Electronic Supplementary Material (ESI) for CrystEngComm.

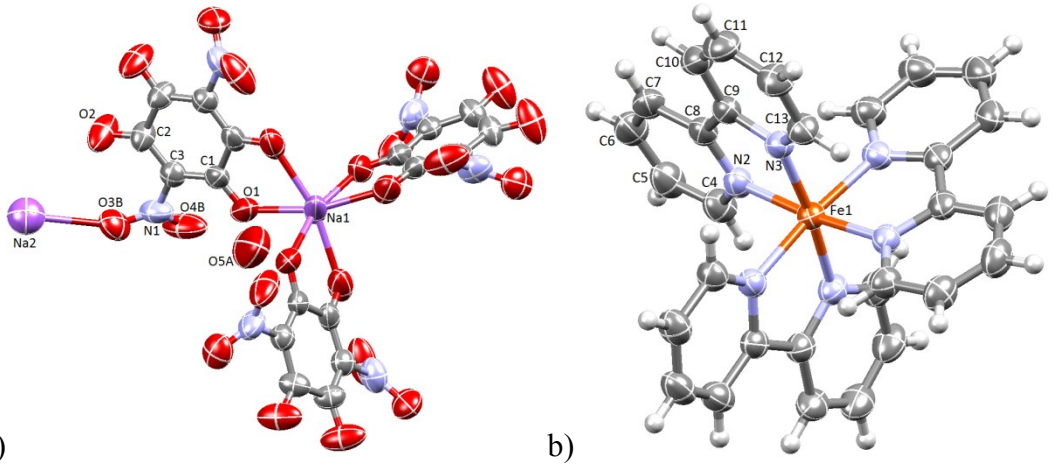
Nitranilic acid as a basis for construction of coordination polymers: from discrete monomers to 3D networks

Supplement

Valentina Milašinović and Krešimir Molčanov

Ruđer Bošković Institute, Bijenička 54, Zagreb HR-10000, Croatia

e-mail: kmolcano@irb.hr



a) b)

Figure S1 ORTEP-3 drawing of **1** with the atom numbering scheme: (a) basic structural unit of coordination polymer and (b) $[Fe(bpy)_3]^{2+}$ cation. Displacement ellipsoids are drawn for the probability of 30% and hydrogen atoms are shown as spheres of arbitrary radii.

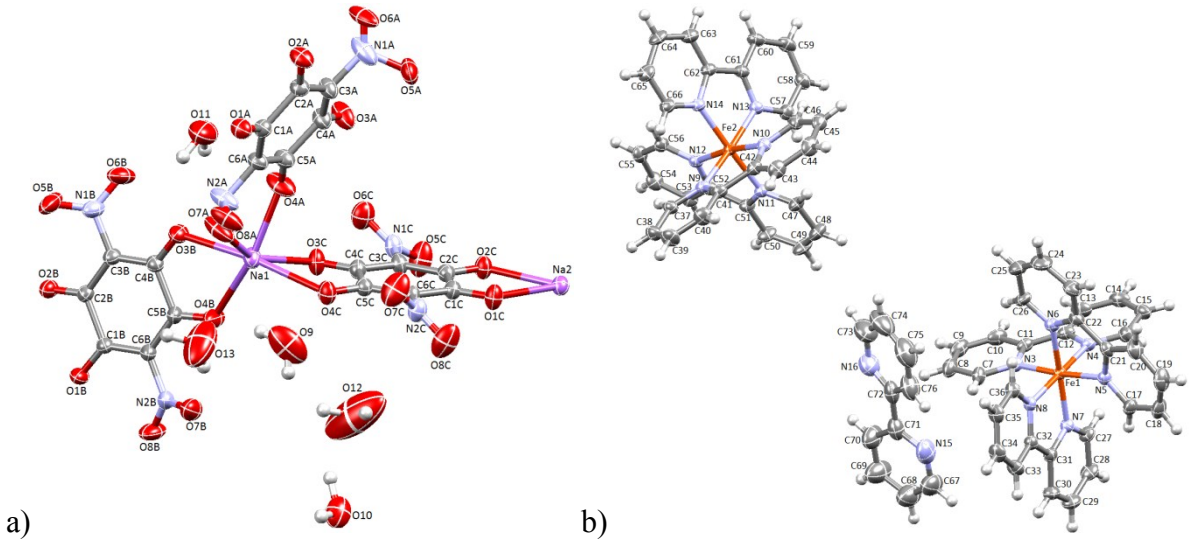
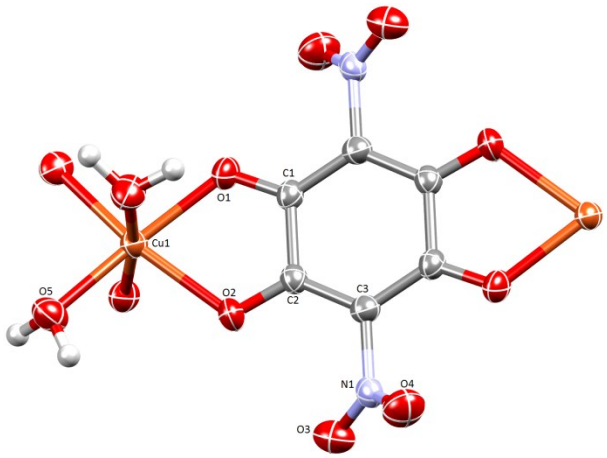


Figure S2 ORTEP-3 drawing of **2** with the atom numbering scheme: (a) basic structural unit of coordination polymer and (b) $[Fe(bpy)_3]^{2+}$ cations and 2,2′-bipyridine. Displacement ellipsoids are drawn for the probability of 30% and hydrogen atoms are shown as spheres of arbitrary radii.



