	0.99	2.42	3.130(2)	128.3	*x*, *y*, *z*
C15–H15B···O4	0.99	2.34	3.333(2)	176.6	1 – *x*, 1 – *y*, 1 – *z*
C18–H18A···O4	0.99	2.53	3.422(2)	150.5	1 – *x*, 2 – *y*, 1 – *z*
C18–H18B···O7	0.99	2.57	3.250(2)	125.6	*x*, *y*, *z*

Table S22. Geometrical parameters (Å, °) for π···π stacking interactions in **s**tructures **5**·H_2O, **7** and **10**·2H_2O.

*Cg*I···*Cg*J	*Cg*I···*Cg*J distance	α	β ,γ	*Cg*I-Perp (offset distance)	Ring slippage	Symmetry transformation for acceptors
5·H_2O						
*Cg*3···*Cg*5	3.590(3)	4.3(2)	17.0, 13.5	3.4912(17)	1.051	*x*, *y*, *z*
*Cg*3···*Cg*5	3.651(3)	4.3(2)	23.2, 26.3	3.2729(17)	1.437	1 + *x*, *y*, *z*
*Cg*3 and *Cg*5 are N1/C2–C6 and C12–C17 ring centroids, respectively						
7						
*Cg*5···*Cg*6	3.6516(10)	1.87(9)	22.9, 21.8	3.3903(7)	1.418	*x*, *y*, *z*
*Cg*6···*Cg*11	4.0992(11)	7.72(9)	33.0, 28.7	3.5965(7)	2.231	–1 + *x*, *y*, *z*
*Cg*11···*Cg*12	3.7133(11)	5.64(9)	17.0, 22.4	3.4340(8)	1.087	*x*, *y*, *z*
*Cg*5, *Cg*6, *Cg*11 and *Cg*12 are N1/C2–C6, N2/C9–C13, N3/C16–C20 and N4/C23–C27 ring centroids, respectively						
10·2H_2O						
*Cg*1···*Cg*2	3.6492(8)	2.69(7)	20.9, 18.6	3.4589(6)	1.303	1 – *x*, 1 – *y*, 1 – *z*
*Cg*1···*Cg*2	3.5617(8)	2.69(7)	18.4, 18.5	3.3773(6)	1.124	1 – *x*, 2 – *y*, 1 – *z*
*Cg*1 and *Cg*2 are N1/C2–C6 and N2/C9–C13 ring centroids, respectively						

CgI···CgJ, α, β, γ and CgI-Perp are the centroid-to-centroid distance between rings I and J (Å), the inter-ring dihedral angle (°), slip angles (°), and the perpendicular distance of CgI from ring J (Å) , respectively. Ring slippage is in Å.

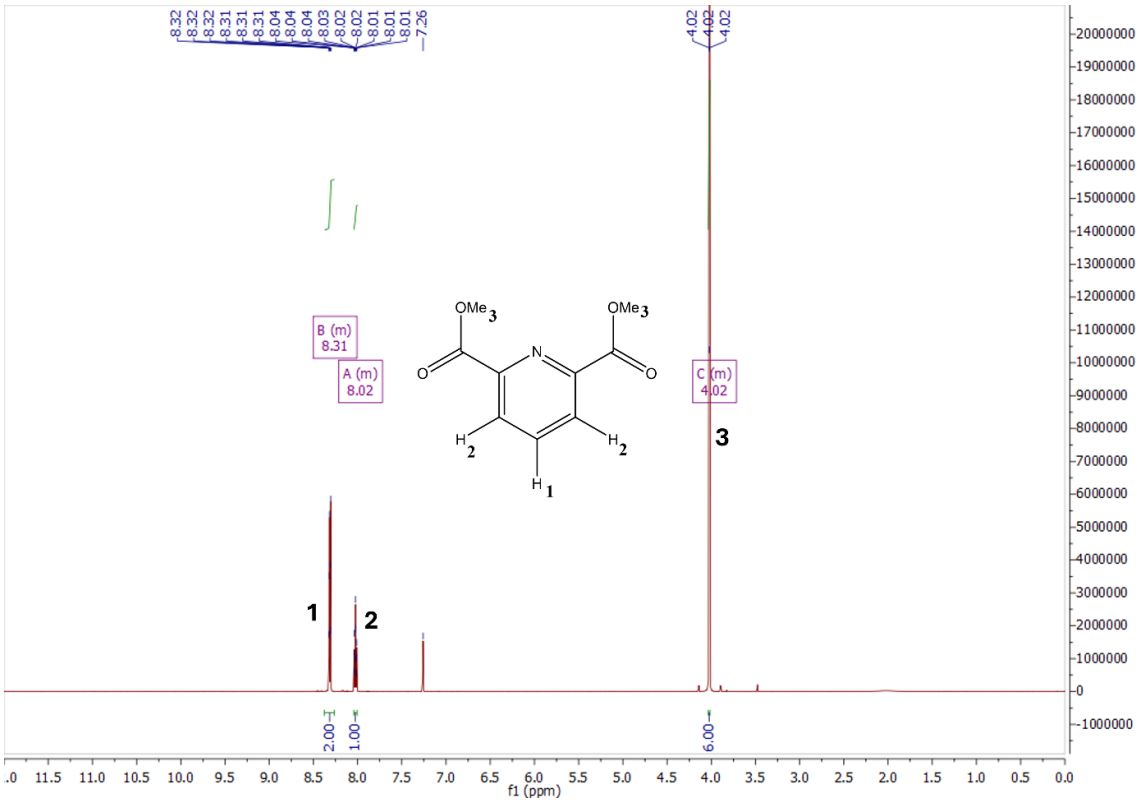


Figure S20. ^{1}H NMR of **b** in $CDCl_3$.

