Electronic Supplementary Material (ESI) for CrystEngComm.

Nitrochloranilic acid: a novel asymmetrically substituted quinoid bridging ligand for design of coordination polymers

Supplement

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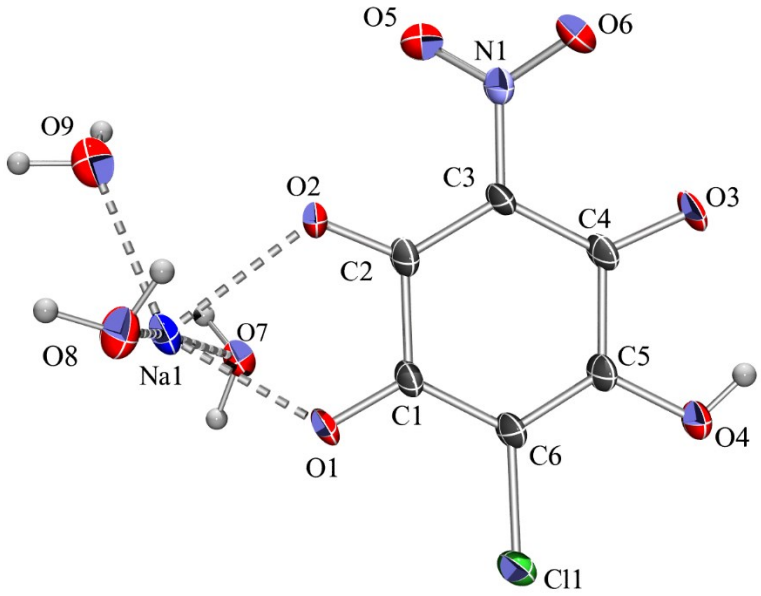


Figure S1 ORTEP-3 drawing of the asymmetric unit of **1**. Displacement ellipsoids are drawn for the probability of 50 % and hydrogen atoms are shown as spheres of arbitrary radii.

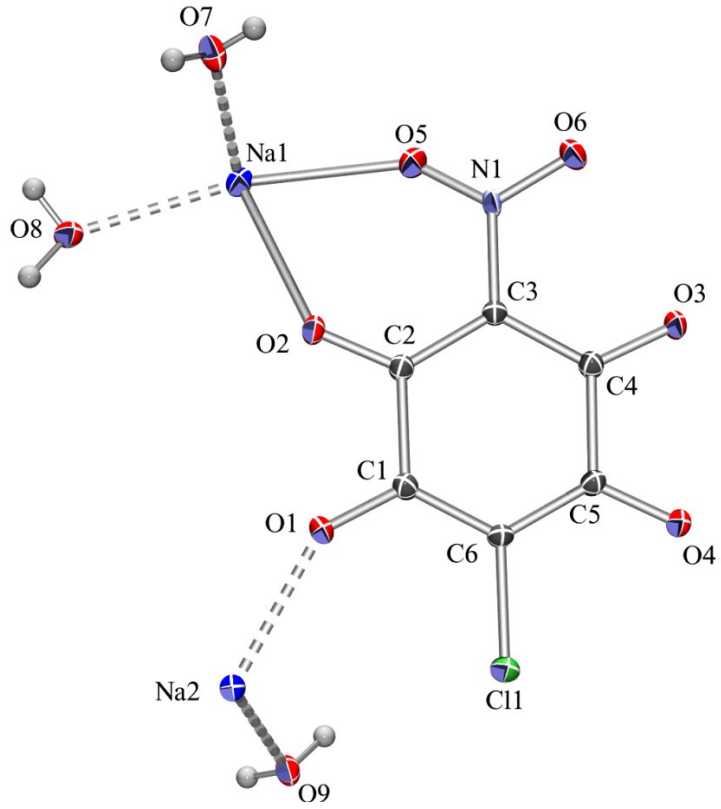


Figure S2 ORTEP-3 drawing of the asymmetric unit of **2**. Displacement ellipsoids are drawn for the probability of 50 % and hydrogen atoms are shown as spheres of arbitrary radii.

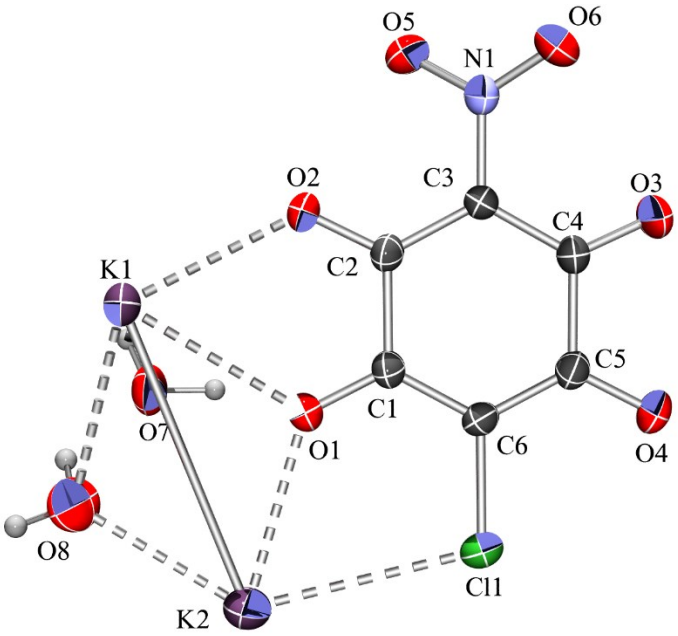


Figure S3 ORTEP-3 drawing of the asymmetric unit of **3**. Displacement ellipsoids are drawn for the probability of 50 % and hydrogen atoms are shown as spheres of arbitrary radii.

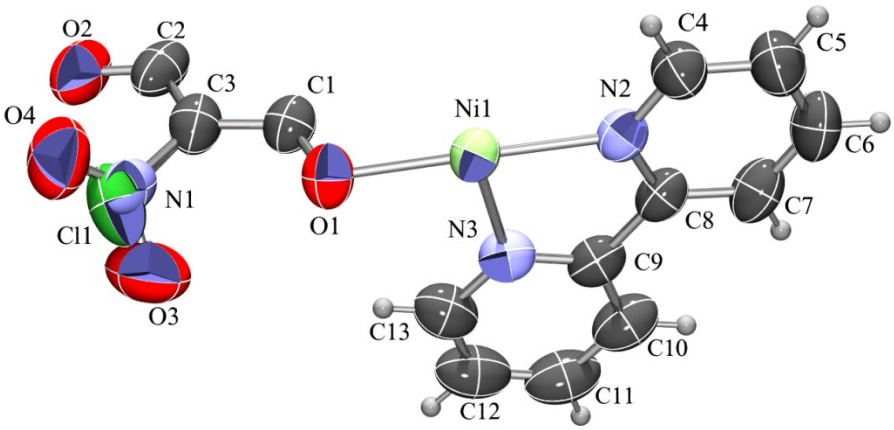


Figure S4 ORTEP-3 drawing of the asymmetric unit of **4**. Ethanol molecule has been omitted for clarity. Displacement ellipsoids are drawn for the probability of 50 % and hydrogen atoms are shown as spheres of arbitrary radii.