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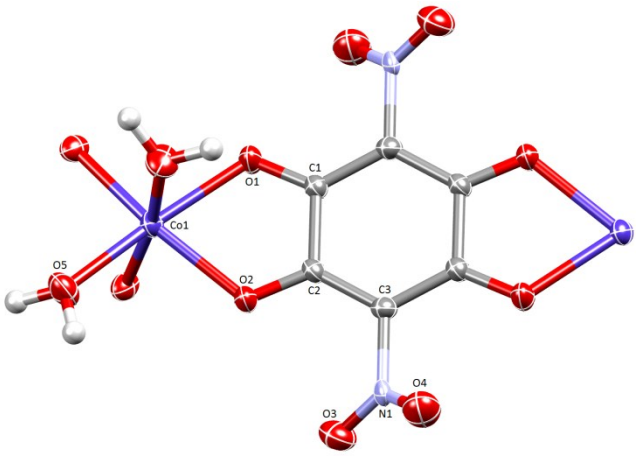

4

Figure S3 ORTEP-3 drawings of complexes in **3** and **4** with the atom numbering schemes. Displacement ellipsoids are drawn for the probability of 50% and hydrogen atoms are shown as spheres of arbitrary radii.

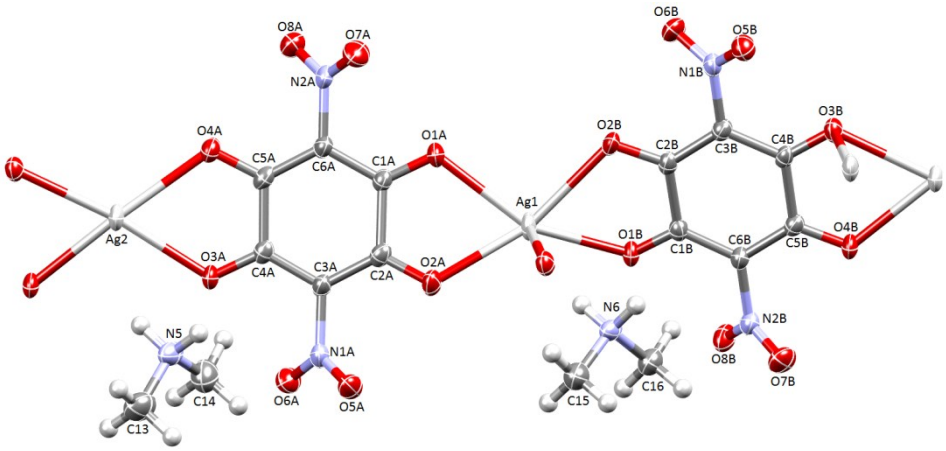

Figure S4 ORTEP-3 drawing of an asymmetric unit of **5** with the atom numbering scheme. Displacement ellipsoids are drawn for the probability of 70% and hydrogen atoms are shown as spheres of arbitrary radii.

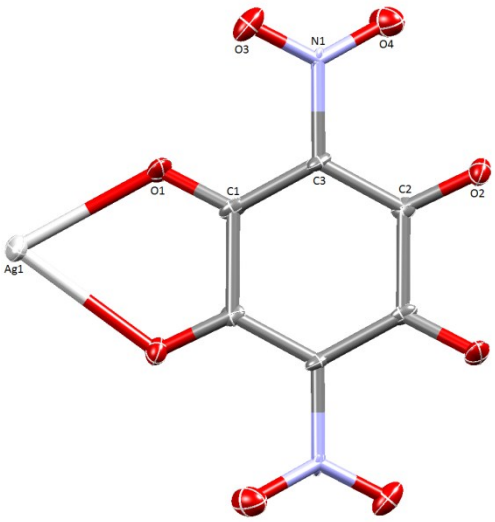

Figure S5 ORTEP-3 drawing of a basic structural unit of **6** with the atom numbering scheme. Displacement ellipsoids are drawn for the probability of 70% and hydrogen atoms are shown as spheres of arbitrary radii.

