Electronic Supplementary Information (ESI)

New Journal of Chemistry

Vanadium and zinc complexes of 5-cyanopicolinate and pyrazine derivatives: synthesis, structural elucidation and *in vitro* insulino-mimetic activity study

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Supplementary material

Crystallographic data: **Figs. S1–S8 and Tables S1–S10**

Table S1: Selected crystallographic data for $NH_4[VO_2(picCN)_2]$ (**3**), $NH_4[VO_2(prz)_2]$ (**4**), $NH_4[VO_2(przNH_2)_2]\cdot H_2O$ (**5**$\cdot H_2O$), $[Zn(picCN)_2(H_2O)_2]$ (**6**), $[Zn(picCN)_2(4apy)_2]\cdot C_7H_8$ (**7**$\cdot C_7H_8$), $[Zn(picCN)_2(4apy)]$ (**8**), $[Zn(picCN)_2(py)_2]$ (**9**) in $[Zn(picCN)_2(phen)]\cdot C_7H_8\cdot$2MeOH (**10**$\cdot C_7H_8\cdot$2MeOH).

	3	**4**	**5**$\cdot H_2O$	**6**	**7**$\cdot C_7H_8$	**8**	**9**	**10**$\cdot C_7H_8\cdot$2MeOH
Formula	$C_{14}H_{10}N_5O_6V$	$C_{10}H_{10}N_5O_6V$	$C_{10}H_14N_7O_7V$	$C_{14}H_{10}N_4O_6Zn$	$C_{31}H_{26}N_8O4Zn$	$C_{19}H_{12}N_6O_4Zn$	$C_{24}H_{16}N_6O_4Zn$	$C_{35}H_{30}N_6O_6Zn$
M_r	395.21	347.17	395.22	395.63	639.97	453.72	517.80	696.02
T (K)	293(2)	293(2)	150(2)	150(2)	293(2)	150(2)	293(2)	150(2)
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	P–1	$P2_1/c$	P–1	P–1	$P2_1/c$	$Pna2_1$	$P2_1/c$
a (Å)	13.9268(3)	7.89910(10)	9.2182(2)	5.0190(4)	10.5093(2)	10.13000(10)	19.2608(4)	13.0350(3)
b (Å)	8.7933(2)	8.15860(10)	11.9215(3)	6.4793(4)	11.7016(2)	11.4236(2)	7.14690(10)	29.0574(7)
c (Å)	13.3931(3)	12.3149(2)	14.0719(3)	12.6014(6)	12.5825(2)	17.9233(3)	17.3723(4)	20.4786(5)
α (°)	90.00	74.5170(10)	90.00	91.545(4)	81.1590(10)	90.00	90.00	90.00
β (°)	97.667(2)	85.1740(10)	98.587(2)	99.276(5)	86.7830(10)	114.1460(10)	90.00	118.529(2)
γ (°)	90.00	64.5960(10)	90.00	110.230(6)	72.6540(10)	90.00	90.00	90.00
Volume (Å^3)	1625.49(6)	690.463(18)	1529.09(6)	377.97(4)	1459.34(4)	1892.63(5)	2391.38(8)	6814.7(3)
Z	4	2	4	1	2	4	4	8
D_c (g/cm^3)	1.615	1.670	1.717	1.738	1.456	1.592	1.438	1.357
μ (mm^{-1})	0.655	0.757	0.703	1.667	0.893	2.168	1.069	0.774
Reflections collected	9720	5540	10701	3548	12042	11961	20962	62321
Reflections unique (R_{int})	3722 (0.0240)	3118 (0.0139)	3493 (0.0289)	1742 (0.0337)	6609 (0.0122)	3880 (0.0239)	5465 (0.0322)	15622 (0.0334)
Parameters	251	211	244	123	398	271	316	888
Flack parameter	-	-	-	-	-	-	–0.004(11)	-
R, wR_2 [I>2σ(I)][a]	0.0333, 0.0873	0.0264, 0.0740	0.0322, 0.0849	0.0365, 0.0667	0.0434, 0.1202	0.0279, 0.0688	0.0342, 0.0788	0.0585, 0.1756
R, wR_2 (all data)[b]	0.0437, 0.0932	0.0289, 0.0758	0.0375, 0.0885	0.0430, 0.0706	0.0486, 0.1271	0.0334, 0.0729	0.0458, 0.0849	0.0994, 0.2059
GOF, S[c]	1.044	1.037, 1.036	1.075, 1.074	1.151, 1.152	1.026	1.060	1.045	1.072, 1.074

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] $S = \{\sum[(F_o^2 - F_c^2)^2]/(n/p)\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined.