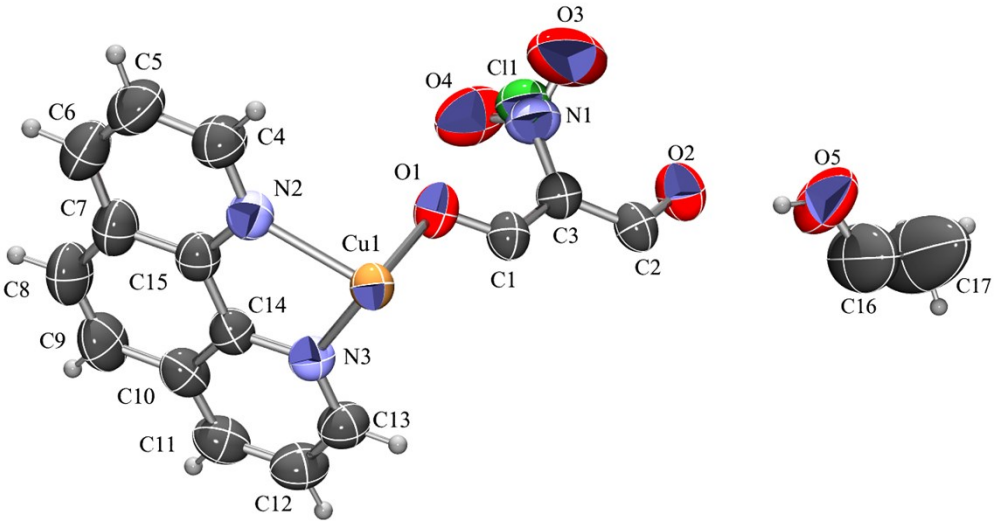


Figure S5 ORTEP-3 drawing of the asymmetric unit of **5**. Displacement ellipsoids are drawn for the probability of 50 % and hydrogen atoms are shown as spheres of arbitrary radii.

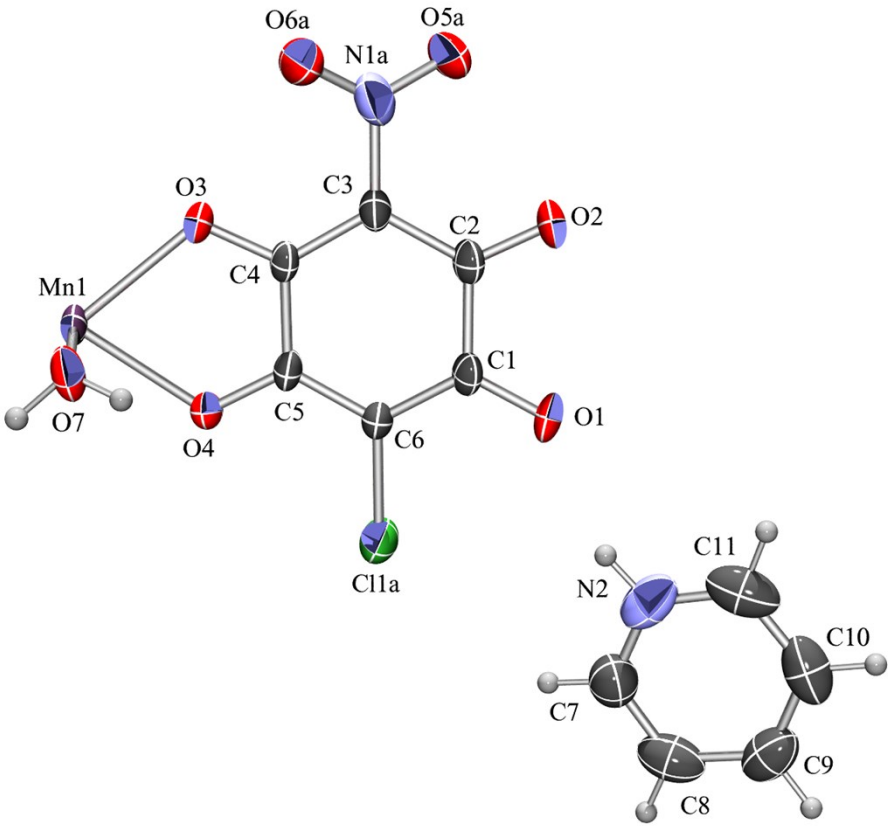
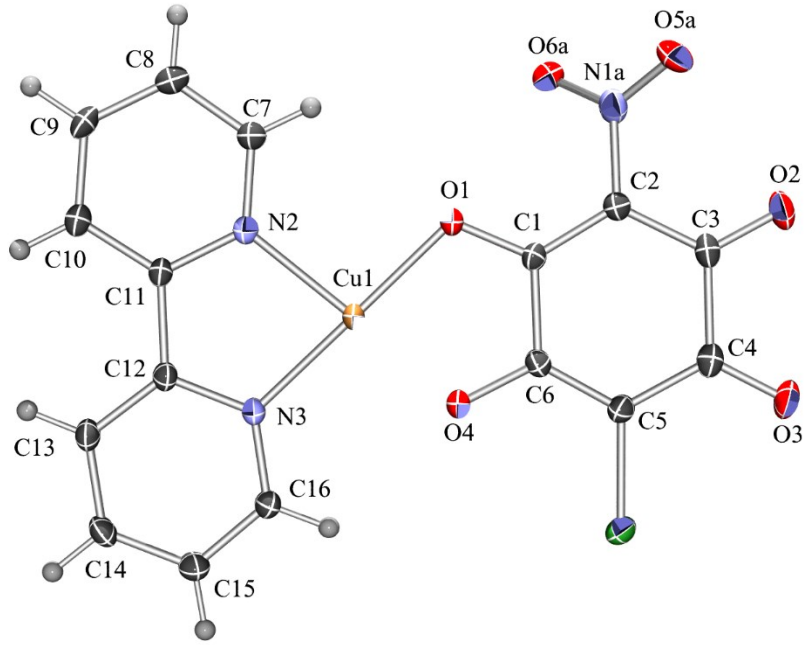
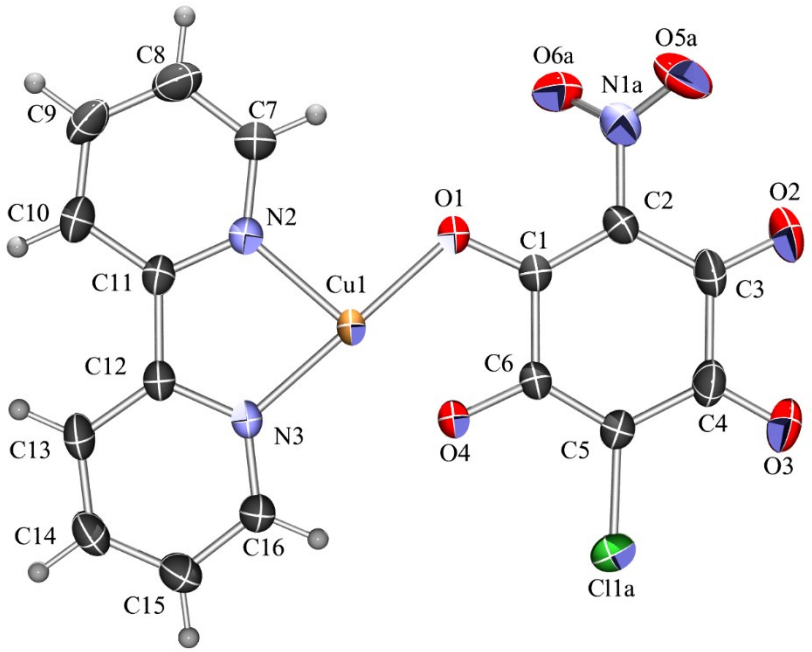


Figure S6 ORTEP-3 drawing of the asymmetric unit of **6**. Displacement ellipsoids are drawn for the probability of 50 % and hydrogen atoms are shown as spheres of arbitrary radii.



a)



b)

Figure S7 ORTEP-3 drawing of the asymmetric unit of **7** at a) 100 K and b) room temperature. Displacement ellipsoids are drawn for the probability of 50 % and hydrogen atoms are shown as spheres of arbitrary radii.