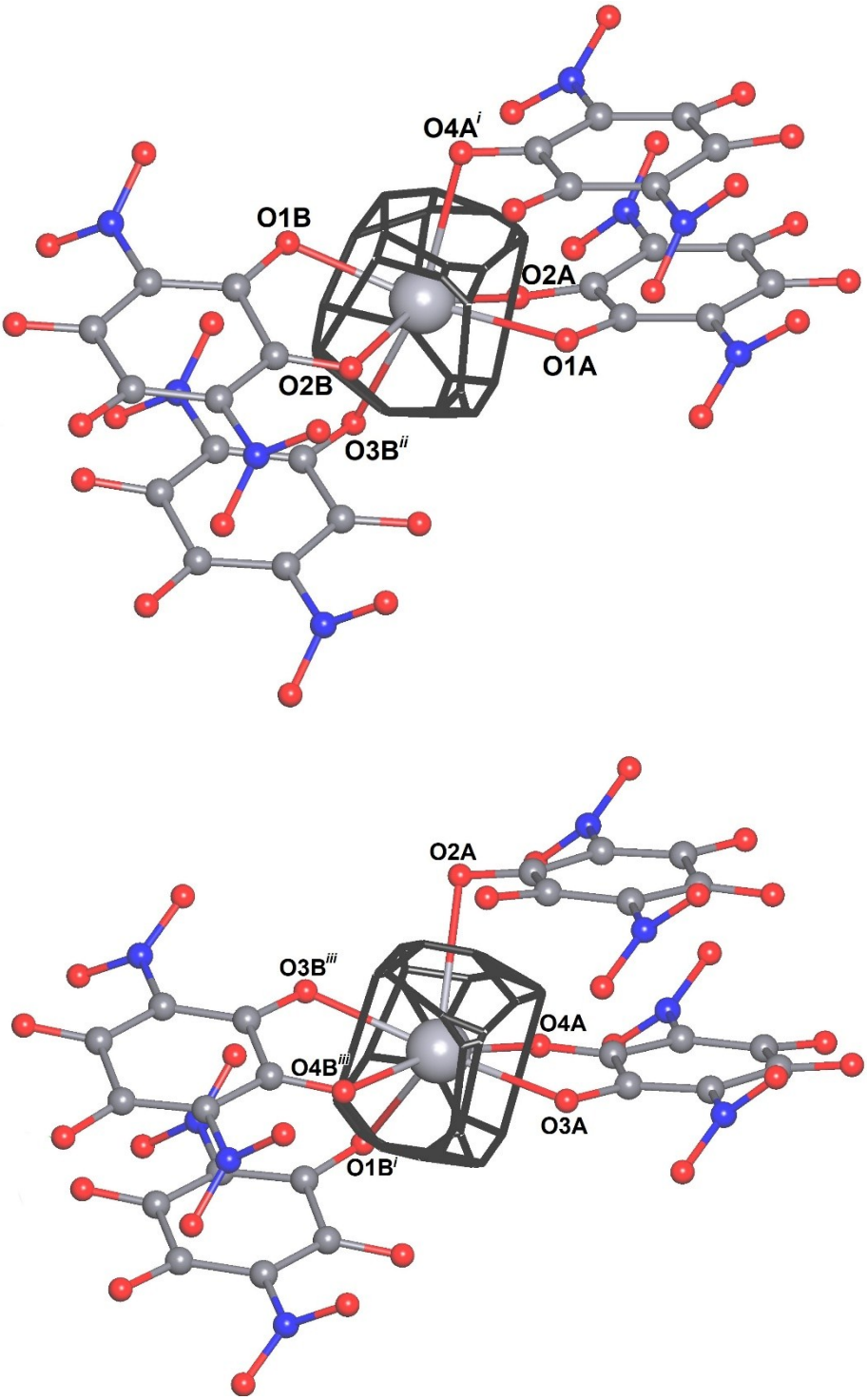

Figure S6 Coordination of silver atoms in **5** represented as Voronoi-Dirichlet polyhedra. a) Ag1 is coordinated by five O atoms and an additional weaker Ag...O contact (Ag1...O4A^{i}); b) Ag2 is coordinated by four O atoms and two additional Ag...O contacts (Ag2...O1B^{i} and Ag2...O2A^{iv}). Faces corresponding to close Ag...O contacts are approximately half-size of those corresponding to Ag-O bonds. Symmetry operators: *i*) 1−*x*, 1−*y*, 1−*z*, *ii*) 1−*x*, 1−*y*, −*z*; *iii*) −1+*x*, *y*, 1+*z*, *iv*) −*x*, −*y*, 1−*z*.