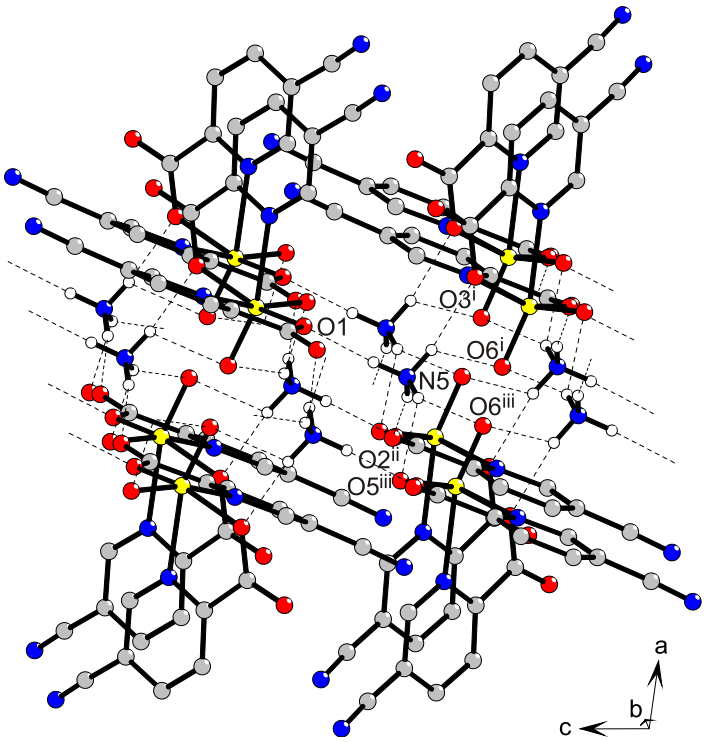

Figure S1: Formation of hydrogen-bonded double layer in **3**, which is parallel to the *ac* plane. Dashed lines indicate N–H···O bonds. Symmetry codes: (i) *–x, −y* + 1½, *z* − ½; (ii) *−x, y* + ½, *−z* + ½; (iii) *−x, y* − ½, *−z* + ½.

Table S2: Hydrogen bonds and other weak intermolecular interactions in **3**.

D–H···*A*	d(*D*–H)	d(H···*A*)	d(*D*···*A*)	<(*DHA*)	Symmetry transformation of the acceptor
N5–H5*A*···O1	0.91(2)	1.93(2)	2.834(2)	175(3)	*x, y, z*
N5–H5*B*···O3	0.90(2)	2.13(2)	3.007(2)	165(3)	*x, −y* + 1½, *z* − ½
N5–H5*B*···O6	0.90(2)	2.47(3)	2.922(2)	111(2)	*x, −y* + 1½, *z* − ½
N5–H5*C*···O2	0.90(2)	2.00(2)	2.877(3)	168(2)	*−x, y* + ½, *−z* + ½
N5–H5*D*···O5	0.89(2)	2.19(2)	2.901(2)	136(3)	*−x, y* − ½, *−z* + ½
N5–H5*D*···O6	0.89(2)	2.35(2)	3.168(2)	153(3)	*−x, y* − ½, *−z* + ½
C4–H4···O4	0.93	2.37	3.096(2)	134	*x, y* – 1, *z*
C6–H6···O5	0.93	2.56	3.085(2)	116	*x, −y* + 1½, *z* + ½
C13–H13···O4	0.93	2.53	3.189(2)	129	*x, −y* + 1½, *z* − ½