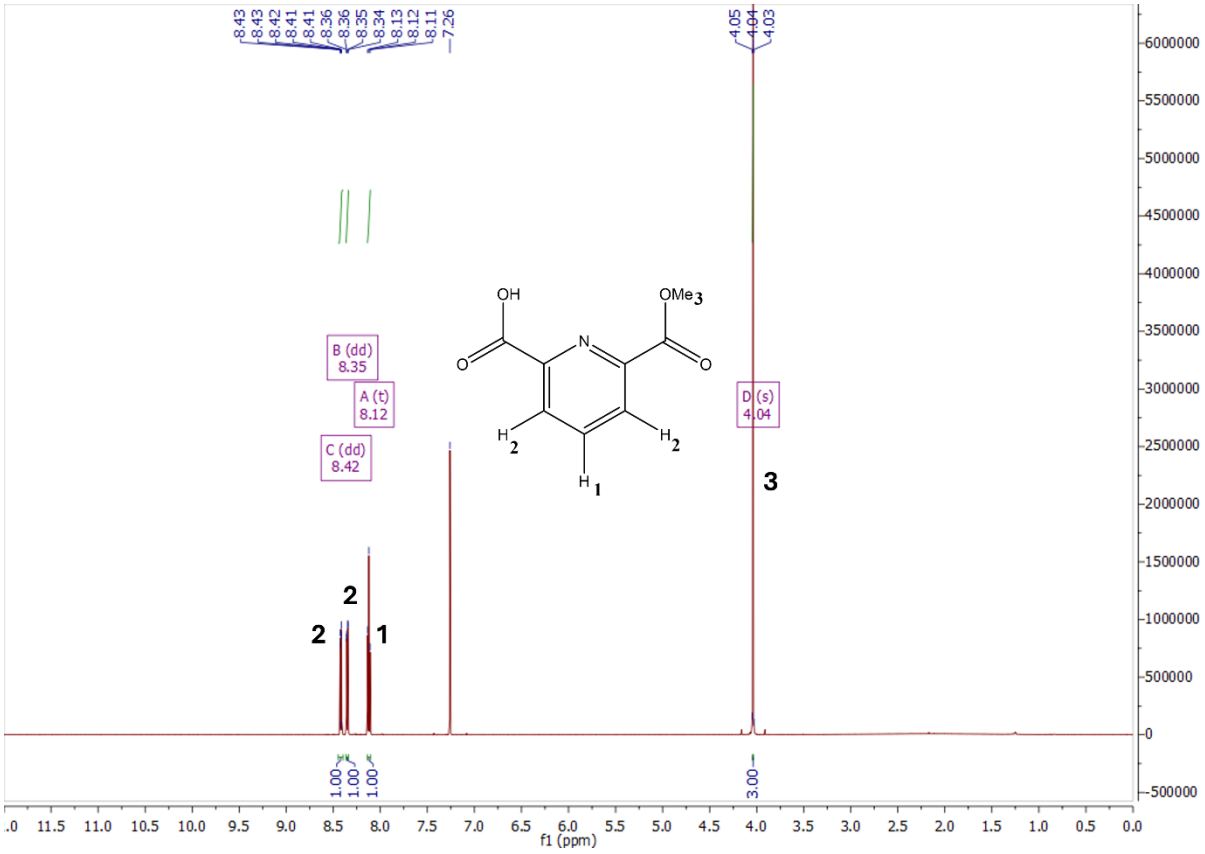


Figure S21. ^{1}H NMR of **c** in $CDCl_3$.