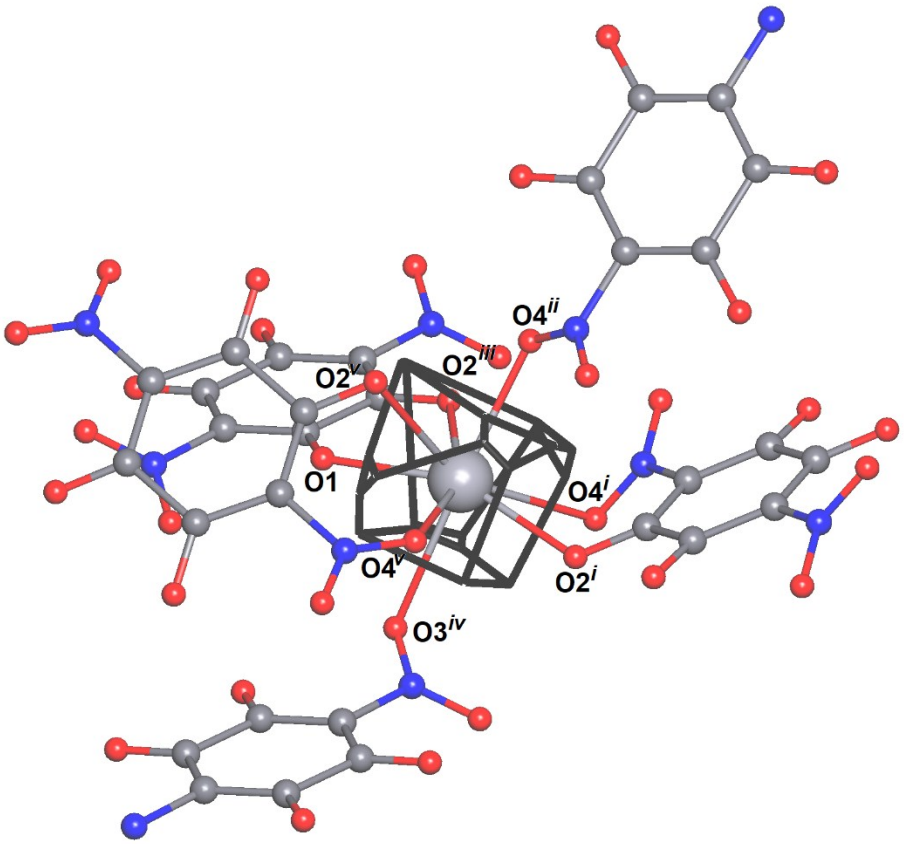

Figure S7 Coordination of silver atom in **6** represented as a Voronoi-Dirichlet polyhedron. Symmetry operators: *i*) 1/2−*x*, −*y*, −1/2+*z*; *ii*) *x*, 1/2−*y*, −1/2+*z*; *iii*) 1−*x*, −*y*, 1−*z*; *iv*) −*x*, −*y*, 1−*z*; *v*) −1/2+*x*, 1/2−*y*, 1−*z*.

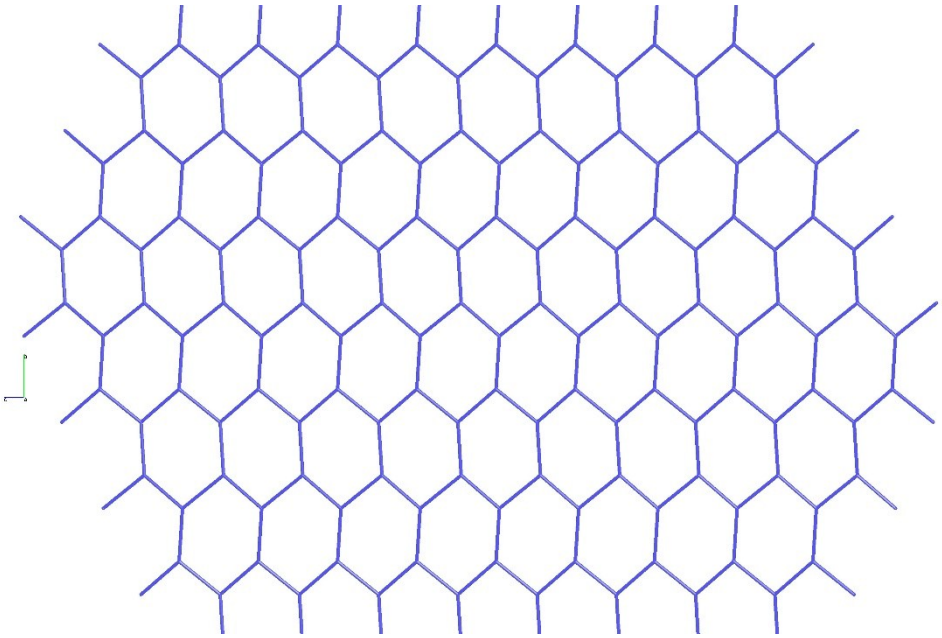

Figure S8 Topological representation of a **hcb** network in **2**.