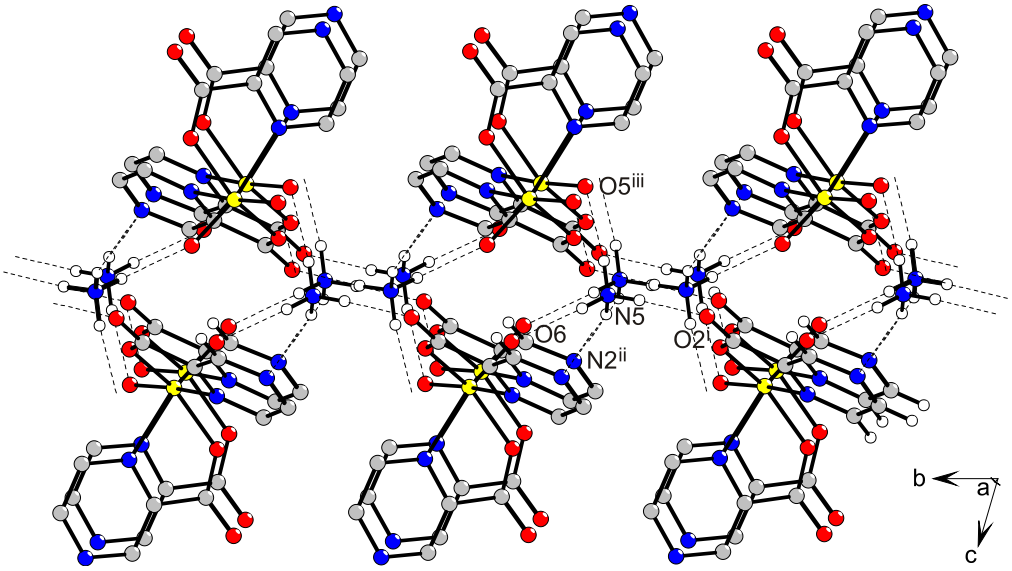

Figure S2: Formation of hydrogen-bonded double layer in **4** parallel to the *ab* plane. Dashed lines indicate N–H···O/N bonds. Symmetry codes: (i) $x, y-1, z$; (ii) $x-1, y, z$; (iii) $-x, -y+1, -z+1$.

Table S3: Hydrogen bonds and other weak intermolecular interactions in **4**.

D–H···*A*	d(*D*–H)	d(H···*A*)	d(*D*···*A*)	<(*DHA*)	Symmetry transformation of the acceptor
N5–H5A···O2	0.90(2)	1.94(2)	2.8380(17)	176(2)	$x, y-1, z$
N5–H5B···O6	0.90(2)	1.98(2)	2.7969(17)	150(3)	x, y, z
N5–H5C···N2	0.89(2)	2.19(2)	3.0448(19)	160(2)	$x-1, y, z$
N5–H5D···O5	0.89(2)	1.99(2)	2.8682(18)	172(2)	$-x, -y+1, -z+1$
C3–H3···O6	0.93	2.49	3.2443(19)	138	$-x+1, -y+1, -z+1$
C3–H3···O5	0.93	2.42	3.1849(19)	139	$x+1, y-1, z$
C8–H8···O5	0.93	2.56	3.322(2)	140	$-x, -y+1, -z+2$
C9–H9···O4	0.93	2.44	3.353(3)	167	$x, y+1, z$

Table S4: Geometrical parameters (Å, °) for π···π stacking interactions in **4**.

*Cg*I···*Cg*J	*Cg*I···*Cg*J	*α*	*β*	*Cg*I-Perp	Symmetry transformation of the acceptor
*Cg*4···*Cg*4	3.6544(11)	0	15.77	–3.5169(8)	$-x+1, -y+1, -z+2$

C*g*I···C*g*J, α, β and C*g*I-Perp are, respectively, the centroid-to-centroid distance between rings I and J, the inter-ring dihedral angle, slip angle and the perpendicular distance of C*g*I from ring C*g*J. *Cg*4 is N3/C7/C8/N4/C9/C10 ring centroid.