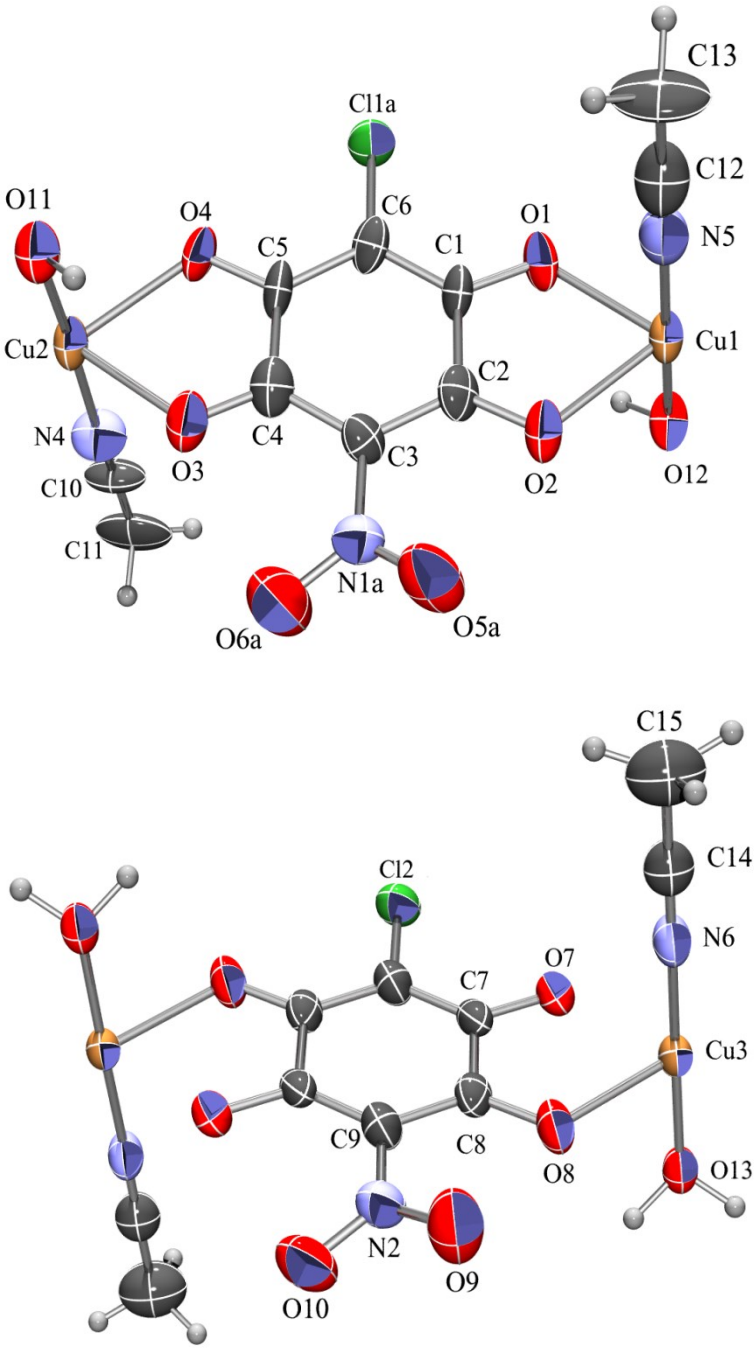


Figure S8 ORTEP-3 drawing of two symmetry-independent polymeric chains in **8**. The chain above has a molecular symmetry *C*s, and the one below has a molecular symmetry C_{2h}. Displacement ellipsoids are drawn for the probability of 50 % and hydrogen atoms are shown as spheres of arbitrary radii.

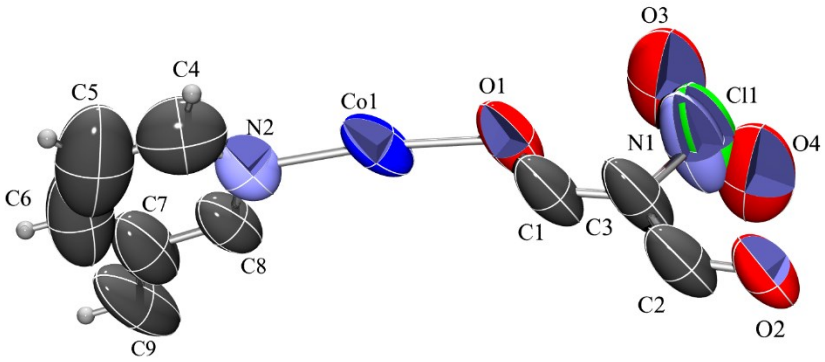


Figure S9 ORTEP-3 drawing of the asymmetric unit of **9**. Ethanol molecule has been omitted for clarity. Displacement ellipsoids are drawn for the probability of 50 % and hydrogen atoms are shown as spheres of arbitrary radii.

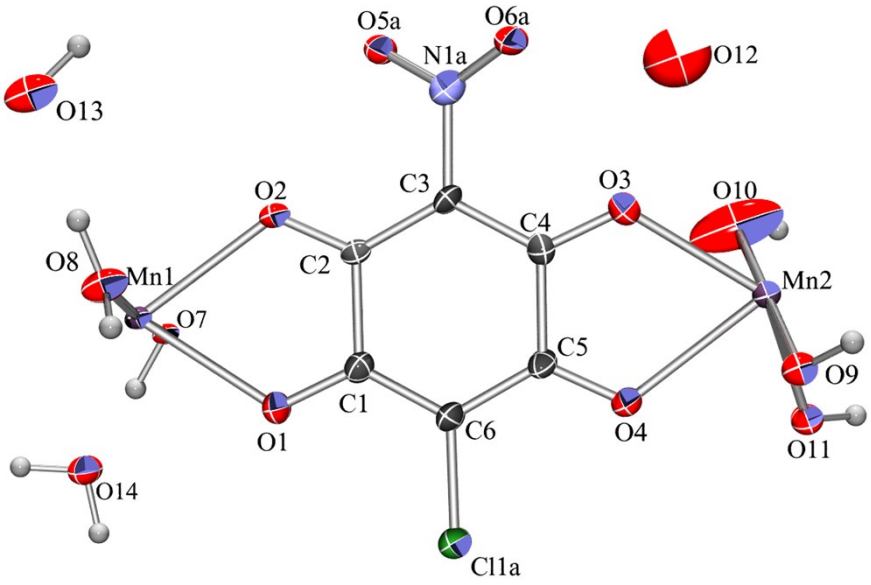


Figure S10 ORTEP-3 drawing of the asymmetric unit of **10**. Displacement ellipsoids are drawn for the probability of 50 % and hydrogen atoms are shown as spheres of arbitrary radii.

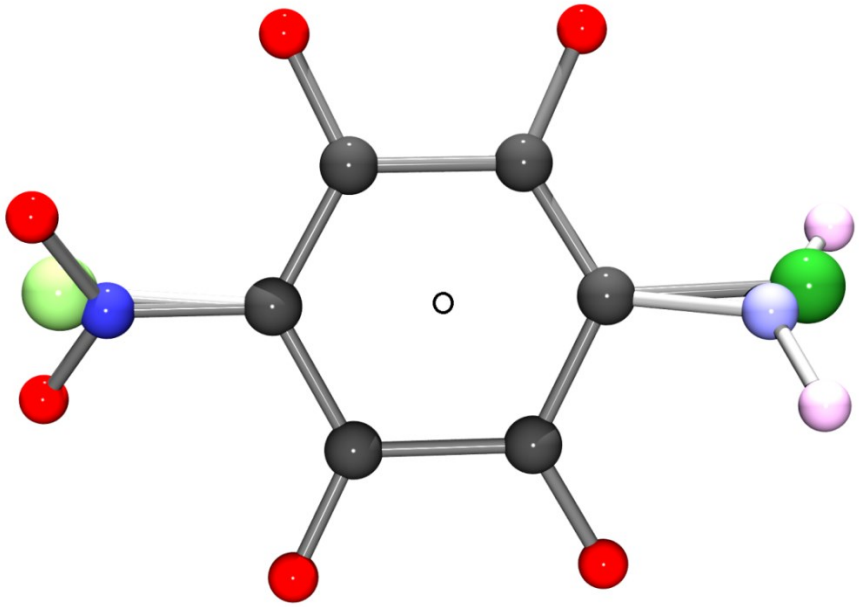


Figure S11 Orientational disorder of nitrochloranilate dianion found in structures **4 - 10**. The minor component (i.e. centrosymmetrically related molecule) has been drawn in lighter shades, and inversion centre has been indicated as an open circle.