Table S1 Geometric parameters of the metal coordination spheres (Å, º). Symmetry operators: *i*) 1-*y*, -1+*x*-*y*, *z*; *ii*) 2-*x*+*y*, 1-*x*, *z*; *iii*) 1+*y*, -1+*x*, 1/2-*z*; *iv*) 2-*x*, 1-*x*+*y*, 1/2-*z*; *v*) *x*-*y*, -*y*,1/2-*z*; *vi*) *x*, *y*, -1+*z*; *vii*) *x*, *y*, 1+*z*; *viii*) 1-*x*, -1/2+*y*, -*z*; *ix*) 1-*x*, 1/2+*y*, -*z*; *x*) 3/2-*x*,*y*,-*z*; *xi*) -1+*x*, *y*,1+*z*; *xii*) 1+*x*, *y*, -1+*z*; *xiii*) 1-*x*, 1-*y*, -*z*; *xiv*) 1-*x*, 1-*y*, 1-*z*: *xv*) 1/2-*x*, -*y*, -1/2+*z*; *xvi*) 1/2-*x*, -*y*, 1/2+*z*; *xvii*) -1/2+*x*, 1/2-*y*, 1-*z*; *xviii*) 1/2+*x*, 1/2-*y*, 1-*z*; *xix*) -*x*, -*y*, 1-*z*; *xx*) 1-*x*, -*y*, 1-*z*; *xxi*) *x*, 1/2-*y*, -1/2+*z*; *xxii*) *x*, 1/2-*y*, 1/2+*z*.

1		**2**			
Na1–O1	2.336(6)	Na1–O3	2.408(4)	Na2–O1	2.450(5)
Na1–O1^{i}	2.336(7)	Na1–O3B	2.509(7)	Na2–O2	2.412(7)
Na1–O1^{ii}	2.336(8)	Na1–O4	2.477(6)	Na2–O1A^{vi}	2.432(6)
Na1–O1^{iii}	2.336(6)	Na1–O4A	2.311(9)	Na2–O2A^{vi}	2.428(4)
Na1–O1^{iv}	2.336(7)	Na1–O4B	2.366(8)	Na2–O1B^{ix}	2.442(7)
Na1–O1^{v}	2.336(8)	Na1–O7A	2.493(6)	Na2–O2B^{ix}	2.420(7)
O1–Na1–O1^{i}	100.3(2)	O3–Na1–O3B	107.69(19)	O1–Na2–O2	65.53(16)
O1–Na1–O1^{ii}	100.3(2)	O3–Na1–O4	64.77(15)	O1–Na2–O1A^{vi}	104.7(2)
O1–Na1–O1^{iii}	165.07(19)	O3–Na1–O4A	88.1(2)	O1–Na2–O2A^{vi}	168.8(3)
O1–Na1–O1^{iv}	92.0(2)	O3–Na1–O4B	88.2(2)	O1–Na2–O1B^{ix}	95.07(17)

O1–Na1–O1^{v}	69.0(2)	O3–Na1–O7A	150.2(3)	O1–Na2–O2B^{ix}	100.80(18)
O1^{i}–Na1–O1^{ii}	100.3(2)	O3B–Na1–O4	168.6(2)	O2–Na2–O1A^{vi}	83.1(2)
O1^{i}–Na1–O1^{iii}	69.0(2)	O3B–Na1–O4A	101.1(2)	O2–Na2–O2A^{vi}	106.25(19)
O1^{i}–Na1–O1^{iv}	165.1(3)	O3B–Na1–O4B	63.7(2)	O2–Na2–O1B^{ix}	106.94(16)
O1^{i}–Na1–O1^{v}	92.0(2)	O3B–Na1–O7A	92.6(2)	O2–Na2–O2B^{ix}	164.30(15)
O1^{ii}–Na1–O1^{iii}	92.0(2)	O4–Na1–O4A	87.5(3)	O1A^{a}–Na2–O2A^{vi}	65.87(16)
O1^{ii}–Na1–O1^{iv}	69.0(2)	O4–Na1–O4B	106.5(2)	O1A^{a}–Na2–O1B^{ix}	160.20(17)
O1^{ii}–Na1–O1^{v}	165.1(2)	O4–Na1–O7A	97.7(2)	O1A^{a}–Na2–O2B^{ix}	108.83(16)
O1^{iii}–Na1–O1^{iv}	100.3(2)	O4A–Na1–O4B	162.3(3)	O2A^{a}–Na2–O1B^{ix}	94.6(2)
O1^{iii}–Na1–O1^{v}	100.3(2)	O4A–Na1–O7A	66.2(2)	O2A^{a}–Na2–O2B^{ix}	88.29(19)
O1^{iv}–Na1–O1^{v}	100.3(2)	O4B–Na1–O7A	120.9(3)	O1B^{d}–Na2–O2B^{ix}	65.07(19)
Na1–O1–C1	119.2(5)	Na1–O3–C4	121.5(3)	Na2–O1–C1	120.1(3)
		Na1–O3B–C4B	120.4(3)	C1A–O1A–Na2^{vii}	120.7(4)
		Na1–O4–C5	119.3(3)	C1B–O1B–Na2^{viii}	121.7(3)
		Na1–O4A–C5A	141.7(4)	Na2–O2–C2	122.2(3)
		Na1–O4B–C5B	125.7(5)	C2A–O2A–Na2^{vii}	119.6(4)
		Na1–O7A–N2A	141.4(6)	C2B–O2B–Na2^{viii}	121.9(3)