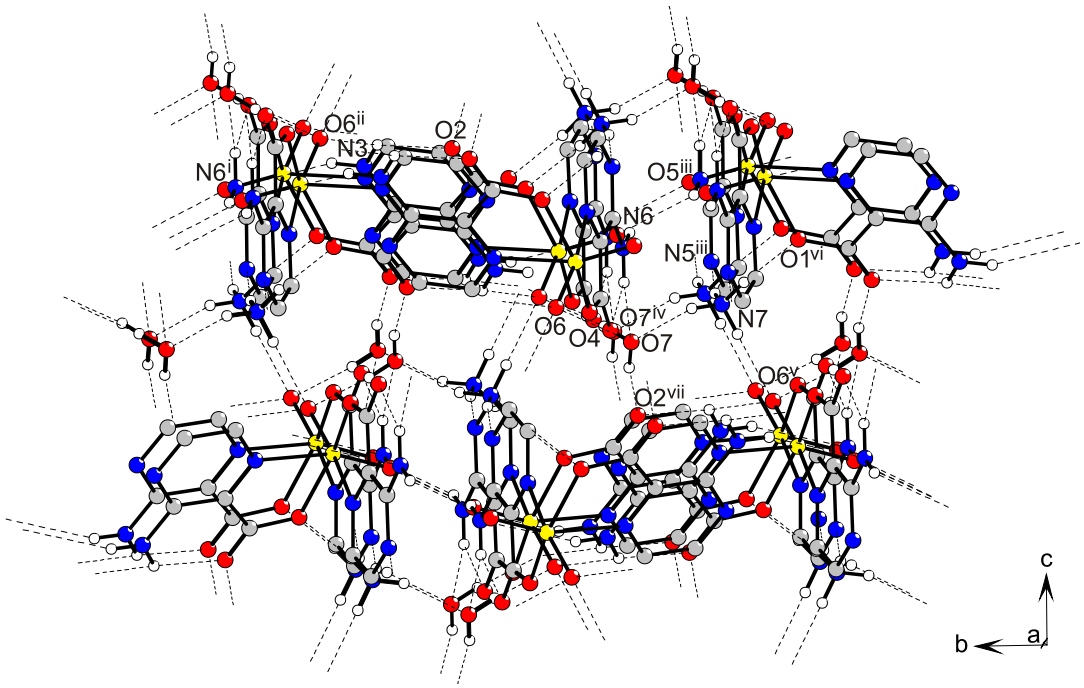

Figure S3: The network of hydrogen bonds formed in **5**·H_2O. Dashed lines indicate N–H···O and O–H···O hydrogen bonds. Symmetry codes: (i) −*x* + 2, −*y* + 2, −*z* + 2; (ii) −*x* + 1, −*y* + 2, −*z* + 2; (iii) −*x* + 2, −*y* + 1, −*z* + 2: (iv) *x* + 1, *y*, *z*; (v) −*x* + 1, *y* – ½, −*z* + 1½; (vi) −*x* + 1, −*y* + 1, −*z* + 2; (vii) *x*, −*y* + 1½, *z* − ½.

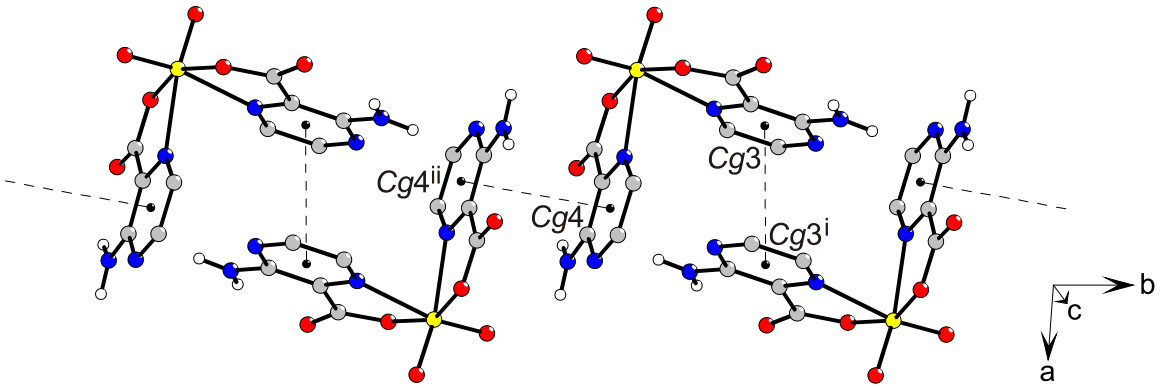

Figure S4: A chain of $[VO_2(przNH_2)_2]^-$ anions part of the **5**·H_2O crystal structure, connected by π···π stacking interactions. Dashed lines indicate centroid-to-centroid distances. Symmetry codes: (i) −*x* + 2, −*y* + 2, −*z* + 2; (ii) −*x* + 2, −*y* + 1, −*z* + 2.

Table S5: Hydrogen bonds and other weak intermolecular interactions in **5**·H_2O.

D–H···*A*	d(*D*–H)	d(H···*A*)	d(*D*···*A*)	<(*D*H*A*)	Symmetry transformation of the acceptor
N3–H3A···N6	0.88	2.53	3.352(2)	156	−*x* + 2, −*y* + 2, −*z* + 2
N3–H3B···O2	0.88	2.16	2.789(2)	128	*x*, *y*, *z*
N3–H3B···O6	0.88	2.44	2.877(2)	112	−*x* + 1, −*y* + 2, −*z* + 2
N6–H6A···O5	0.88	2.35	2.978(2)	129	−*x* + 2, −*y* + 1, −*z* + 2
N6–H6B···O4	0.88	2.09	2.737(2)	130	*x*, *y*, *z*
N6–H6B···O7	0.88	2.48	3.060(2)	124	*x* + 1, *y*, *z*
N7–H71N···O6	0.87(1)	1.95(1)	2.821(2)	178(2)	−*x* + 1, *y* – ½, −*z* + 1½
N7–H73N···N5	0.88(1)	2.09(1)	2.966(2)	170(2)	−*x* + 2, −*y* + 1, −*z* + 2
N7–H72N···O7	0.87(1)	1.98(1)	2.819(2)	161(2)	*x*, *y*, *z*
N7–H74N···O1	0.89(1)	2.02(1)	2.901(2)	174(2)	−*x* + 1, −*y* + 1, −*z* + 2
O7–H75O···O6	0.84(1)	1.98(1)	2.8079(18)	171(2)	*x*, *y*, *z*
O7–H76O···O2	0.84(1)	2.01(1)	2.8229(18)	163(2)	*x*, −*y* + 1½, *z* − ½
C4–H4···O4	0.95	2.28	3.162(2)	154	–*x* + 2, *y* + ½, –*z* + 1½