Table S1 Bond lengths in the nitrochloranilate dianion (Å) in compounds **4**–**8**, **9** and **10**.

Bond	**4**	**5**	**6**	**7_RT**	**7_100K**	**9**	**10**
C1–C2	1.539(3)	1.545(4)	1.523(10)	1.513(3)	1.513(4)	1.559(2)	1.551(7)
C2–C3	1.387(4)	1.414(3)	1.426(9)	1.363(3)	1.367(4)	1.408(3)	1.429(9)
C3–C4	1.410(4)	1.386(3)	1.410(9)	1.443(3)	1.441(3)	1.383(2)	1.408(9)
C4–C5	1.545(4)	1.540(3)	1.509(9)	1.555(4)	1.561(4)	1.559(2)	1.535(8)
C5–C6			1.387(9)	1.431(3)	1.437(4)		1.419(9)
C6–C1			1.415(9)	1.388(3)	1.385(3)		1.398(9)
C1–O1			1.243(8)	1.269(2)	1.275(3)		1.249(8)
C2–O2	1.256(3)	1.229(3)	1.225(8)	1.289(2)	1.291(3)	1.240(2)	1.215(7)
C4–O3	1.236(4)	1.251(3)	1.259(8)	1.215(3)	1.220(3)	1.229(2)	1.234(8)
C5–O4			1.265(7)	1.218(3)	1.222(3)		1.233(7)
C3–Cl1A	1.738(7)	1.746(3)	1.70(4)	1.739(2)	1.740(3)	1.703(2)	1.675(11)
C6–N1A			1.49(6)	1.425(5)	1.436(5)		1.501(18)
N1A–O5A			1.41(8)	1.201(4)	1.209(4)		1.21(2)
N1A–O6A			0.97(9)	1.246(4)	1.251(4)		1.19(2)
C6–Cl1B			1.730(9)	1.830(13)	1.821(14)		1.698(7)
C3–N1B	1.458(16)	1.410(11)	1.49(5)	1.42(3)	1.45(3)	1.534(3)	1.50(3)
N1B–O5B	1.237(18)	1.165(14)	1.21(7)	1.18(4)	1.18(4)	1.178(4)	1.21(3)
N1B–O6B	1.181(15)	1.201(14)	1.18(5)	1.14(4)	1.16(4)	1.172(5)	1.21(3)

Table S2 Geometric parameters of the metal coordination spheres (Å, º). Symmetry operators: (*i*) 1−*x*, −*y*, −*z*; (*ii*) *x*, −1+*y*, *z*; (*iii*) *x*, *y*, −1+*z*; (*iv*) *x*, *y*, 1+*z*; (*v*) *x*, 1+*y*, *z*; (*vi*) 3/2−*x*, −1/2+*y*,1/2−*z*; (*vii*) 1/2+*x*, 1/2−*y*, 1/2+*z*; (*viii*) −1+*x*, *y*, *z*; (*ix*) 1/2−*x*, −1/2+*y*, 1/2−*z*; (*x*) 1−*x*, *y*, 3/2−*z*; (*xi*) 1−*x*, *y*, 1/2−*z*; (*xii*) −*x*, 2−*y*, 1−*z*; (*xiii*) −*x*, 1−*y*, −*z*; (*xiv*) 1−*x*, 1−*y*, −*z*; (*xv*) 3/2−*x*, 3/2−*y*, 1−*z*; (*xvi*) −1/2+*x*, 3/2−*y*, −1/2+*z*; (*xvii*) 1−*x*, *y*, 1−*z*; (*xviii*) *x*, −*y*, *z*; (*xix*) *x*, 1−*y*, *z*.

2				**3**			
Na1–O2	2.3642(15)	Na2–O1	2.3227(16)	K1–O1	2.8165(18)	K2–Cl1	3.2017(8)
Na1–O5	2.3148(18)	Na2–O3^{ii}	2.3680(16)	K1–O2	2.7454(17)	K2–O1	2.697(2)
Na1–O7	2.3317(16)	Na2–O4^{ii}	2.3929(16)	K1–O8	2.885(3)	K2–O8	2.681(2)
Na1–O8	2.3621(17)	Na2–O7^{iv}	2.3658(16)	K1–O2^{vi}	2.8662(19)	K2–O5^{viii}	2.721(2)
Na1–O8^{i}	2.4216(16)	Na2–O9	2.3456(16)	K1–O5^{vi}	2.8960(19)	K2–O7^{ix}	2.937(3)
Na1–O9^{iii}	2.4256(16)	O1–Na2–O9	107.53(6)	K1–O4^{i}	2.9075(19)	K2–O6^{i}	2.852(3)
O2–Na1–O5	69.25(6)	O1–Na2–O7^{iv}	109.36(6)	K1–O4^{vii}	2.755(2)	Cl1–K2–O1	60.27(4)
O2–Na1–O9^{iii}	166.74(6)	O9–Na2–O7^{iv}	84.13(5)	O1–K1–O2	56.74(5)	Cl1–K2–O8	135.17(7)
O5–Na1–O8	166.85(6)	O4^{ii}–Na2–O7^{iv}	95.87(6)	O1–K1–O8	71.12(6)	Cl1–K2–O5^{viii}	86.83(4)
O7–Na1–O8	92.74(6)	C4–O3– Na2^{v}	121.58(12)	O1–K1–O2^{vi}	149.98(6)	Cl1–K2–O7^{ix}	139.91(5)
O8–Na1–O9^{iii}	84.07(6)	O1–Na2–O3^{ii}	87.26(5)	O1–K1–O5^{vi}	134.68(6)	Cl1–K2–O6^{i}	72.06(5)
Na1–O7–Na2^{iii}	96.21(6)	O9–Na2–O3^{ii}	115.44(6)	O1–K1–O4^{i}	81.02(5)	O1–K2–O8	76.15(7)
O5–Na1–O6	121.82(16)	O3^{ii}–Na2–O4^{ii}	66.14(5)	O1–K1–O4^{vii}	121.52(6)	O1–K2–O5^{viii}	144.66(6)
Na1–C3–C2	119.54(15)	Na2–O1–C1	145.34(12)	O2–K1–O8	122.16(7)	O1–K2–O7^{ix}	149.20(7)
O2–Na1–O7	109.82(6)	C5–O4–Na2^{v}	120.05(12)	O2–K1–O2^{vi}	115.49(5)	O1–K2–O6^{i}	91.05(6)
O2–Na1–O8^{i}	86.31(5)	O1–Na2–O4^{ii}	153.26(6)	O2–K1–O5^{vi}	168.58(6)	O8–K2–O5^{viii}	131.13(8)
O5–Na1–O9^{iii}	109.06(6)	O9–Na2–O4^{ii}	83.10(5)	O2–K1–O4^{i}	76.14(6)	O8–K2–O7^{ix}	83.92(8)
O7–Na1–O9^{iii}	83.11(5)	O3^{ii}–Na2–O7^{iv}	149.90(6)	O2–K1–O4^{vii}	73.03(5)	O8–K2–O6^{i}	121.53(8)
O8–Na1–O8^{i}	93.49(6)	Na2–O9–Na1^{iv}	94.24(5)	O8–K1–O2^{vi}	122.24(6)	O5^{viii}–K2–O7^{ix}	65.36(7)
Na1–O8–Na1^{i}	86.52(5)			O8–K1–O5^{vi}	67.97(6)	O5^{viii}–K2–O6^{i}	90.45(6)
O2–Na1–O8	97.83(6)			O8–K1–O4^{i}	120.78(7)	O7^{ix}–K2–O6^{i}	79.54(7)
O5–Na1–O7	89.61(6)			O8–K1–O4^{vii}	123.23(7)	K2–Cl1–C6	103.06(7)
O5–Na1–O8^{i}	88.22(6)			O2^{vi}–K1–O5^{vi}	55.12(5)	K2–O1–C1	132.64(15)
O7–Na1–O8^{i}	161.73(6)			O2^{vi}–K1–O4^{i}	69.06(5)	K1–O8–K2	102.92(8)
O9^{iii}–Na1–O8^{i}	80.47(5)			O2^{vi}–K1–O4^{vii}	76.01(6)		
Na1–O2–C2	135.30(12)			O5^{vi}–K1–O4^{i}	103.82(6)		
Na1–O5–Na1	144.23(13)			O5^{vi}–K1–O4^{vii}	97.20(5)		
				O4^{i}–K1–O4^{vii}	115.94(6)		
				K1–O1–K2	104.34(6)		
				K1–O1–C1	123.02(15)		
				K1–O2–C2	126.17(15)		

