Supporting Information for New As-rich arsenato-polyoxovanadate clusters: solvothermal synthesis and selected properties of $[V_6^{IV}As_8^{III}O_{26}]^{4-}$ cluster containing compounds

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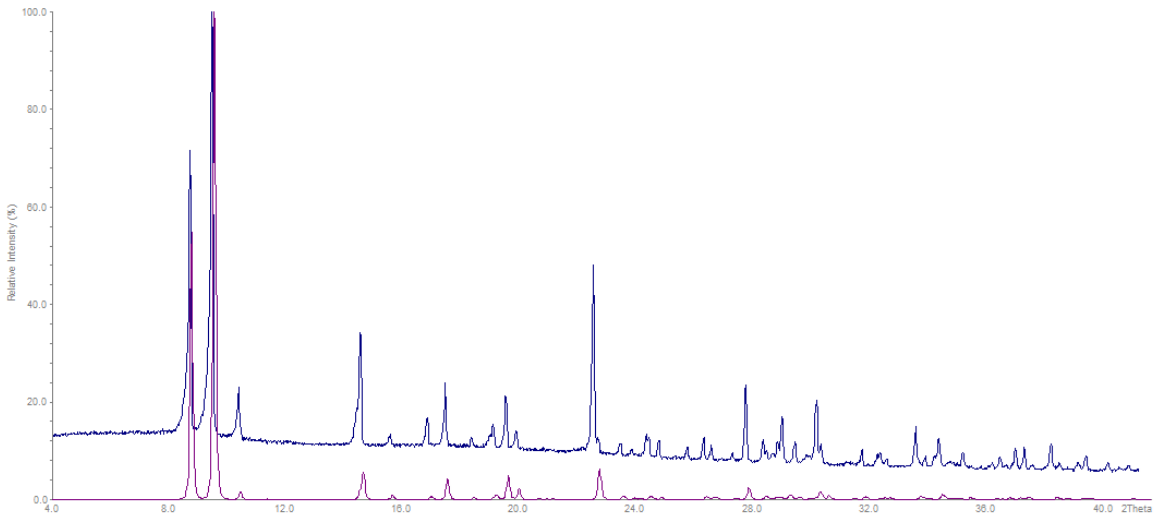