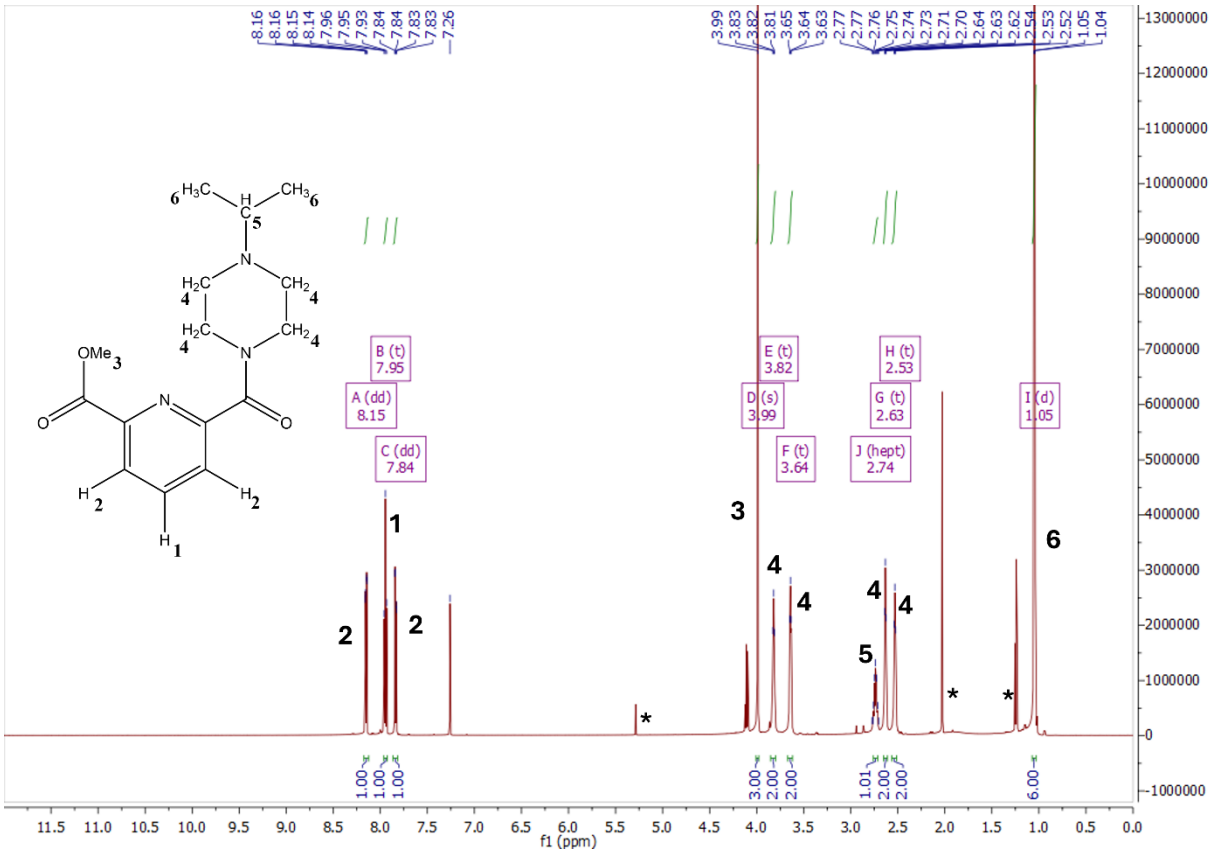


Figure S22. ^{1}H NMR of **d1** in $CDCl_3$.