Table S6: Geometrical parameters (Å, °) for π···π stacking interactions in **5**·H_2O.

*Cg*I···*Cg*J	*Cg*I···*Cg*J	*α*	*β*	*Cg*I-Perp	Symmetry transformation of the acceptor
*Cg*3···*Cg*3	3.5669(10)	0	25.00	–3.2326(7)	−*x* + 2, −*y* + 2, −*z* + 2
*Cg*4···*Cg*4	3.9506(9)	0	31.27	3.3765(7)	−*x* + 2, –*y* + 1, −*z* + 2

C*g*I···C*g*J, α, β and C*g*I-Perp are, respectively, the centroid-to-centroid distance between rings I and J, the inter-ring dihedral angle, slip angle and the perpendicular distance of C*g*I from ring J. *Cg*3 and *Cg*4 are N1/C2/C3/N2/C4/C5 and N4/C7/C8/N5/C9/C10 ring centroids, respectively.

Table S7: Hydrogen bonds and other weak intermolecular interactions in **6**.

D–H···*A*	d(*D*–H)	d(H···*A*)	d(*D*···*A*)	<(*D*H*A*)	Symmetry transformation of the acceptor
O3–H3A···O1	0.83(2)	1.91(2)	2.695(2)	158(3)	*x* − 1, *y*, *z*
O3–H3B···O2	0.81(2)	1.88(2)	2.663(2)	162(4)	−*x* + 1, −*y*, −*z* + 1
C6–H6···O3	0.93	2.45	3.347(3)	144	−*x*, −*y* + 1, −*z* + 1

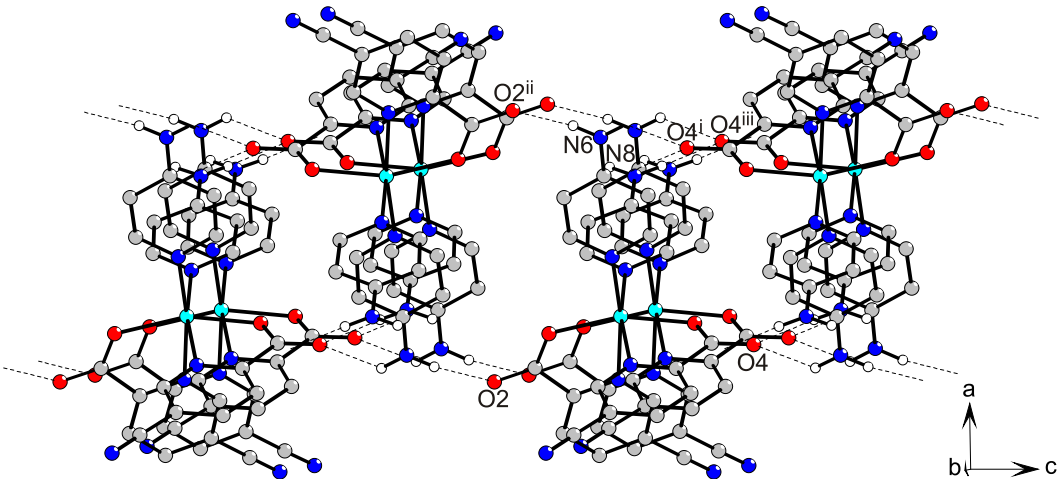

Figure S5: Formation of hydrogen-bonded layer in **7**·C_7H_8. Dashed lines indicate N–H···O bonds. Symmetry codes: (i) −*x* + 1, −*y* + 1, −*z* + 2; (ii) −*x* + 1, −*y* + 1, −*z* + 1; (iii) −*x* + 1, −*y*, −*z* + 2.