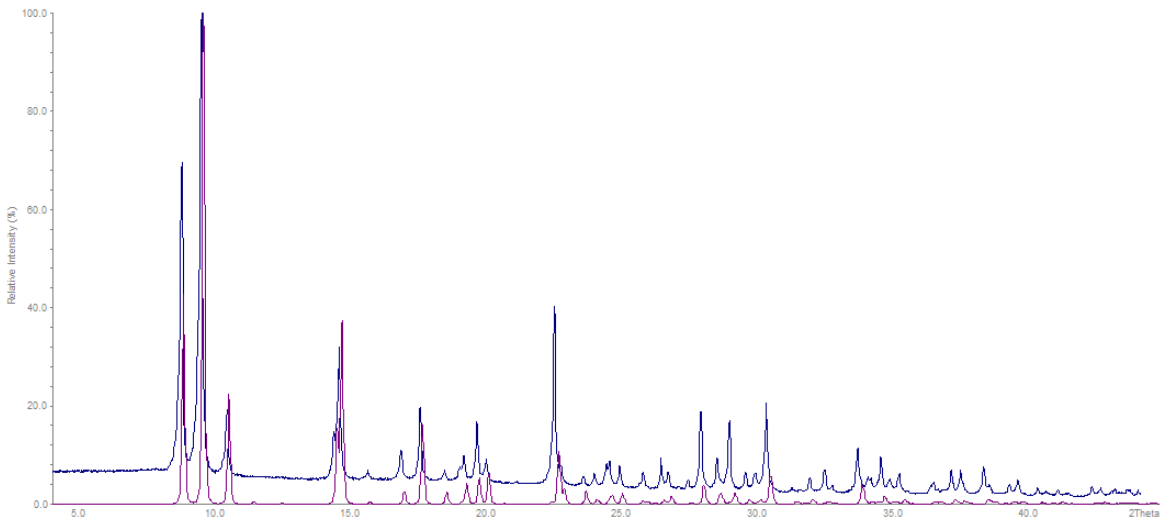

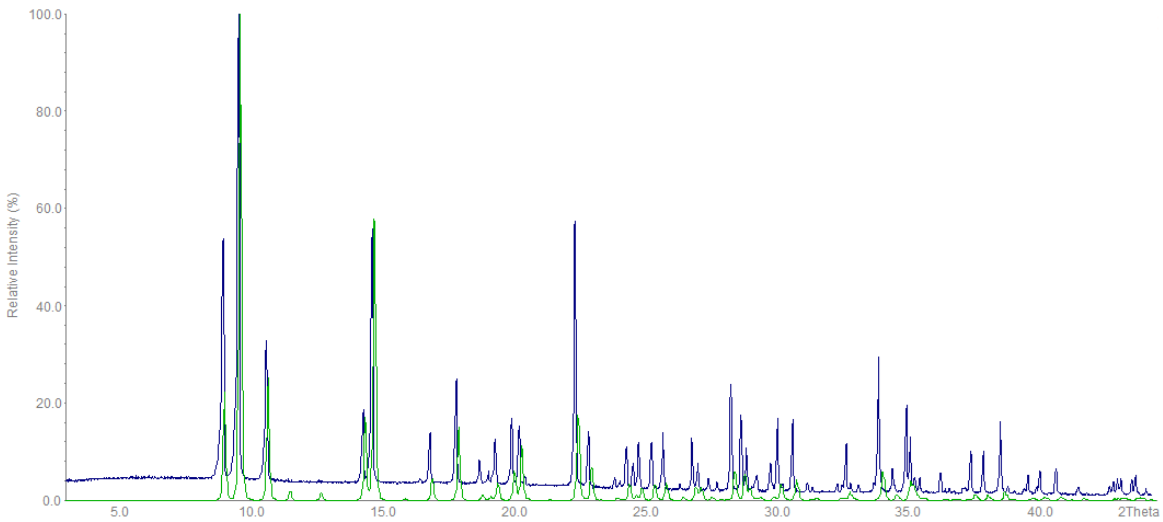

Figure S1: Experimental and calculated X-ray powder patterns of **I** (top), **II** (middle), and **III** (bottom). The lower patterns in the graphs correspond to the calculated diffractograms.

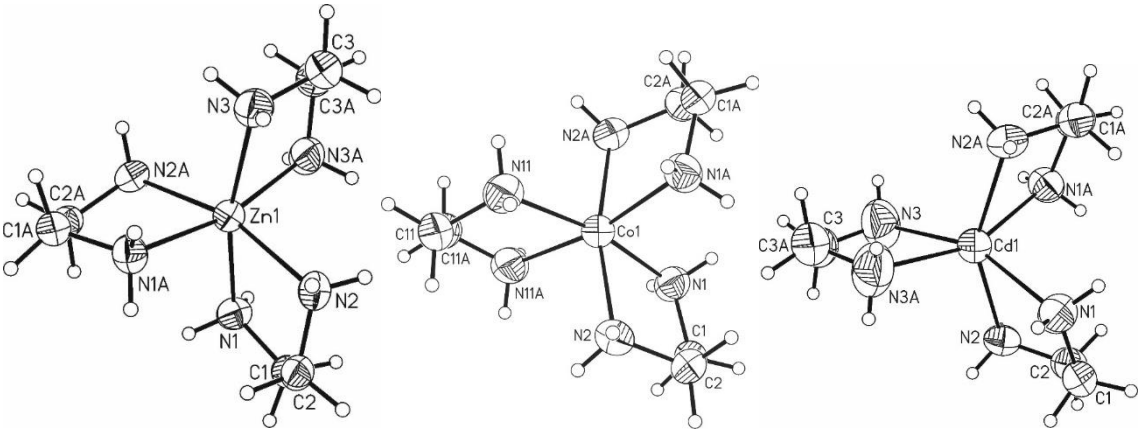

Figure S2: ORTEP plots of the $[M(en)_3]^{2+}$ complexes in the structures of I, II, and III with labelling and displacement ellipsoids drawn at the 50% probability level.