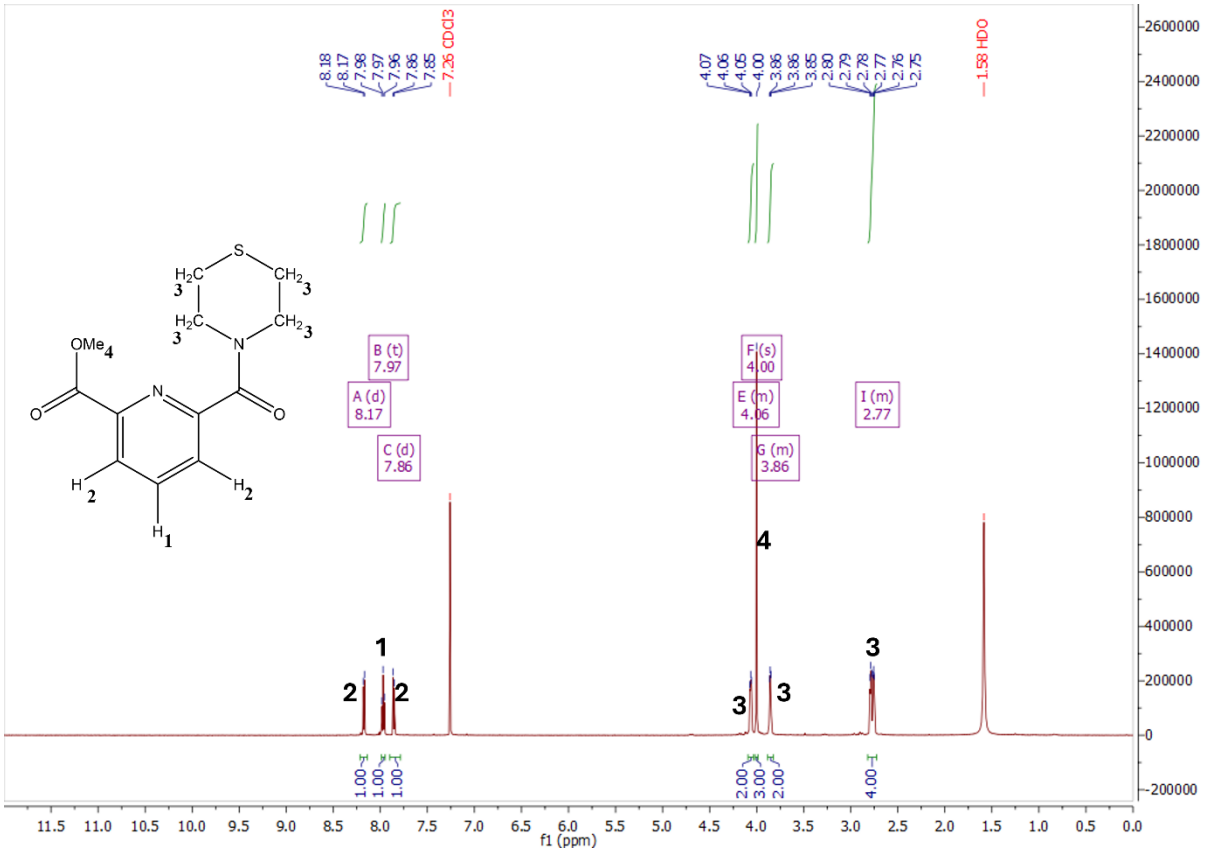


Figure S23. ^{1}H NMR of **d2** in $CDCl_3$.

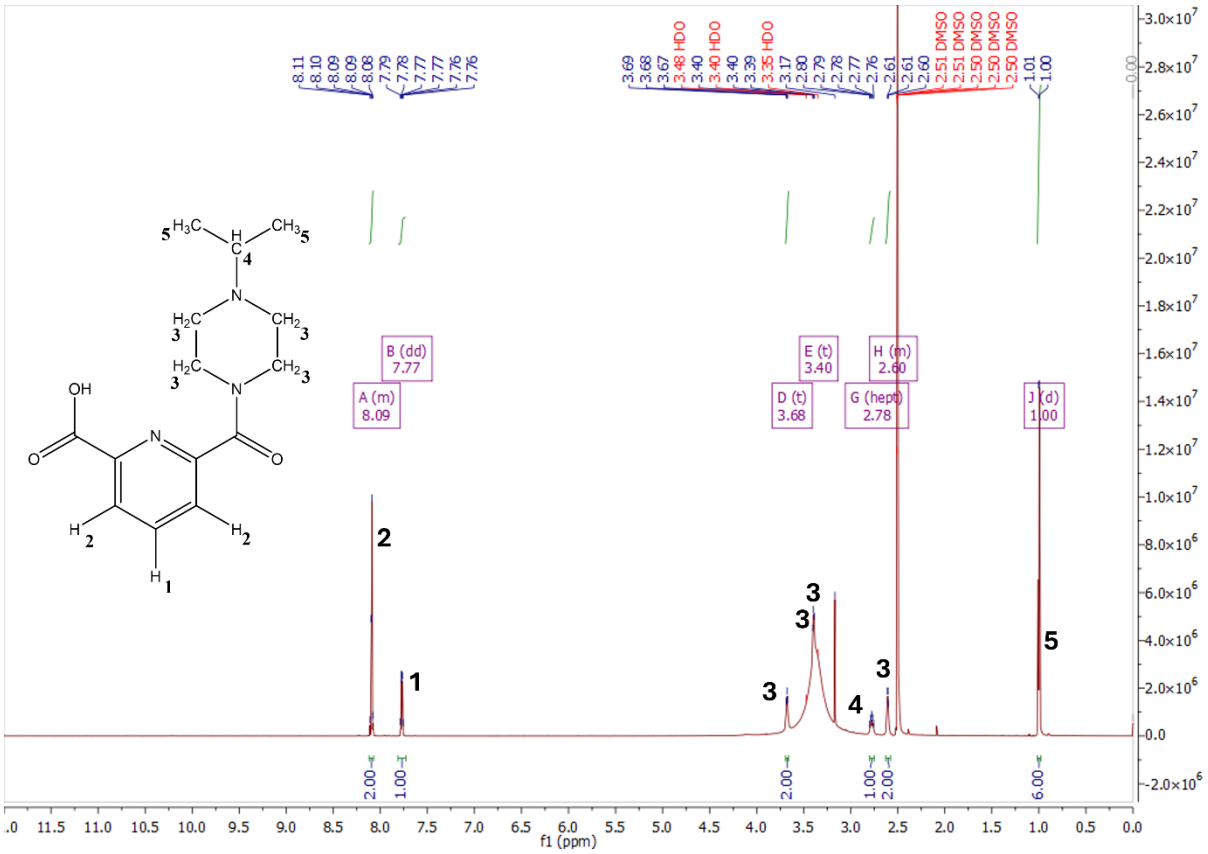


Figure S24. ^{1}H NMR of **e1** in DMSO-d_6.