	3	**4**	**5**			
M*1–O1	2.050(2)	2.115(2)	Ag1–O1A	2.431(2)	Ag2–O3A	2.343(2)
M*1–O2	2.146(2)	2.075(2)	Ag1–O1B	2.330(3)	Ag2–O4A	2.402(3)
M*1–O5	2.019(2)	2.072(3)	Ag1–O2A	2.364(3)	Ag2–O3B^{xi}	2.404(3)
M*1–O1^{x}	2.050(2)	2.115(2)	Ag1–O2B	2.480(3)	Ag2–O4B^{xi}	2.324(3)
M*1–O2^{x}	2.146(2)	2.075(2)	Ag1–O3B^{xiii}	2.640(3)	Ag2–O1B^{xiv}	2.837(3)
M*1–O5^{x}	2.019(2)	2.072(3)	Ag1–O4A^{xiv}	2.801(3)	O3A–Ag2–O4A	67.95(8)
O1–M*1–O2	77.32(8)	76.96(9)	O1A–Ag1–O1B	153.38(9)	O3A–Ag2–O3B^{xi}	171.65(9)
O1–M*1–O5	172.41(9)	172.25(10)	O1A–Ag1–O2A	67.53(8)	O3A–Ag2–O4B^{xi}	106.54(9)
O1–M*1–O1^{x}	97.63(8)	98.57(10)	O1A–Ag1–O2B	96.32(8)	O3A–Ag2–O1B^{xiv}	114.91(8)
O1–M*1–O2^{x}	91.15(8)	91.68(9)	O1A–Ag1–O3B^{xiii}	102.30(8)	O4A–Ag2–O3B^{xi}	118.49(8)
O1–M*1–O5^{x}	88.45(9)	87.33(10)	O1A–Ag1–O4A^{xiv}	88.21(8)	O4A–Ag2–O4B^{xi}	165.50(9)
O2–M*1–O5	98.11(8)	97.94(10)	O1B–Ag1–O2A	135.51(8)	O4A–Ag2–O1B^{xiv}	77.47(8)
O2–M*1–O1^{x}	91.15(8)	91.68(9)	O1B–Ag1–O2B	66.95(8)	O3B^{xi}–Ag2–O4B^{xi}	68.51(8)
O2–M*1–O2^{x}	162.58(8)	162.70(11)	O1B–Ag1–O3B^{xiii}	96.66(8)	O3B^{xi}–Ag2–O1B^{xiv}	72.69(8)

O2–M*1–O5^{x}	94.63(9)	94.56(10)	O1B–Ag1–O4A^{xiv}	79.35(8)	O4B^{xi}–Ag2–O1B^{xiv}	93.73(8)
O5–M*1–O1^{x}	88.45(9)	87.33(10)	O2A–Ag1–O2B	152.83(9)	C1B–O1B–Ag2^{xiv}	104.7(2)
O5–M*1–O2^{x}	94.63(9)	94.56(10)	O2A–Ag1–O3B^{xiii}	78.39(8)	Ag2–O3A–C4A	119.3(2)
O5–M*1–O5^{x}	85.87(10)	87.26(11)	O2A–Ag1–O4A^{xiv}	91.32(8)	C4B–O3B–Ag2^{xii}	116.9(2)
O1^{x}–M*1–O2^{x}	77.32(8)	76.96(9)	O2B–Ag1–O3B^{xiii}	84.38(8)	Ag2^{xii}–O3B–Ag1^{xiii}	88.95(8)
O1^{x}–M*1–O5^{x}	172.41(9)	172.25(10)	O2B–Ag1–O4A^{xiv}	110.55(8)	Ag2–O4A–C5A	117.1(2)
O2^{x}–M*1–O5^{x}	98.11(8)	97.94(10)	O3B^{xiii}–Ag1–O4A^{xiv}	160.91(7)	Ag2–O4A–Ag1^{xiv}	82.41(7)
M*1–O1–C1	116.25(18)	115.07(19)	Ag1–O1A–C1A	116.5(2)	C5B–O4B–Ag2^{xii}	119.7(2)
M*1–O2–C2	113.42(18)	116.16(19)	Ag1–O1B–C1B	118.1(2)		
			Ag1–O1B–Ag2^{xiv}	82.88(7)		
			Ag1–O2A–C2A	117.2(2)		
			Ag1–O2B–C2B	115.0(2)		
			C4B–O3B–Ag1^{xiii}	108.8(2)		
			C5A–O4A–Ag1^{xiv}	101.5(2)		

6	
Ag1–O1	2.370(3)
Ag1–O2^{xv}	2.406(3)
Ag1–O4^{xv}	2.778(3)
Ag1–O2^{xvii}	2.854(3)
Ag1–O4^{xvii}	2.654(3)
Ag1–O3^{xix}	2.635(3)
Ag1–O2^{xx}	2.532(3)
Ag1–O4^{xxi}	2.508(3)
O1–Ag1–O2^{xv}	156.38(10)
O1–Ag1–O4^{xv}	124.46(10)
O1–Ag1–O2^{xvii}	72.55(9)
O1–Ag1–O4^{xvii}	94.92(10)
O1–Ag1–O3^{xix}	72.79(10)
O1–Ag1–O2^{xx}	65.05(10)
O1–Ag1–O4^{xxi}	108.94(10)
O2^{xv}–Ag1–O4^{xv}	61.08(9)