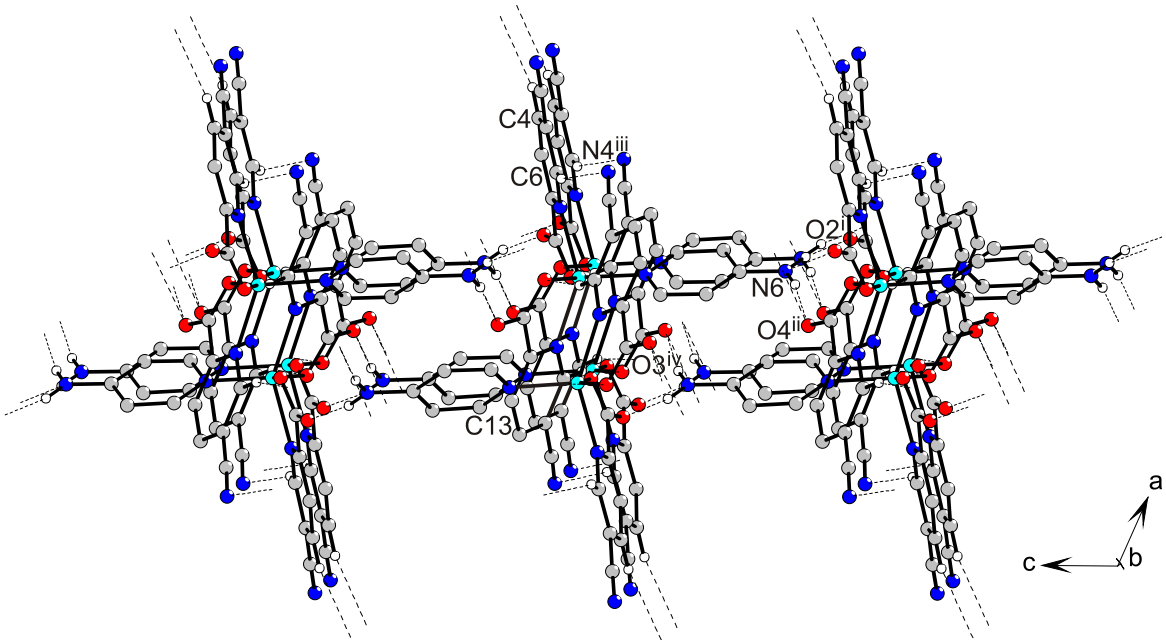

Figure S6: 3D Network of hydrogen-bonded and with weak C–H···O/N interactions connected molecules in **8**. Dashed lines indicate N–H···O and C–H···O/N interactions. Symmetry codes: (i) *x*, −*y* + 1½, *z* − ½; (ii) *x*, −*y* + ½, *z* − ½; (iii) –*x* + 1, *y* – ½, –*z* + ½; (iv) –*x* + 1, *y* + ½, –*z* + ½.

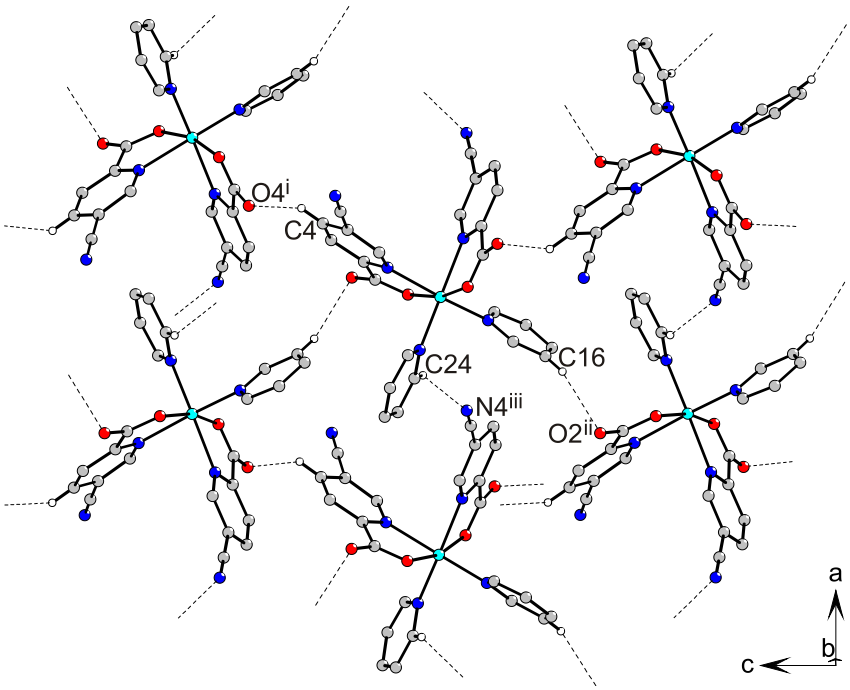

Figure S7: Interactions between adjacent molecules in **9**. Dashed lines indicate weak C–H···O and C–H···N interactions. Symmetry codes: (i) *–x* + ½, *y* + ½, *z* + ½; (ii) *–x*, *–y* + 1, *z* – ½; (iii) *x* – ½, *–y* + 1½, *z*.