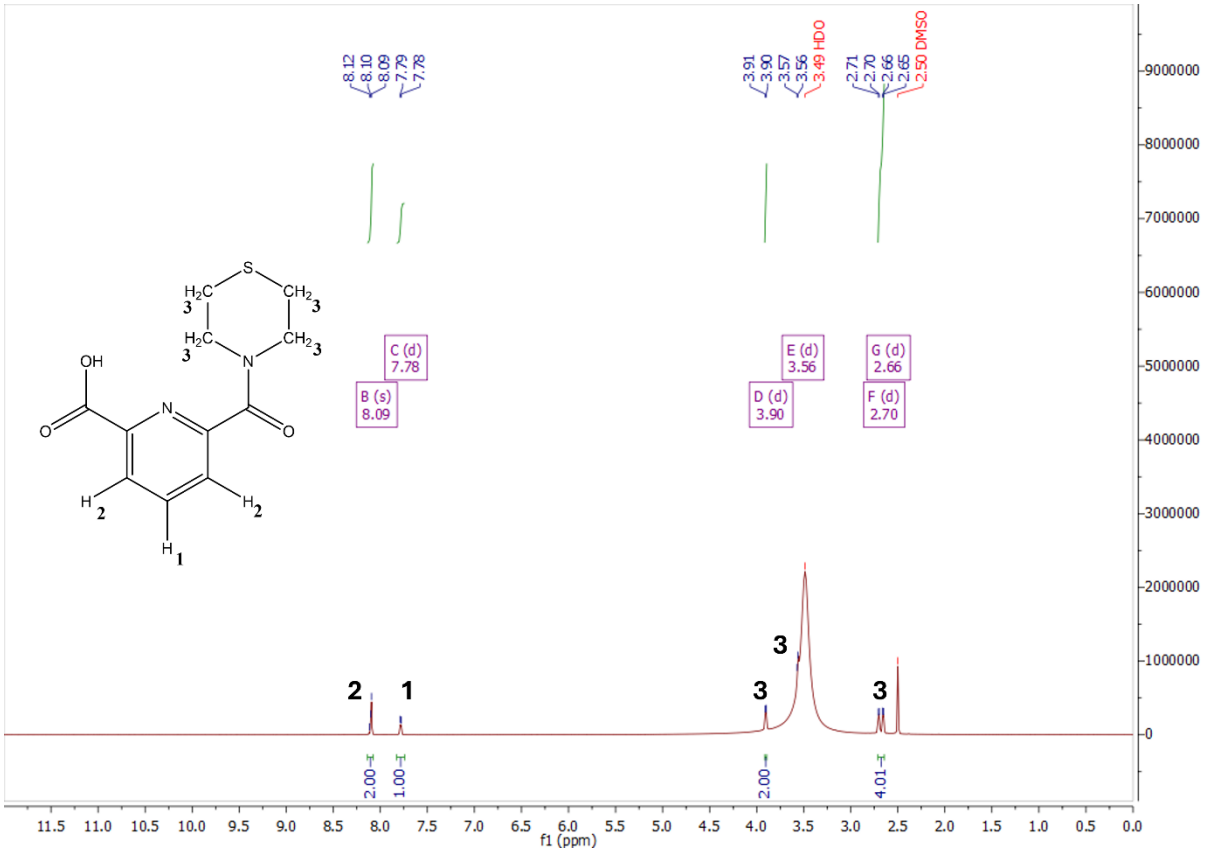


Figure S25. ^{1}H NMR of **e2** in DMSO-d_6.

