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Supporting information for article:

Novel first-row transition-metal phosphates: hydrothermal synthesis and crystal structures

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Table S1 Experimental details

Experiments were carried out at 293 K with Mo *K*α radiation using an Oxford Diffraction Xcalibur diffractometer with a Sapphire3 CCD-detector. Data collection was based on ω scans. Data reduction was performed with *CrysAlis PRO* 1.171.39.46 (Rigaku Oxford Diffraction, 2018). Absorption was corrected by numerical methods based on gaussian integration over a multifaceted crystal model for both data sets. Refinement (with 0 restraints) was carried out on F^2. Extinction was applied using *SHELXL2018*/3 (Sheldrick 2015b), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$.

	(I)	(II)
	Crystal data	
Chemical formula	$Na_2CuNiP_2O_8$	$Mn_2CuP_2O_8$
M_r	358.17	363.36
Crystal system, space group	Monoclinic, $P2_1/n$	Triclinic, $P\bar{1}$
a, *b*, *c* (Å)	5.1300 (1), 8.6729 (2), 6.8473 (2)	4.8292 (5), 5.4051 (5), 6.5968 (6)
α, β, γ (°)	90, 97.104 (3), 90	72.716 (8), 86.579 (8), 69.064 (9)
V (Å^3)	302.31 (1)	153.35 (3)
Z	2	1
F(000)	346	173
No. of reflections for cell measurement	2144	1224
θ range (°) for cell measurement	4.6–30.5	3.2–29.8
μ (mm^{-1})	7.32	8.02
Crystal shape	Asymmetric	Flattened
Colour	Light green	Light green
Crystal size (mm)	0.15 × 0.12 × 0.09	0.10 × 0.05 × 0.05
	Data collection	
Radiation source	fine-focus sealed X-ray tube	fine-focus sealed X-ray tube

Detector resolution (pixels mm^{-1})	16.0630	16.0630
T_{min}, T_{max}	0.447, 0.605	0.600, 0.749
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4614, 863, 741	2449, 846, 723
R_{int}	0.036	0.043
θ values (°)	θ_{max} = 30.0, θ_{min} = 4.6	θ_{max} = 29.9, θ_{min} = 3.2
$(\sin\theta/\lambda)_{max}$ ($Å^{-1}$)	0.703	0.701
Range of *h*, *k*, *l*	$h = -7\rightarrow7$, $k = -12\rightarrow12$, $l = -9\rightarrow9$	$h = -6\rightarrow6$, $k = -7\rightarrow7$, $l = -9\rightarrow9$
	Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.024, 0.065, 1.13	0.032, 0.068, 1.14
No. of reflections	863	846
No. of parameters	68	62
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.026P)^2 + 0.250P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.020P)^2 + 0.006P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	< 0.001	< 0.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	0.58, −0.50	1.19, −0.81
Extinction coefficient	0.015 (2)	0.023 (4)

Computer programs: *CrysAlis PRO* 1.171.39.46 (Rigaku OD, 2018), SHELXT (Sheldrick, 2015a), *SHELXL2018*/3 (Sheldrick, 2015b), *DIAMOND* (Brandenburg, 2006), *WinGX* (Farrugia, 2012).

Table S2 Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$) for I

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.0	0.5	0.5	0.00953 (16)
Ni1	0.0	0.5	0.0	0.00901 (16)
P1	0.55035 (13)	0.31773 (8)	0.21763 (10)	0.00698 (18)
Na1	0.5394 (2)	0.35311 (14)	0.71180 (17)	0.0129 (3)

O1	0.5516 (4)	0.1372 (2)	0.2405 (3)	0.0097 (4)
O2	0.6902 (4)	0.3876 (2)	0.4086 (3)	0.0110 (4)
O3	0.7043 (4)	0.3521 (2)	0.0458 (3)	0.0120 (4)
O4	0.2702 (4)	0.3796 (2)	0.1928 (3)	0.0107 (4)