Table S1. Selected bond lengths (Å) and angles (°) for the M^{2+} coordination in **I**, **II**, and **III**.

Co(1)-N(2)#4	2.166(5)	Co(1)-N(1)	2.171(5)
Co(1)-N(2)	2.166(5)	Co(1)-N(11)#4	2.174(6)
Co(1)-N(1)#4	2.171(5)	Co(1)-N(11)	2.174(6)
N(2)#4-Co(1)-N(2)	165.7(3)	N(1)#4-Co(1)-N(11)#4	168.9(2)
N(2)#4-Co(1)-N(1)#4	78.9(2)	N(1)-Co(1)-N(11)#4	92.9(2)
N(2)-Co(1)-N(1)#4	91.54(19)	N(2)#4-Co(1)-N(11)	96.7(2)
N(2)#4-Co(1)-N(1)	91.54(19)	N(2)-Co(1)-N(11)	94.2(2)
N(2)-Co(1)-N(1)	78.9(2)	N(1)#4-Co(1)-N(11)	92.9(2)
N(1)#4-Co(1)-N(1)	95.9(3)	N(1)-Co(1)-N(11)	168.9(2)
N(2)#4-Co(1)-N(11)#4	94.2(2)	N(11)#4-Co(1)-N(11)	79.2(3)
N(2)-Co(1)-N(11)#4	96.7(2)		

Zn(1)-N(2)#4	2.178(3)	Zn(1)-N(1)#4	2.193(3)
Zn(1)-N(2)	2.178(3)	Zn(1)-N(3)	2.198(3)
Zn(1)-N(1)	2.193(3)	Zn(1)-N(3)#4	2.198(3)
N(2)#4-Zn(1)-N(2)	163.50(15)	N(1)-Zn(1)-N(3)	166.58(12)
N(2)#4-Zn(1)-N(1)	91.04(10)	N(1)#4-Zn(1)-N(3)	92.29(12)
N(2)-Zn(1)-N(1)	78.15(11)	N(2)#4-Zn(1)-N(3)#4	93.89(12)
N(2)#4-Zn(1)-N(1)#4	78.15(10)	N(2)-Zn(1)-N(3)#4	98.91(11)
N(2)-Zn(1)-N(1)#4	91.04(10)	N(1)-Zn(1)-N(3)#4	92.29(12)
N(1)-Zn(1)-N(1)#4	98.58(17)	N(1)#4-Zn(1)-N(3)#4	166.58(12)
N(2)#4-Zn(1)-N(3)	98.91(12)	N(3)-Zn(1)-N(3)#4	78.15(19)
N(2)-Zn(1)-N(3)	93.89(12)		

Cd(1)-N(2)#4	2.343(5)	Cd(1)-N(3)#4	2.361(7)
Cd(1)-N(2)	2.343(5)	Cd(1)-N(1)#4	2.389(5)
Cd(1)-N(3)	2.361(7)	Cd(1)-N(1)	2.390(5)
N(2)#4-Cd(1)-N(2)	150.8(3)	N(2)#4-Cd(1)-N(1)#4	72.71(18)
N(2)#4-Cd(1)-N(3)	109.5(3)	N(2)-Cd(1)-N(1)#4	88.91(17)

N(2)-Cd(1)-N(3)	94.0(3)	N(3)-Cd(1)-N(1)#4	94.5(2)
N(2)#4-Cd(1)-N(3)#4	94.0(3)	N(3)#4-Cd(1)-N(1)#4	158.2(3)
N(2)-Cd(1)-N(3)#4	109.5(3)	N(2)#4-Cd(1)-N(1)	88.91(17)
N(3)-Cd(1)-N(3)#4	73.3(4)		

Table S2. Selected bond lengths (Å) and angles (°) for the $[As_8V_6O_{26}]^{6-}$ anion in **I**. The ORTEP plot with atom labelling is shown below with the displacement ellipsoids drawn at the 50 % probability level.