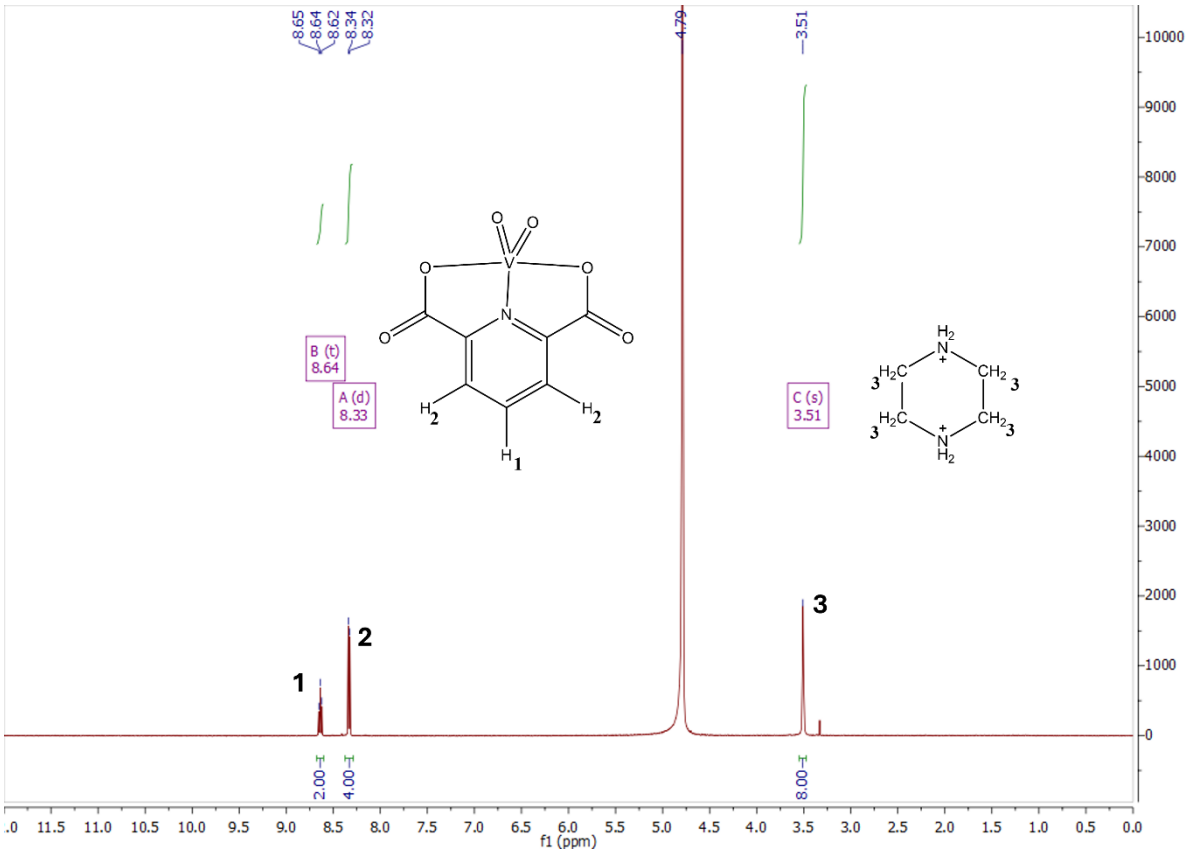


Figure S26. ^{1}H NMR spectra of **1**·6H_2O in D_2O.

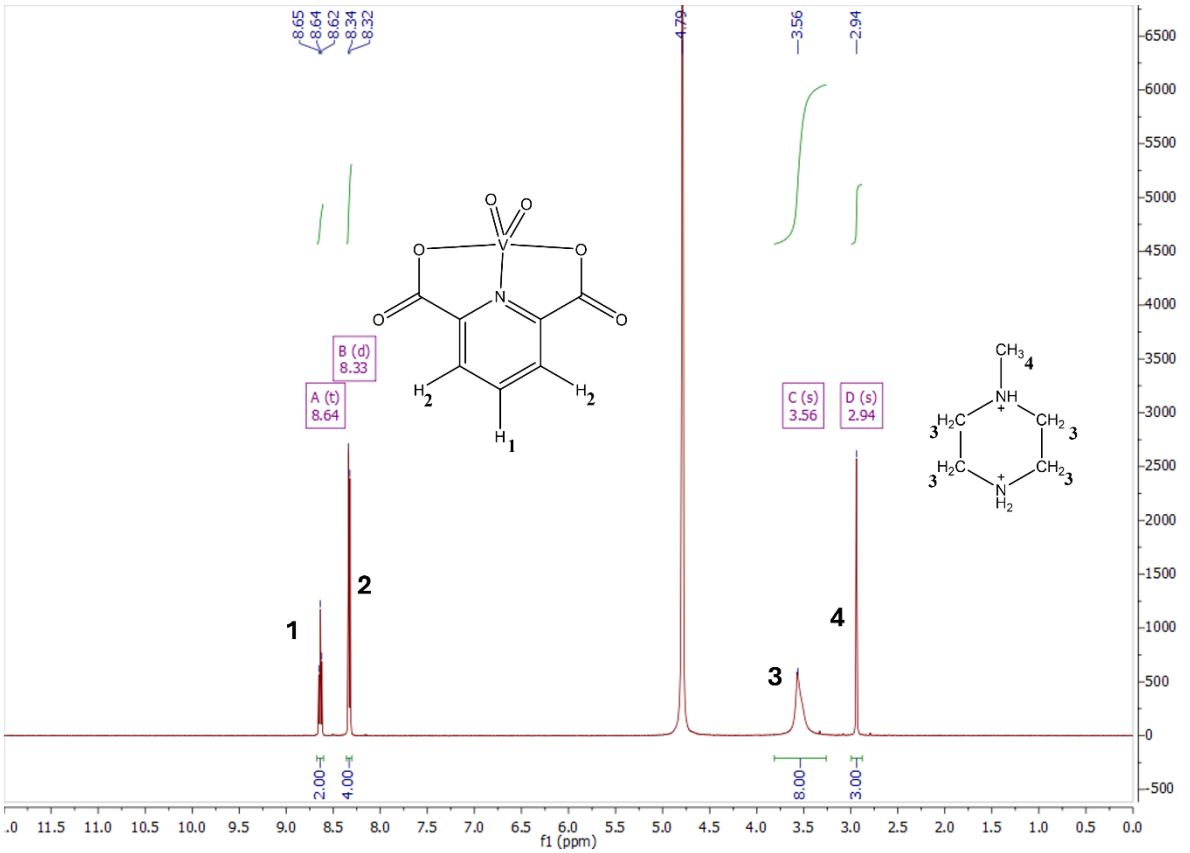


Figure S27. ^{1}H NMR of **2**·5H_2O in D_2O.