4		**5**		**6**	
Ni1–O1	2.067(2)	Cu1–O1	2.1749(17)	Mn1–O3	2.191(5)
Ni1–N2	2.075(2)	Cu1–N2	2.1541(19)	Mn1–O4	2.147(5)
Ni1–N3	2.077(2)	Cu1–N3	2.004(2)	Mn1–O7	2.183(6)
O1–Ni1–N2	169.78(7)	Cu1–O1^{xi}	2.1749(17)	O3–Mn1–O4	74.50(18)
O1–Ni1–N3	93.68(8)	Cu1–N2^{xi}	2.1541(19)	O3–Mn1–O7	91.7(2)
O1–Ni1–O1^{x}	78.74(8)	Cu1–N3^{xi}	2.004(2)	O3–Mn1–O3^{xii}	180.00
O1–Ni1–N2^{x}	94.44(8)	O1–Cu1–N2	94.08(7)	O3–Mn1–O4^{xii}	105.50(18)
O1–Ni1–N3^{x}	91.77(8)	O1–Cu1–N3	92.35(7)	O3–Mn1–O7^{xii}	88.3(2)
N2–Ni1–N3	78.80(8)	O1–Cu1–O1^{xi}	75.08(7)	O4–Mn1–O7	89.4(2)
N2–Ni1–O1^{x}	94.44(8)	O1–Cu1–N2^{xi}	166.31(7)	O4–Mn1–O3^{xii}	105.50(18)
N2–Ni1–N2^{x}	93.28(8)	O1–Cu1–N3^{xi}	91.86(7)	O4–Mn1–O4^{xii}	180.00
N2–Ni1–N3^{x}	96.30(8)	N2–Cu1–N3	80.09(8)	O4–Mn1–O7^{xii}	90.6(2)
N3–Ni1–O1^{x}	91.77(8)	N2–Cu1–O1^{xi}	166.31(7)	O7–Mn1–O3^{xii}	88.3(2)
N3–Ni1–N2^{x}	96.30(8)	N2–Cu1–N2^{xi}	97.79(7)	O7–Mn1–O4^{xii}	90.6(2)
N3–Ni1–N3^{x}	172.94(8)	N2–Cu1–N3^{xi}	96.39(8)	O7–Mn1–O7^{xii}	180.00
O1^{x}–Ni1–N2^{x}	169.78(7)	N3–Cu1–O1^{xi}	91.86(7)	Mn1–O3–C4	115.8(4)
O1^{x}–Ni1–N3^{x}	93.68(8)	N3–Cu1–N2^{xi}	96.39(8)	Mn1–O4–C5	116.4(4)
N2^{x}–Ni1–N3^{x}	78.80(8)	N3–Cu1–N3^{xi}	174.69(7)		
Ni1–O1–C1	115.08(17)	O1^{xi}–Cu1–N2^{xi}	94.08(7)		
Ni1–N2–C4	126.44(17)	O1^{xi}–Cu1–N3^{xi}	92.35(7)		
Ni1–N2–C8	114.94(17)	N2^{xi}–Cu1–N3^{xi}	80.09(8)		
Ni1–N3–C9	115.22(17)	Cu1–O1–C1	116.08(15)		
Ni1–N3–C13	125.41(18)	Cu1–N2–C4	131.83(18)		
		Cu1–N2–C15	110.29(15)		
		Cu1–N3–C13	126.61(16)		
		Cu1–N3–C14	115.02(16)		

9		**10**			
Co1–O1	2.087(11)	Mn1–O1	2.242(5)	Mn2–O3	2.266(5)
Co1–N2	2.046(13)	Mn1–O2	2.316(5)	Mn2–O4	2.368(5)
Co1–O2^{xv}	2.064(10)	Mn1–O7	2.242(5)	Mn2–O9	2.159(6)
O1–Co1–N2	173.4(5)	Mn1–O8	2.106(6)	Mn2–O10	2.141(9)
O1–Co1–O2^{xv}	77.2(4)	Mn1–O7^{xvii}	2.310(5)	Mn2–O11	2.180(7)
N2–Co1–N2^{xi}	80.3(5)	Mn1–O1^{xviii}	2.242(5)	Mn2–O3^{xix}	2.266(5)
O1^{xi}–Co1–N2^{xi}	173.4(5)	Mn1–O2^{xviii}	2.316(5)	Mn2–O4^{xix}	2.368(5)
N2^{xi}–Co1–O2^{xv}	90.9(4)	O1–Mn1–O2	69.29(15)	O2–Mn2–O4	67.95(15)
Co1–O1–C1	117.8(11)	O1–Mn1–O7	87.67(16)	O3–Mn2–O9	99.39(19)
O1–Co1–O1^{xi}	89.2(4)	O1–Mn1–O8	97.08(18)	O3–Mn2–O10	80.5(2)
O1–Co1–O2^{xvi}	94.7(4)	O1–Mn1–O7^{xvii}	140.19(13)	O3–Mn2–O11	138.42(14)
N1–Co1–O2^{xv}	97.8(4)	O1–Mn1–O1^{xviii}	75.66(18)	O3–Mn2–O3^{xix}	76.89(18)
C2–O2– Co1^{xv}	115.6(10)	O1–Mn1–O2^{xviii}	144.80(16)	O3–Mn2–O4^{xix}	143.12(16)
O1–Co1–N2^{xi}	95.5(5)	O2–Mn1–O7	93.97(11)	O4–Mn2–O9	76.41(12)
N2–Co1–O1^{xi}	95.5(5)	O2–Mn1–O8	84.30(11)	O4–Mn2–O10	103.62(13)
N2–Co1–O2^{xvi}	90.9(4)	O2–Mn1–O7^{xvii}	74.17(11)	O4–Mn2–O11	78.18(10)
O1^{xi}–Co1–O2^{xvi}	77.2(4)	O2–Mn1–O1^{xviii}	144.80(16)	O4–Mn2–O3^{xix}	143.12(16)
O2^{xv} –Co1–O2^{xvi}	168.7(4)	O2–Mn1–O2^{xviii}	145.28(14)	O4–Mn2–O4^{xix}	141.86(15)
Co1–N2–C8	113.4(10)	O7–Mn1–O8	174.0(2)	O9–Mn2–O10	179.9(3)
		O7–Mn1–O7^{xvii}	79.50(18)	O9–Mn2–O11	95.2(3)
		O7–Mn1–O1^{xviii}	87.67(16)	O9–Mn2–O3^{xix}	99.39(19)
		O7–Mn1–O2^{xviii}	93.97(11)	O9–Mn2–O4^{xix}	76.41(12)
		O8–Mn1–O7^{xvii}	94.5(2)	O10–Mn2–O11	85.0(3)
		O8–Mn1–O1^{xviii}	97.08(18)	O10–Mn2–O3^{xix}	80.5(2)
		O8–Mn1–O2^{xviii}	84.30(11)	O10–Mn2–O4^{xix}	103.62(13)
		O7^{xvii}–Mn1–O1^{xviii}	140.19(13)	O11–Mn2–O3^{xix}	138.42(14)
		O7^{xvii}–Mn1–O2^{xviii}	74.17(11)	O11–Mn2–O4^{xix}	78.18(10)
		O1^{xviii}–Mn1–O2^{xviii}	69.29(15)	O3^{xix}–Mn2–O4^{xix}	67.95(15)
		Mn1–O1–C1	121.3(4)	Mn2–O3–C4	121.3(4)
		Mn1–O2–C2	119.3(4)	Mn2–O4–C5	117.9(4)
		Mn1–O7–Mn1^{xvii}	100.51(19)		