As(1)-O(3)	1.702(4)	As(2)-O(4)	1.723(4)
As(1)-O(2)	1.799(4)	As(2)-O(2)	1.788(4)
As(1)-O(1)	1.810(4)	As(2)-O(5)	1.792(4)
V(1)-O(6)	1.605(6)	V(2)-O(7)	1.600(4)
V(1)-O(5)#1	1.962(4)	V(2)-O(3)	1.921(4)
V(1)-O(5)	1.962(4)	V(2)-O(4)	1.935(4)
V(1)-O(1)#1	1.964(4)	V(2)-O(1)#3	2.000(4)
V(1)-O(1)	1.964(4)	V(2)-O(5)#2	2.001(4)
O(1)-V(2)#2	2.000(4)	O(5)-V(2)#3	2.001(4)
O(3)-As(1)-O(2)	102.6(2)	O(4)-As(2)-O(2)	101.3(2)
O(3)-As(1)-O(1)	101.12(19)	O(4)-As(2)-O(5)	101.52(19)
O(2)-As(1)-O(1)	95.28(18)	O(2)-As(2)-O(5)	96.55(18)
O(6)-V(1)-O(5)#1	107.93(12)	O(7)-V(2)-O(3)	106.7(2)
O(6)-V(1)-O(5)	107.93(12)	O(7)-V(2)-O(4)	105.6(2)
O(5)#1-V(1)-O(5)	144.1(2)	O(3)-V(2)-O(4)	89.60(18)
O(6)-V(1)-O(1)#1	109.06(12)	O(7)-V(2)-O(1)#3	107.5(2)
O(5)#1-V(1)-O(1)#1	91.40(17)	O(3)-V(2)-O(1)#3	145.09(17)
O(5)-V(1)-O(1)#1	76.96(17)	O(4)-V(2)-O(1)#3	87.94(17)
O(6)-V(1)-O(1)	109.06(12)	O(7)-V(2)-O(5)#2	107.8(2)
O(5)#1-V(1)-O(1)	76.96(17)	O(3)-V(2)-O(5)#2	87.88(17)
O(5)-V(1)-O(1)	91.41(17)	O(4)-V(2)-O(5)#2	145.87(17)
O(1)#1-V(1)-O(1)	141.9(2)	O(1)#3-V(2)-O(5)#2	75.26(16)
As(1)-O(1)-V(1)	132.8(2)	As(2)-O(4)-V(2)	128.7(2)
As(1)-O(1)-V(2)#2	122.1(2)	As(2)-O(5)-V(1)	132.1(2)
V(1)-O(1)-V(2)#2	103.74(18)	As(2)-O(5)-V(2)#3	123.2(2)
As(2)-O(2)-As(1)	127.3(2)	V(1)-O(5)-V(2)#3	103.77(18)
As(1)-O(3)-V(2)	128.6(2)		