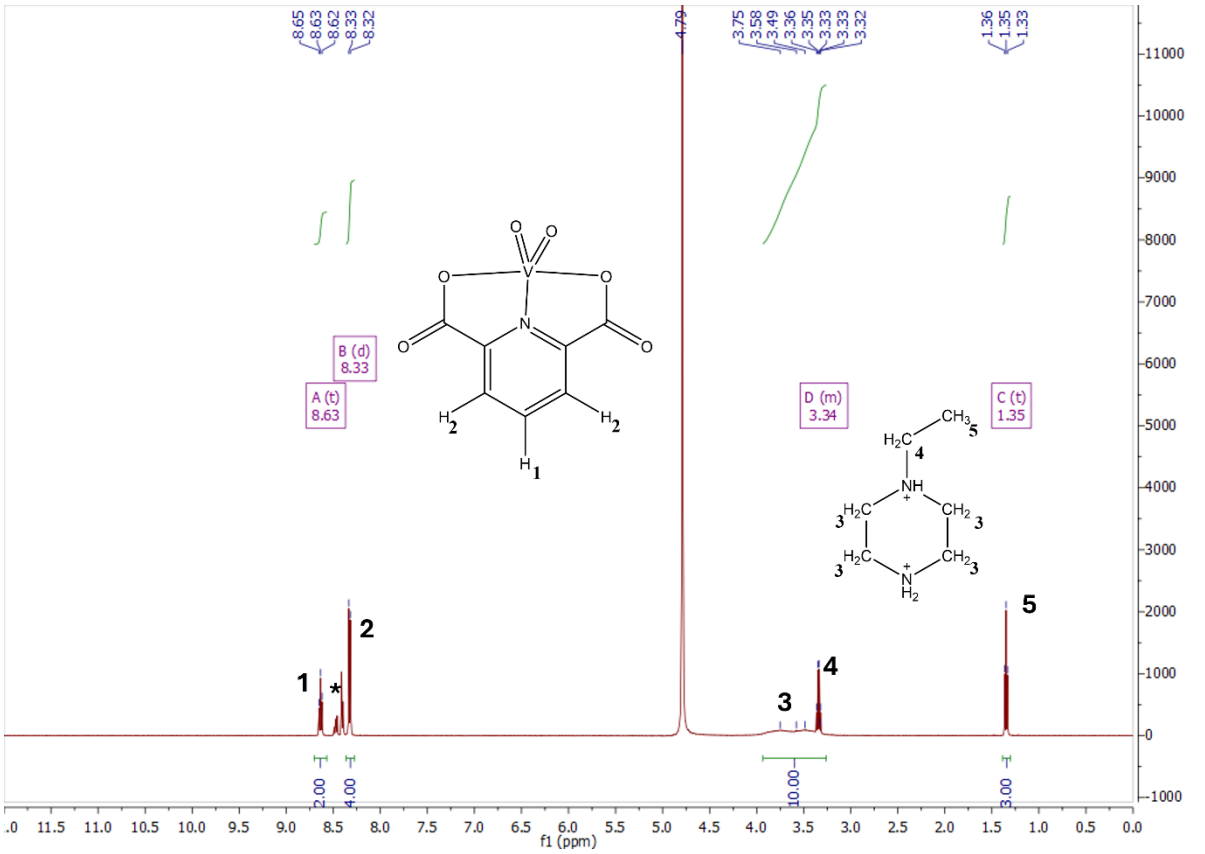


Figure S28. ^{1}H NMR of **3**·3H_2O in D_2O.