Table S8: Hydrogen bonds and other weak intermolecular interactions in $[Zn(picCN)_2(4apy)_2]\cdot C_7H_8$ (**7**·C_7H_8), $[Zn(picCN)_2(4apy)]$ (**8**) and $[Zn(picCN)_2(py)_2]$ (**9**).

D–H···*A*	d(*D*–H)	d(H···*A*)	d(*D*···*A*)	<(*DHA*)	Symmetry transformation of the acceptor
7·C_7H_8					
N6–H6A···O4	0.86	2.34	3.020 (2)	136	−*x* + 1, −*y* + 1, −*z* + 2
N6–H6B···O2	0.86	2.06	2.881 (3)	159	−*x* + 1, −*y* + 1, −*z* + 1
N8–H8A···O4	0.86	2.11	2.956 (3)	168	−*x* + 1, −*y*, −*z* + 2
C27–H27···*Cg*5		2.52	3.4272(1)	166	*x*, *y*, *z*
C30–H30···*Cg*3		2.74	3.5186(1)	142	*x*, *y* + 1, *z*
8					
N6–H6A···O2	0.88	2.08	2.937 (2)	165	*x*, −*y* + 1½, *z* − ½
N6–H6B···O4	0.88	2.02	2.888 (2)	169	*x*, −*y* + ½, *z* − ½
C4–H4···O4	0.93	2.45	3.376(3)	164	−*x* + 2, −*y* + 1, −*z* + 1
C6–H6···N4	0.93	2.37	3.225(3)	149	*–x* + 1, *y* – ½, *–z* + ½
C13–H13···O3	0.93	2.52	3.445(2)	165	*–x* + 1, *y* + ½, *–z* + ½
9					
C4–H4···O4	0.93	2.38	3.014(4)	125	*–x* + ½, *y* + ½, *z* + ½
C16–H16···O2	0.93	2.54	3.383(5)	151	*–x*, *–y* + 1, *z* – ½
C24–H24···N4	0.93	2.57	3.314(6)	137	*x* – ½, *–y* + 1½, *z*

*Cg*3 and *Cg*5 are N1/C2–C6 and N5/C15–C19 ring centroids, respectively.

Table S9: Geometrical parameters (Å, °) for π···π stacking interactions in $[Zn(picCN)_2(4apy)_2]\cdot C_7H_8$ (**7**·C_7H_8) and $[Zn(picCN)_2(phen)]\cdot C_7H_8\cdot 2MeOH$ (**10**·C_7H_8·2MeOH).

*Cg*I···*Cg*J	*Cg*I···*Cg*J	*α*	*β* ,*γ*	*Cg*I-Perp	Symmetry transformation of the acceptor
7·C_7H_8					
*Cg*6···*Cg*7	3.8672(1)	8	21.1, 29.0	–3.3831	*x*, *y* – 1, *z*
10·C_7H_8·2MeOH					
*Cg*5···*Cg*17	3.8752(17)	8.35(15)	26.82, 18.98	3.6646 (12)	*x*, −*y* + ½, *z* + ½
*Cg*12···*Cg*18	3.9270(19)	9.69(17)	27.79, 19.11	–3.7106(13)	–*x* + 1, –*y*, –*z* + 1

C*g*I···C*g*J, α, β and C*g*I-Perp are, respectively, the centroid-to-centroid distance between rings I and J, the inter-ring dihedral angle, slip angle and the perpendicular distance of C*g*I from ring J. In **7**·C_7H_8 *Cg*6 and *Cg*7 are N7/C20–C24 and C26–C31 ring centroids, respectively. In **10**·C_7H_8·2MeOH *Cg*5, *Cg*12, *Cg*17 and *Cg*18 are N3/C9–C13, N7/C28–C32, C58–C63 and C65–C70 ring centroids, respectively.