	7_RT	**7_100K**
Cu1–O1	1.9370(15)	1.9387(16)
Cu1–O2	1.9329(16)	1.9363(18)
Cu1–N2	1.9626(18)	1.9651(18)
Cu1–N3	1.9639(17)	1.9618(18)
Cu1–O6A^{xiii}	2.5934(19)	2.5415(18)
Cu1–O2^{xiv}	2.8871(17)	2.8174(17)
O1–Cu1–O2	84.19(6)	84.04(7)
O1–Cu1–N2	96.80(7)	97.00(7)
O1–Cu1–N3	176.44(7)	176.36(7)
O1–Cu1–O6A^{xiii}	92.96(6)	92.10(6)
O1–Cu1–O2^{xiv}	95.20(6)	94.72(6)
O2–Cu1–N2	176.63(7)	176.45(7)
O2–Cu1–N3	96.78(7)	96.77(7)
O2–Cu1–O6A^{xiii}	82.80(6)	82.22(7)
O2–Cu1–O2^{xiv}	86.96(6)	86.99(6)
N2–Cu1–N3	82.43(7)	82.40(8)
N2–Cu1–O6A^{xiii}	100.36(7)	101.11(7)
N2–Cu1–O2^{xiv}	89.73(6)	89.55(6)
N3–Cu1–O6A^{xiii}	83.77(7)	84.51(7)
N3–Cu1–O2^{xiv}	88.28(6)	88.86(6)
O6A^{xiii}–Cu1–O2^{xiv}	166.18(5)	166.56(6)
Cu1–O1–C1	112.69(13)	112.83(15)
Cu1–O2–C2	111.80(13)	111.85(16)
Cu1–O2– Cu1^{xiv}	93.04(6)	93.01(7)
C2–O2– Cu1^{xiv}	104.14(11)	104.20(14)
N1A–O6A– Cu1^{xiii}	115.8(2)	114.0(2)
Cu1–N2–C7	125.28(14)	125.18(16)
Cu1–N2–C11	114.56(13)	114.62(15)
Cu1–N3–C12	114.53(13)	114.79(15)
Cu1–N3–C16	125.31(15)	125.25(15)

Purity of the samples checked by powder X-ray diffraction

PXRD experiments were performed on an Xcalibur Nova R single-crystal diffractometer using microfocus Cu*K*α radiation (beam width 0.3 x 0.3 mm) and a Ruby CCD detector. The samples were placed in a glass capillary with internal diameter of 0.3 mm and wall thickness of 0.01 mm, and measurements were done in a transmission geometry. The raw diffractometer data were processed by *CrysAlis PRO* program package.

Results of PXRD experiments are shown in Figs. S12-S18. It is evident that the samples are rather poorly crystalline, and it seems that the bulk is in most cases amorphous. Compound **10** is almost all amorphous, as it produced no diffraction pattern at all.

Samples **2** and **5** contain a large amount of sodium chloride (crystals of which are visible under a loupe), while the bulk of sample **3** is potassium hydrogen carbonate (crystals of compound **3** are unstable hydrates, which decompose within weeks). Samples **4**, **7** and **9** are relatively pure compounds **4**, **7** and **9**, while sample **6** contains, besides compound **6**, at least one unidentified crystalline substance (however, no single crystals of that phase have been found).

PXRD of compounds **1** and **8** wasn't measured, because only a few single crystals were isolated of these compounds were isolated, and was therefore no bulk samples. In the case of **1** the crystals were grown by addition of *conc*. HCl to solid sodium nitrochloranilate (compound **2**); the crystals are not stable in the acidic medium, so most of them decomposed quckly. Of compound **8** only a handful of single crystals were grown on walls of a test tube; the rest of the sample was liquid with a little amorphous precipitate.

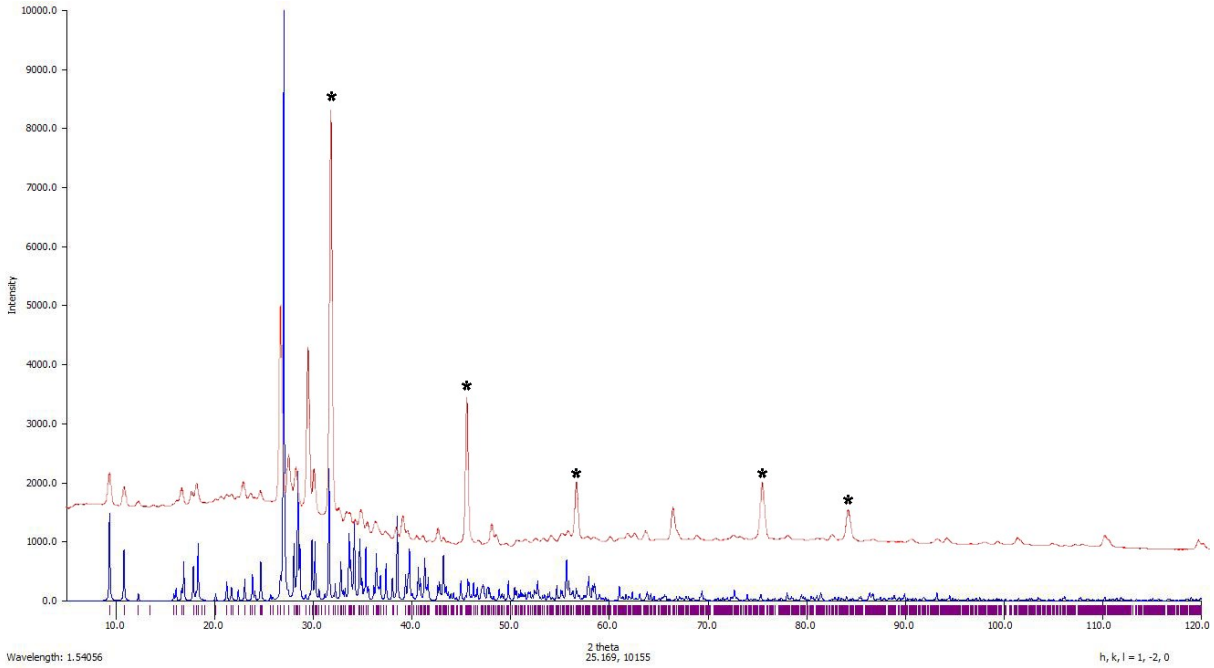


Figure S12 Comparison of experimental (red) and calculated powder diffraction patterns of compound **2**. Diffraction maxima marked by an asterisk (*) belong to sodium chloride.