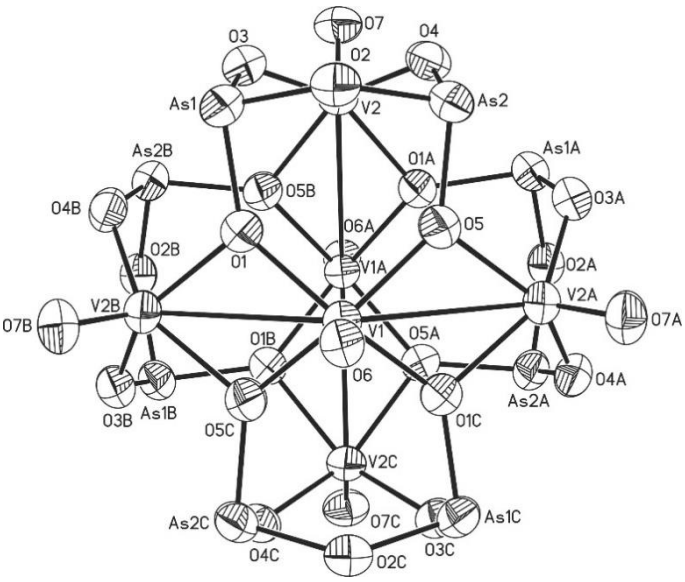

Table S3. Selected bond lengths (Å) and angles (°) for the $[As_8V_6O_{26}]^{6-}$ anion in **II**. The ORTEP plot with atom labelling is shown below with the displacement ellipsoids drawn at the 50 % probability level.

As(1)-O(1)	1.709(2)	As(2)-O(4)	1.724(2)
As(1)-O(3)	1.800(2)	As(2)-O(3)	1.791(2)
As(1)-O(2)	1.815(2)	As(2)-O(5)	1.795(2)
V(1)-O(6)	1.602(2)	V(2)-O(7)	1.606(3)
V(1)-O(1)	1.920(2)	V(2)-O(5)	1.957(2)
V(1)-O(4)	1.937(2)	V(2)-O(5)#3	1.957(2)
V(1)-O(2)#1	1.996(2)	V(2)-O(2)	1.959(2)
V(1)-O(5)#2	2.001(2)	V(2)-O(2)#3	1.959(2)
V(1)-V(2)#2	3.1134(6)	V(2)-V(1)#2	3.1135(6)
O(2)-V(1)#2	1.996(2)	V(2)-V(1)#1	3.1135(6)
O(5)-V(1)#1	2.001(2)	O(4)-As(2)-O(3)	101.53(11)
O(1)-As(1)-O(3)	102.79(11)	O(4)-As(2)-O(5)	101.53(10)
O(1)-As(1)-O(2)	101.07(10)	O(3)-As(2)-O(5)	96.57(10)
O(3)-As(1)-O(2)	95.35(10)	O(7)-V(2)-O(5)	108.13(6)
O(6)-V(1)-O(1)	106.69(11)	O(7)-V(2)-O(5)#3	108.13(6)
O(6)-V(1)-O(4)	105.39(11)	O(5)-V(2)-O(5)#3	143.75(13)
O(1)-V(1)-O(4)	89.63(10)	O(7)-V(2)-O(2)	109.23(6)
O(6)-V(1)-O(2)#1	107.49(11)	O(5)-V(2)-O(2)	91.19(9)
O(1)-V(1)-O(2)#1	145.11(9)	O(5)#3-V(2)-O(2)	76.96(9)
O(4)-V(1)-O(2)#1	87.98(9)	O(7)-V(2)-O(2)#3	109.23(6)
O(6)-V(1)-O(5)#2	108.02(11)	O(5)-V(2)-O(2)#3	76.96(9)
O(1)-V(1)-O(5)#2	87.91(9)	O(5)#3-V(2)-O(2)#3	91.19(9)
O(4)-V(1)-O(5)#2	145.76(9)	O(2)-V(2)-O(2)#3	141.54(12)
O(2)#1-V(1)-O(5)#2	75.13(9)	As(2)-O(3)-As(1)	126.79(13)
As(1)-O(1)-V(1)	128.31(12)	As(2)-O(4)-V(1)	128.38(12)
As(1)-O(2)-V(2)	132.73(12)	As(2)-O(5)-V(2)	132.24(12)
As(1)-O(2)-V(1)#2	121.91(11)	As(2)-O(5)-V(1)#1	122.95(11)
V(2)-O(2)-V(1)#2	103.83(10)	V(2)-O(5)-V(1)#1	103.76(10)