O2^{xv}–Ag1–O2^{xvii}	112.41(9)
O2^{xv}–Ag1–O4^{xvii}	71.26(10)
O2^{xv}–Ag1–O3^{xix}	84.67(10)
O2^{xv}–Ag1–O2^{xx}	130.21(10)
O2^{xv}–Ag1–O4^{g}	94.05(10)
O4^{xv}–Ag1–O2^{xvii}	153.88(9)
O4^{xv}–Ag1–O4^{xvii}	130.74(10)
O4^{xv}–Ag1–O3^{xix}	90.21(10)
O4^{xv}–Ag1–O2^{xx}	70.21(9)
O4^{xv}–Ag1–O4^{xxi}	85.55(10)
O2^{xvii}–Ag1–O4^{xvii}	57.46(10)
O2^{xvii}–Ag1–O3^{xix}	115.07(10)
O2^{xvii}–Ag1–O2^{xx}	106.50(9)
O2^{xvii}–Ag1–O4^{xxi}	69.25(10)
O4^{xvii}–Ag1–O3^{xix}	73.09(10)
O4^{xvii}–Ag1–O2^{xx}	158.53(10)
O4^{xvii}–Ag1–O4^{xxi}	110.44(10)
O3^{xix}–Ag1–O2^{xx}	105.93(10)
O3^{xix}–Ag1–O4^{xxi}	175.67(11)
O2^{xx}–Ag1–O4^{xxi}	71.78(10)
Ag1–O1–C1	123.6(3)
C2–O2–Ag1^{xvi}	122.0(3)
C2–O2–Ag1^{xviii}	101.2(2)
C2–O2–Ag1^{xx}	117.8(3)
Ag1^{xvi}–O2–Ag1^{xviii}	100.52(10)
Ag1^{xvi}–O2–Ag1^{xx}	110.14(11)
Ag1^{xviii}–O2–Ag1^{xx}	100.26(10)
N1–O3–Ag1^{xix}	119.8(2)
N1–O4–Ag1^{xvi}	99.2(2)
N1–O4–Ag1^{xviii}	128.9(2)
N1–O4–Ag1^{xxii}	119.6(2)
Ag1^{xvi}–O4–Ag1^{xviii}	96.57(10)

Ag1^{xvi}–O4–Ag1^{xxii}	102.97(10)
Ag1^{xviii}–O4–Ag1^{xxii}	103.30(12)

***** In two isostructural compounds **3** and **4** M denotes Cu and Co, respectively.

Table S2 Geometric parameters of hydrogen bonds.

	D–H / Å	H···*A* / Å	*D*···*A* / Å	*D*–H···*A* / º	Symm. op. on *A*
1					
C4–H4···N2	0.93	2.55	3.060(8)	115	1-*x*+*y*, 1-*x*, *z*
C5–H5···O2	0.93	2.58	3.280(10)	132	*x*, *x*-*y*, 1/2+*z*
C7–H7···O5B	0.93	2.48	3.19(6)	133	*y*, 1-*x*+*y*, 1-*z*
C12–H12···O2	0.93	2.47	3.336(7)	154	*x*, *x*-*y*, 1/2+*z*
C13–H13···O3B	0.93	2.57	3.321(13)	138	*x*, *x*-*y*, 1/2+*z*
C13–H13···O4A	0.93	2.48	3.14(3)	128	*x*, *x*-*y*, 1/2+*z*
C13–H13···N3	0.93	2.52	3.034(6)	115	1-*y*, *x*-*y*, *z*
2					
O9–H9A···O13	0.96	2.03	2.894(19)	148	*x*, *y*, *z*
O9–H9B···O12	0.79	2.44	2.91(2)	119	*x*, *y*, *z*
O10–H10A···O12	1.00	1.92	2.78(2)	142	*x*, *y*, *z*
O10–H10B···O3A	1.02	2.44	2.820(10)	101	1+*x*, *y*, *z*
O10–H10B···O4A	1.02	1.90	2.845(9)	152	1+*x*, *y*, *z*
O10–H10B···O11	1.02	2.48	2.972(12)	109	1+*x*, *y*, *z*
O11–H11A···O3B	0.97	2.20	2.941(10)	132	*x*, *y*, *z*
O11–H11A···O6B	0.97	2.58	2.985(10)	105	*x*, *y*, *z*
O11–H11B···O6B	0.97	2.53	2.985(10)	108	*x*, *y*, *z*
O12–H12A···O3A	0.97	2.25	2.93(2)	125	1+*x*, *y*, *z*
O12–H12B···O9	0.97(4)	2.45(5)	2.91(2)	109(3)	*x*, *y*, *z*
O13–H13A···O4B	0.92	2.45	2.806(18)	103	*x*, *y*, *z*
O13–H13A···O7B	0.92	2.35	3.240(14)	161	*x*, *y*, *z*
C16–H16···N16	0.93	2.48	3.217(9)	137	-1+*x*, *y*, *z*
3					
O5–H5A···O1	0.93(6)	2.22(6)	3.023(3)	144(7)	1/2+ *x*, -*y*, *z*
O5–H5A···O4	0.93(6)	2.26(7)	2.993(4)	135(5)	2-*x*, -1/2+*y*, 1/2-*z*
O5–H5B···O2	0.92(5)	2.36(6)	3.047(3)	132(4)	2-*x*, -*y*,-*z*
O5–H5B···O3	0.92(5)	2.15(4)	2.991(4)	152(5)	2-*x*, -*y*,-*z*
4					
O5–H5A···O1	0.94(6)	2.17(5)	2.941(4)	138(6)	1/2+ *x*, -*y*, *z*
O5–H5A···O4	0.94(6)	2.32(6)	3.003(4)	129(4)	2-*x*, -1/2+*y*, 1/2-*z*
O5–H5B···O2	0.94(4)	2.56(7)	3.086(4)	116(4)	2-*x*, -*y*,-*z*
O5–H5B···O3	0.94(4)	2.07(4)	2.970(4)	161(6)	2-*x*, -*y*,-*z*
5					
N5–H5A···O2B	0.89	2.05	2.878(4)	155	1-*x*, 1-*y*, 1-*z*
N5–H5A···O6B	0.89	2.30	2.904(4)	125	1-*x*, 1-*y*, 1-*z*
N5–H5B···O3A	0.89	2.04	2.822(4)	146	*x*, *y*, *z*
N5–H5B···O6A	0.89	2.38	2.996(4)	126	*x*, *y*, *z*
N6–H6A···O1B	0.89	2.28	3.003(4)	138	*x*, *y*, *z*
N6–H6A···O8B	0.89	2.27	2.881(4)	126	*x*, *y*, *z*
N6–H6A···O3B	0.89	2.46	3.119(4)	131	2-*x*, 1-*y*, -*z*