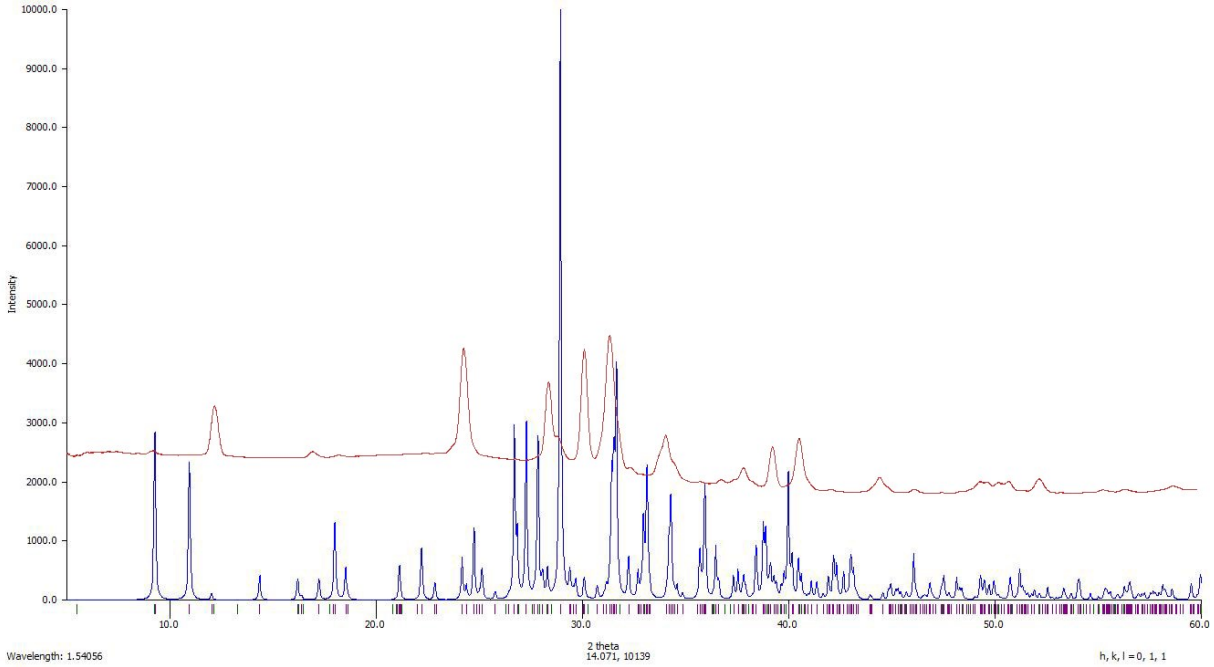


Figure S13 Comparison of experimental (red) and calculated powder diffraction patterns of compound **3**. Diffraction maxima of the experimental sample correspond to potassium hydrogen carbonate, while the crystals of compound **3** have decomposed.

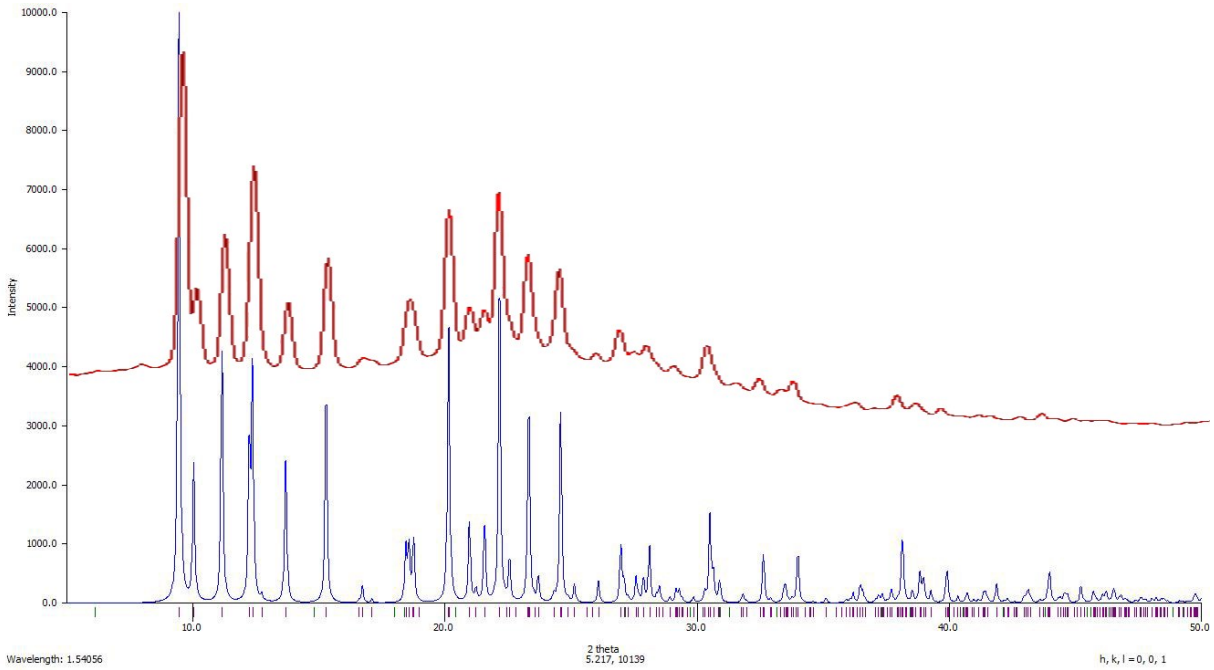


Figure S14 Comparison of experimental (red) and calculated powder diffraction patterns of compound **4**.

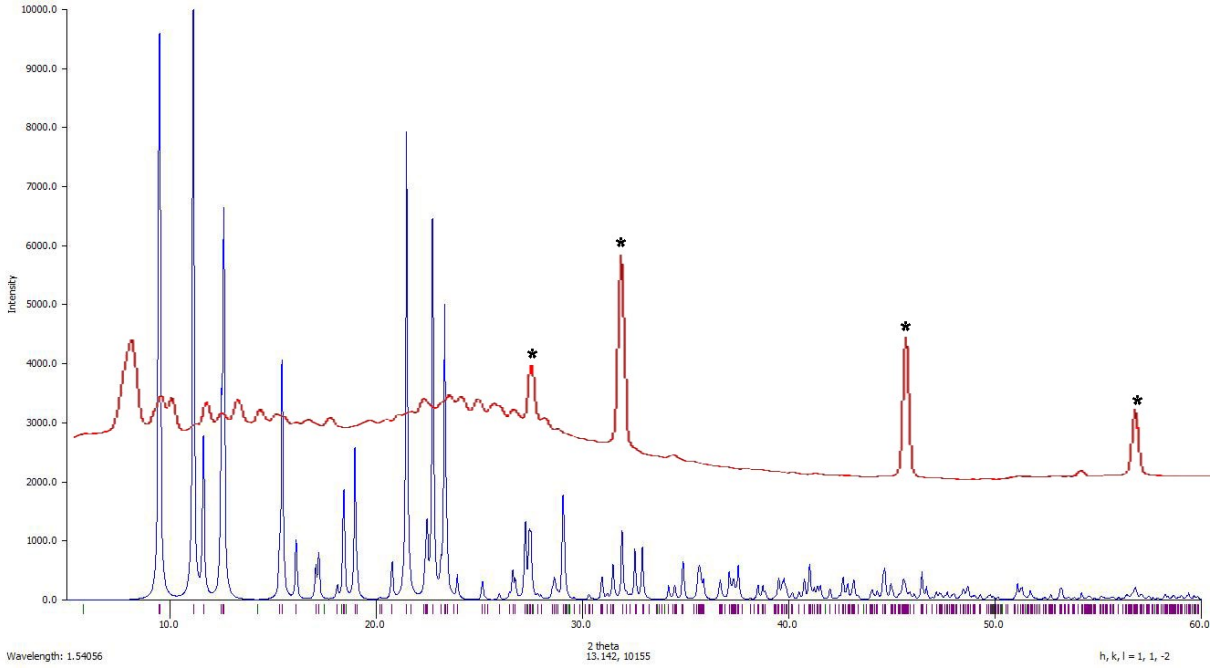


Figure S15 Comparison of experimental (red) and calculated powder diffraction patterns of compound **5**. Diffraction maxima marked by an asterisk (*) belong to sodium chloride.