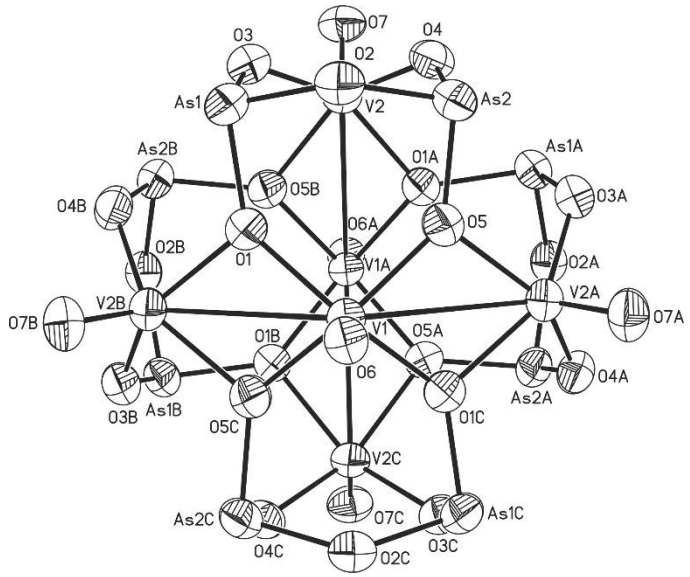

Table S4. Selected bond lengths (Å) and angles (°) for the $[As_8V_6O_{26}]^{6-}$ anion in **III**. The ORTEP plot with atom labelling is shown below with the displacement ellipsoids drawn at the 50 % probability level.

As(1)-O(1)	1.706(4)	As(2)-O(4)	1.716(4)
As(1)-O(3)	1.798(4)	As(2)-O(3)	1.797(4)
As(1)-O(2)	1.820(4)	As(2)-O(5)	1.798(4)
O(1)-As(1)-O(3)	102.46(19)	O(4)-As(2)-O(3)	101.37(19)
O(1)-As(1)-O(2)	101.66(17)	O(4)-As(2)-O(5)	102.01(18)
O(3)-As(1)-O(2)	95.78(18)	O(3)-As(2)-O(5)	96.39(18)
V(1)-O(6)	1.603(4)	V(2)-O(7)	1.612(6)
V(1)-O(1)	1.932(4)	V(2)-O(5)#3	1.959(4)
V(1)-O(4)	1.938(4)	V(2)-O(5)	1.959(4)
V(1)-O(2)#1	1.992(4)	V(2)-O(2)	1.959(4)
V(1)-O(5)#2	2.004(4)	V(2)-O(2)#3	1.959(4)
V(1)-V(2)#2	3.1041(10)	O(7)-V(2)-O(5)#3	108.18(12)
O(6)-V(1)-O(1)	107.0(2)	O(7)-V(2)-O(5)	108.18(12)
O(6)-V(1)-O(4)	105.5(2)	O(5)#3-V(2)-O(5)	143.6(2)
O(1)-V(1)-O(4)	89.37(18)	O(7)-V(2)-O(2)	109.20(11)
O(6)-V(1)-O(2)#1	107.5(2)	O(5)#3-V(2)-O(2)	77.38(17)
O(1)-V(1)-O(2)#1	144.88(17)	O(5)-V(2)-O(2)	90.76(17)
O(4)-V(1)-O(2)#1	87.68(16)	O(7)-V(2)-O(2)#3	109.21(11)
O(6)-V(1)-O(5)#2	108.3(2)	O(5)#3-V(2)-O(2)#3	90.76(17)
O(1)-V(1)-O(5)#2	87.59(16)	O(5)-V(2)-O(2)#3	77.38(17)
O(4)-V(1)-O(5)#2	145.46(17)	O(2)-V(2)-O(2)#3	141.6(2)
O(2)#1-V(1)-O(5)#2	75.60(16)	As(2)-O(3)-As(1)	126.6(2)
As(1)-O(1)-V(1)	128.6(2)	As(2)-O(4)-V(1)	129.0(2)
As(1)-O(2)-V(2)	133.3(2)	As(2)-O(5)-V(2)	133.4(2)
As(1)-O(2)-V(1)#2	121.9(2)	As(2)-O(5)-V(1)#1	122.6(2)
V(2)-O(2)-V(1)#2	103.54(18)	V(2)-O(5)-V(1)#1	103.09(18)