N6–H6B···O2A	0.89	2.35	3.023(4)	132	1+*x*, *y*, *z*
N6–H6B···O5A	0.89	2.34	2.956(4)	127	1+*x*, *y*, *z*
N6–H6B···O4A	0.89	2.36	3.016(4)	131	1-*x*, 1-*y*, 1-*z*
C13–H13B···O6B	0.96	2.55	3.054(5)	113	1-*x*, 1-*y*, 1-*z*

Table S3 Geometric parameters of π interactions. Symmetry operators: *i*) *x*-*y*, 2–*y*, 1/2–*z*; *ii*) 1–*x*, *x*–*y*, *z*.

π···*π*	Cg[a]···Cg / Å	*α*[b]	*β*[c]	Cg···plane(Cg2) / Å	Offset/ Å[d]	Symm. op. on Cg2
1						
C1→C1^{i}···N2→C8	3.975(3)	0.0(2)	5.1	3.9587(19)	0.354	1–*x*+*y*, *y*, –1/2+*z*
Fe1→N3^{ii}···N2→C8	3.872(3)	0.0(2)	31.0	3.319(2)	1.994	1–*x*+*y*, 1–*x*, *z*
N3→C13···N3→C13	3.828(3)	0.0(2)	26.3	3.4308(19)	1.697	1–*x*, –*y*, 1–*z*
2						
N6→C26···N11→C51	3.860(4)	12.1(3)	29.2	3.674(3)	1.885	–1+*x*, *y*, –1+*z*
C7→C31···N13→C61	3.968(2)	16.1(2)	36.9	3.7059(19)	2.38	1–*x*, –1/2+*y*, 1–*z*
N8→C36···N15→C71	3.949(3)	22.1(2)	38.7	3.7062(17)	–	1–*x*, –1/2+*y*, –*z*
N14→C66···N8→C36	3.949(3)	22.1(2)	20.2	3.0821(18)	–	1–*x*, 1/2+*y*, –*z*
N16→C73···N5→C21	3.817(5)	14.9(4)	15.2	3.466(5)	1.001	1+*x*, *y*, *z*
5						
C1B→C6B···C1B→C6B	3.521(2)	0.00(16)	27.1	3.1350(14)	1.602	1–*x*, 1–*y*, –*z*
C1B→C6B···C1B→C6B	3.334(2)	0.00(16)	16.8	3.1920(14)	0.963	2–*x*, 1–*y*, –*z*
C1A→C6A···C1A→C6A	3.462(2)	0.03(15)	20.3	3.2459(14)	1.204	–*x*, 1–*y*, 1–*z*
C1A→C6A···C1A→C6A	3.428(2)	0.03(15)	22.5	3.1672(14)	1.311	–1–*x*, 1–*y*, 1–*z*

[a] Cg = centre of gravity of the aromatic ring.

[b] α = angle between planes of two interacting rings.

[c] β = angle between Cg···Cg line and normal to the plane of the first interacting ring.

[d] Offset can be calculated only for the strictly parallel rings ($\alpha = 0.00°$). For slightly inclined rings ($\alpha \leq 5°$) an approximate value is given.