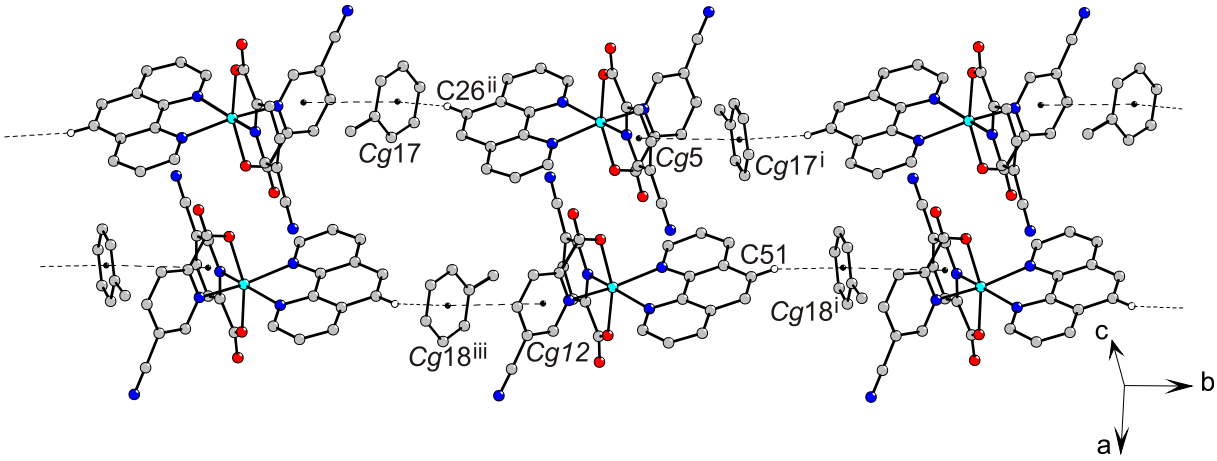

Figure S8: C–H···π and π···π stacking interactions in **10**·C_7H_8·2MeOH spreading along *b* axis. Dashed lines indicate C–H···π interactions and centroid-to-centroid distances.
Symmetry codes: (i) –*x*, –*y*, –*z* + 1; (ii) *x*, −*y* + ½, *z* + ½; (iii) –*x* + 1, –*y*, –*z* + 1.

Table S10: Hydrogen bonds and other weak intermolecular interactions in $[Zn(picCN)_2(phen)]\cdot C_7H_8\cdot 2MeOH$ (**10**$\cdot C_7H_8\cdot 2MeOH$).

D–H···*A*	d(*D*–H)	d(H···*A*)	d(*D*···*A*)	<(*D*H*A*)	Symmetry transformation of the acceptor
O9–H9···O2	0.84	1.88	2.721 (4)	177	$x + 1, y, z$
O10–H10A···O6	0.84	1.89	2.721 (4)	170	$x, y, z - 1$
O11*A*–H11*A*···O4	0.84	2.02	2.67 (2)	134	$x + 1, -y + ½, z - ½$
O11*B*–H11*B*···O4	0.84	1.95	2.77 (3)	166	$x + 1, -y + ½, z - ½$
O12*A*–H12*A*···O8	0.84	2.02	2.785 (13)	152	x, y, z
O12*B*–H12*B*···O8	0.84	1.95	2.682 (10)	144	x, y, z
C4–H4···N4	0.95	2.51	3.414(5)	160	$x - 1, -y + ½, z - ½$
C6–H6···O7	0.95	2.52	3.156(4)	124	$x - 1, y, z$
C11–H11···N2	0.95	2.51	3.420(5)	161	$x + 1, -y + ½, z + ½$
C15–H15···O6	0.95	2.41	3.106(5)	130	x, y, z
C17–H17···O10	0.95	2.26	3.185(5)	166	$-x + 1, -y, -z + 1$
C24–H24···O8	0.95	2.41	3.148(5)	135	$x - 1, y, z$
C30–H30···N8	0.95	2.51	3.422(5)	162	$-x + 2, -y, -z + 2$
C37–H37···N10	0.95	2.50	3.416(5)	162	$-x, -y, -z + 1$
C39–H39···O1	0.95	2.52	3.146(4)	123	x, y, z
C41–H41···O2	0.95	2.37	3.095(5)	133	x, y, z
C43–H43···O11*A*	0.95	2.49	3.16(3)	130	$x - 1, y, z$
C48–H48···O9	0.95	2.21	3.1531(5)	171	x, y, z
C50–H50···O4	0.95	2.42	3.150(5)	133	$x + 1, y, z$
C26–H26···*Cg*17	0.95	2.79	3.703(4)	162	$-x, -y, -z + 1$
C51–H51···*Cg*18	0.95	2.74	3.657(4)	162	$x, -y + ½, z + ½$

*Cg*17 and *Cg*18 are C58–C63 and C65–C70 ring centroids, respectively.