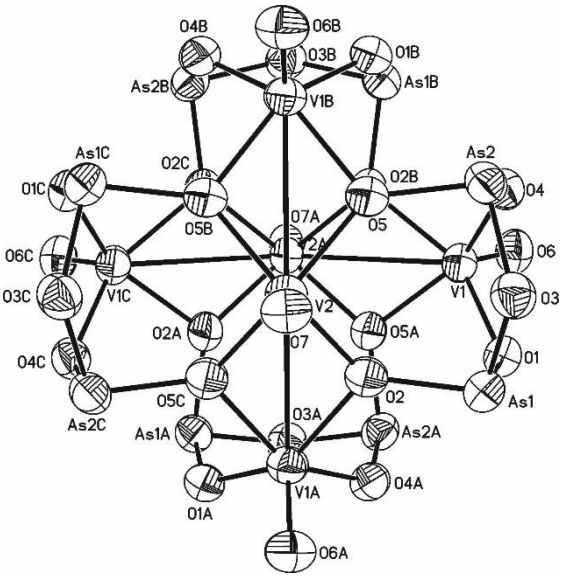

Table S5. Hydrogen bonds [Å and °] for **I**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1C)...O(7)#3	0.91	2.53	3.251(7)	136.5
N(1)-H(1D)...O(6)	0.91	2.14	2.981(6)	152.3
C(2)-H(2B)...O(6)#4	0.99	2.65	3.639(7)	173.3
N(2)-H(2C)...O(7)#5	0.91	2.18	3.034(7)	155.5
N(2)-H(2D)...O(4)#6	0.91	2.15	3.026(6)	160.4
N(11)-H(11C)...O(7)#5	0.91	2.50	3.302(8)	147.3
N(11)-H(11D)...O(4)#7	0.91	2.34	3.210(7)	161.4
C(11)-H(11B)...O(7)#6	0.99	2.61	3.603(9)	175.8

Table S6. Hydrogen bonds [Å and °] for **II**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1N)...O(7)	0.91	2.14	2.997(3)	156.2
N(1)-H(2N)...O(6)#1	0.91	2.56	3.254(4)	133.8
N(2)-H(3N)...O(4)#5	0.91	2.16	3.024(3)	158.9
N(2)-H(4N)...O(6)#6	0.91	2.18	3.038(4)	156.0
N(3)-H(5N)...O(4)#7	0.91	2.35	3.216(4)	158.4
N(3)-H(6N)...O(6)#6	0.91	2.49	3.299(4)	147.6
C(3)-H(3A)...O(6)#5	0.99	2.58	3.565(5)	173.6

Table S7. Hydrogen bonds [Å and °] for **III**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

N(1)-H(1C)...O(7)#3	0.91	2.53	3.251(7)	136.5
N(1)-H(1D)...O(6)	0.91	2.14	2.981(6)	152.3
C(2)-H(2B)...O(6)#4	0.99	2.65	3.639(7)	173.3
N(2)-H(2C)...O(7)#5	0.91	2.18	3.034(7)	155.5
N(2)-H(2D)...O(4)#6	0.91	2.15	3.026(6)	160.4
N(11)-H(11C)...O(7)#5	0.91	2.50	3.302(8)	147.3
N(11)-H(11D)...O(4)#7	0.91	2.34	3.210(7)	161.4
C(11)-H(11B)...O(7)#6	0.99	2.61	3.603(9)	175.8