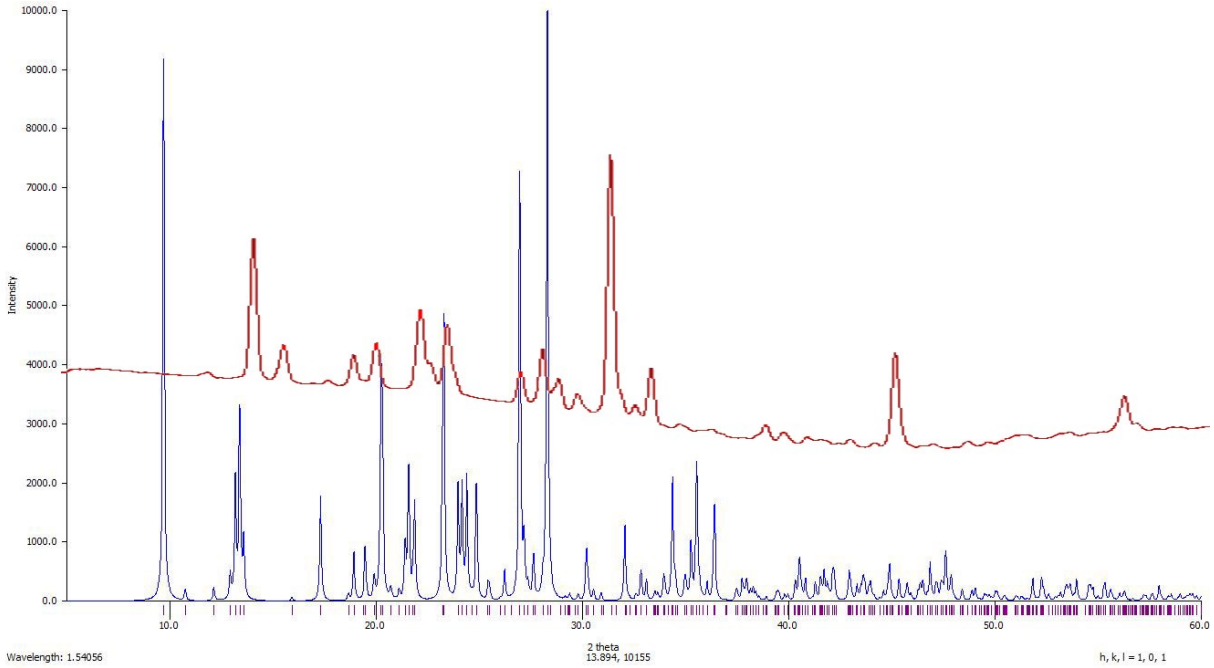


Figure S16 Comparison of experimental (red) and calculated powder diffraction patterns of compound **6**.

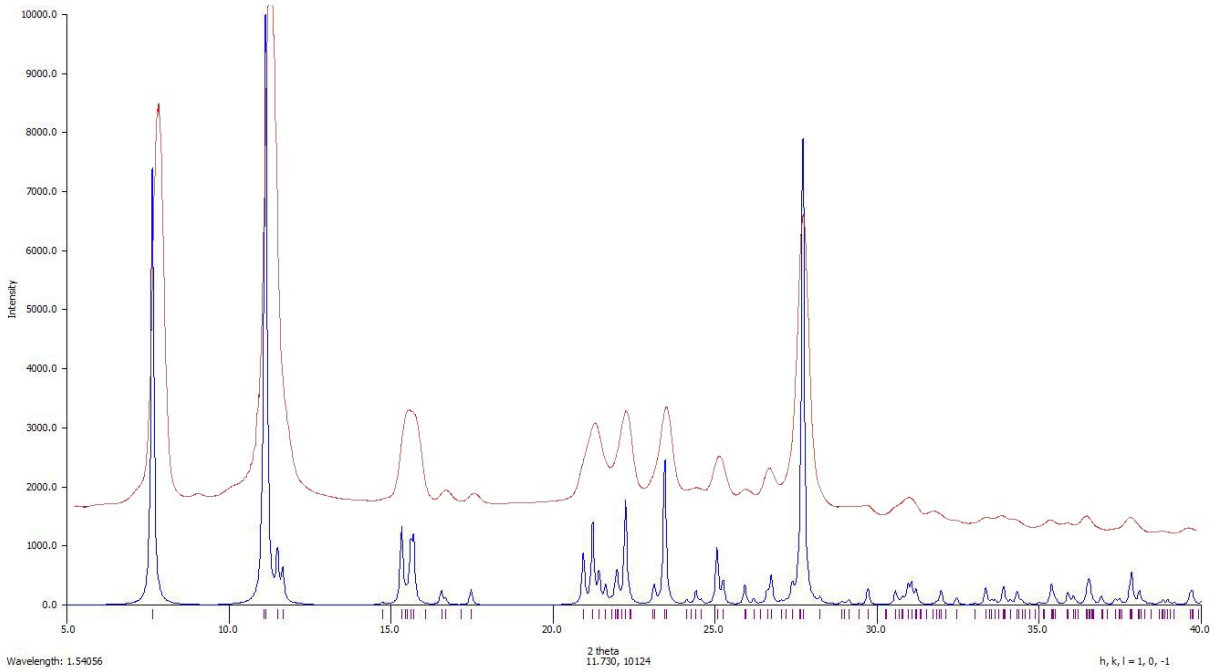


Figure S17 Comparison of experimental (red) and calculated powder diffraction patterns of compound **7**.

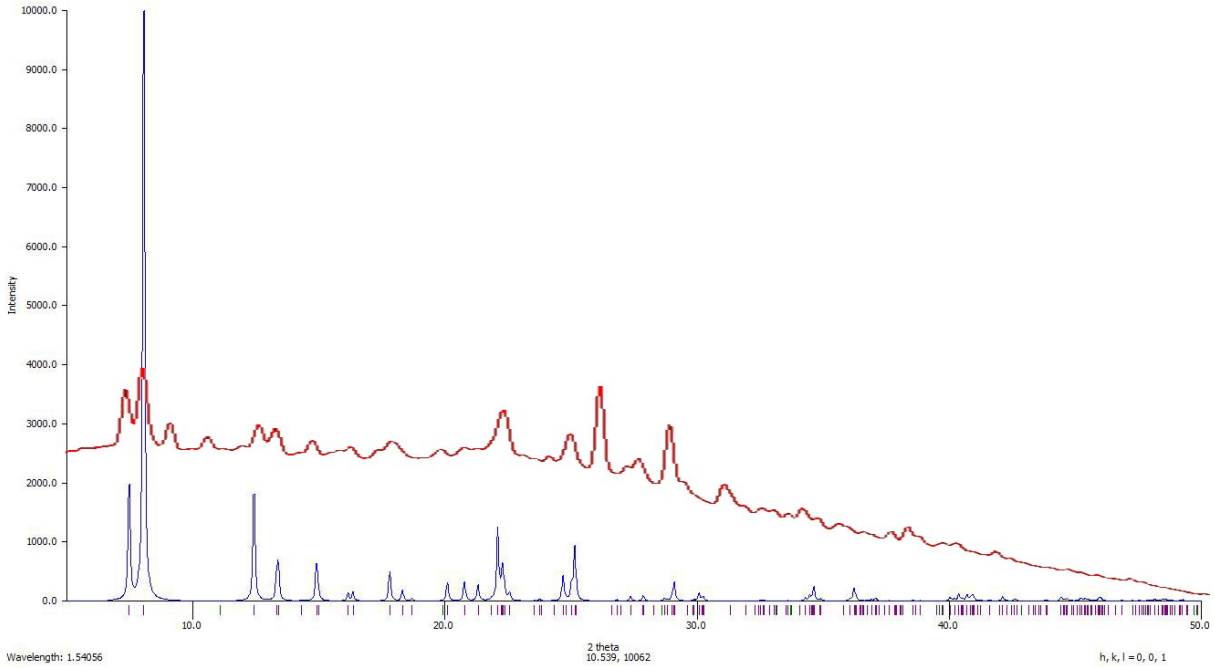


Figure S18 Comparison of experimental (red) and calculated powder diffraction patterns of compound **9**.