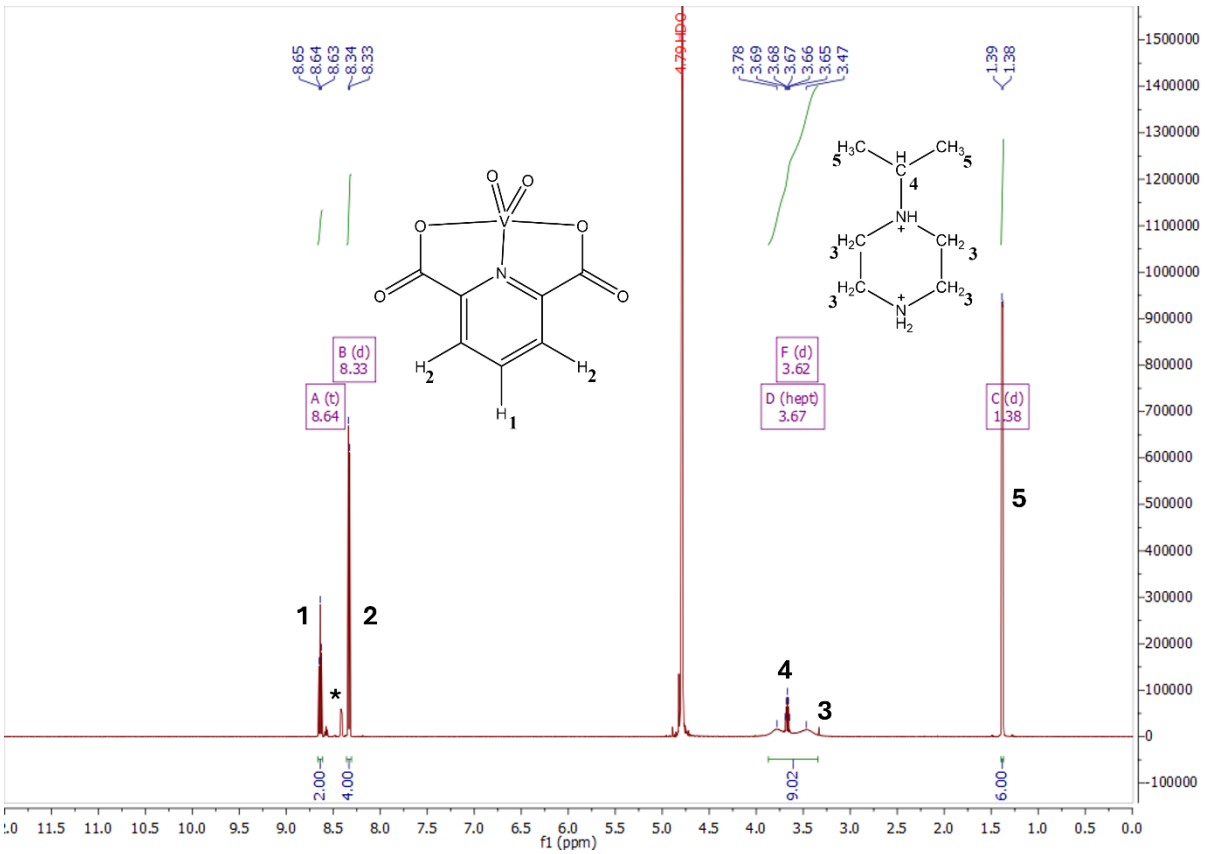


Figure S29. ^{1}H NMR of **4**·H_2O in D_2O.

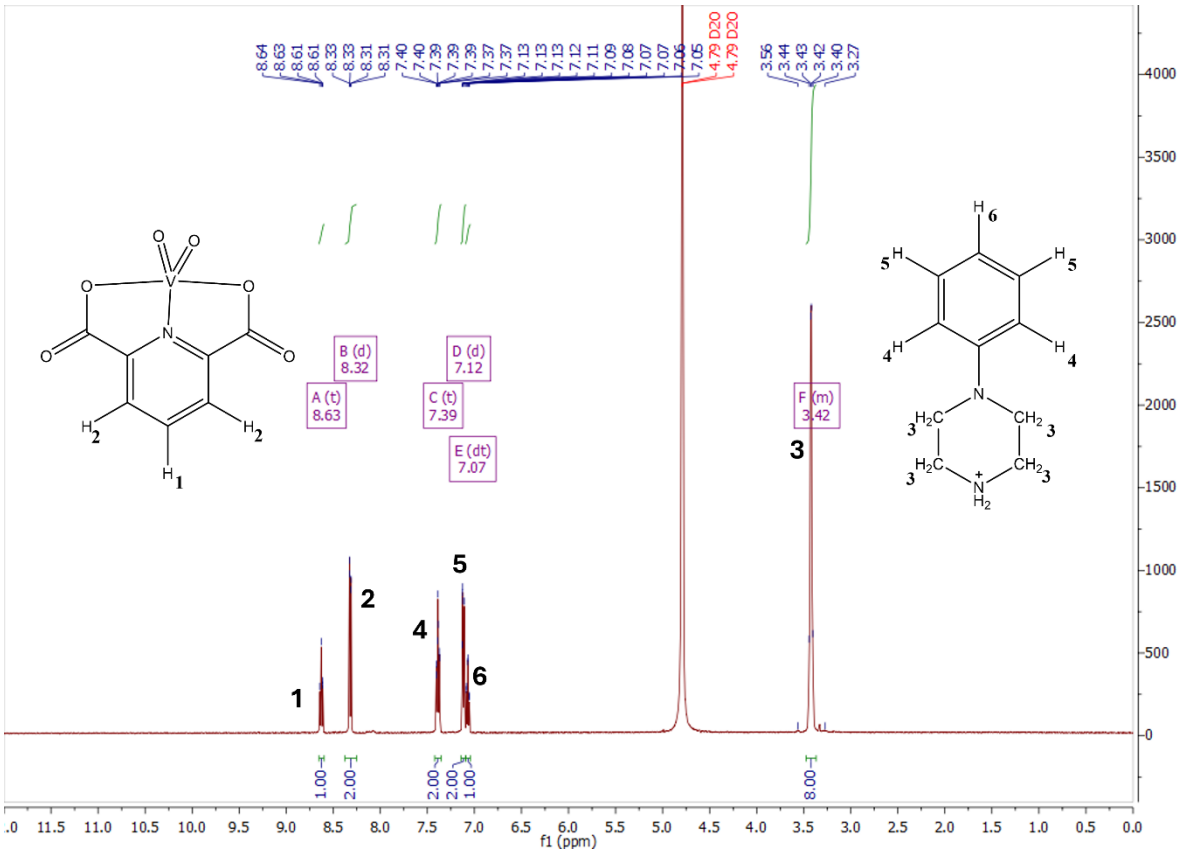


Figure S30. ^{1}H NMR of **5**·H_2O in D_2O.