Table S3 Atomic displacement parameters (Å^2) for I

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0097 (3)	0.0084 (3)	0.0095 (3)	−0.00294 (17)	−0.00285 (18)	0.00193 (17)
Ni1	0.0085 (3)	0.0094 (3)	0.0090 (3)	−0.00042 (18)	0.00037 (19)	0.00068 (18)
P1	0.0071 (3)	0.0065 (3)	0.0073 (3)	−0.0007 (3)	0.0002 (2)	0.0000 (2)
Na1	0.0121 (5)	0.0139 (6)	0.0126 (5)	0.0009 (4)	0.0011 (4)	−0.0001 (5)
O1	0.0123 (9)	0.0057 (9)	0.0107 (9)	0.0005 (7)	0.0001 (7)	−0.0012 (7)
O2	0.0117 (9)	0.0122 (10)	0.0090 (9)	−0.0041 (8)	0.0005 (7)	−0.0008 (7)
O3	0.0124 (9)	0.0141 (10)	0.0098 (9)	−0.0032 (8)	0.0025 (8)	0.0000 (8)
O4	0.0100 (9)	0.0092 (10)	0.0126 (9)	0.0015 (7)	0.0003 (7)	0.0005 (7)

Table S4 Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for II

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.5	0.0	0.5	0.01030 (19)
Mn1	0.21184 (13)	0.73817 (12)	0.19171 (9)	0.00965 (18)
P	0.8665 (2)	0.3392 (2)	0.28146 (15)	0.0064 (2)
O1	1.1796 (6)	0.3337 (5)	0.3316 (4)	0.0096 (5)
O2	0.7335 (5)	0.2257 (5)	0.4930 (4)	0.0073 (5)
O3	0.8902 (6)	0.1502 (5)	0.1410 (4)	0.0100 (6)
O4	0.6756 (6)	0.6372 (5)	0.1722 (4)	0.0124 (6)

Table S5 Atomic displacement parameters (Å^2) for II

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0083 (3)	0.0090 (4)	0.0134 (4)	−0.0048 (3)	−0.0019 (3)	−0.0005 (3)
Mn1	0.0118 (3)	0.0083 (3)	0.0079 (3)	−0.0027 (2)	−0.0003 (2)	−0.0020 (2)
P	0.0064 (5)	0.0072 (5)	0.0062 (4)	−0.0032 (4)	0.0006 (3)	−0.0018 (4)
O1	0.0073 (12)	0.0116 (14)	0.0111 (13)	−0.0058 (11)	0.0004 (10)	−0.0019 (11)
O2	0.0072 (12)	0.0085 (13)	0.0069 (12)	−0.0038 (10)	0.0012 (10)	−0.0025 (10)
O3	0.0115 (13)	0.0112 (14)	0.0088 (12)	−0.0036 (11)	0.0012 (10)	−0.0059 (11)
O4	0.0125 (14)	0.0098 (14)	0.0123 (14)	−0.0035 (11)	0.0016 (11)	−0.0001 (11)

Table S6 Selected geometric parameters (Å, º)

(I)			
Cu1—O2	1.9029 (19)	P1—O4	1.5239 (19)
Cu1—O2^{i}	1.9029 (19)	P1—O3	1.5251 (19)
Cu1—O1^{ii}	2.0223 (18)	P1—O2	1.5362 (19)
Cu1—O1^{iii}	2.0223 (18)	P1—O1	1.573 (2)
Cu1—O4^{iv}	2.856 (2)	Na1—O2	2.323 (2)
Cu1—O4^{xv}	2.856 (2)	Na1—O3^{viii}	2.338 (2)
Ni1—O3^{iv}	2.0406 (19)	Na1—O4^{ii}	2.351 (2)
Ni1—O3	2.0406 (19)	Na1—O1^{ix}	2.536 (2)
Ni1—O4^{v}	2.0740 (19)	Na1—O4^{x}	2.569 (2)
Ni1—O4^{vi}	2.0740 (19)	Na1—O1^{ii}	2.612 (2)
Ni1—O1^{vii}	2.1821 (19)	Na1—O2^{x}	2.624 (2)
Ni1—O1^{iii}	2.1821 (19)	Na1—O3^{ix}	2.633 (2)
O4—P1—O3	114.60 (11)	O2—P1—O1	108.21 (11)
O4—P1—O2	106.92 (11)	P1—O1—Cu1^{xi}	120.42 (11)

O3—P1—O2	110.34 (11)	P1—O1—Ni1^{xi}	128.63 (11)
O4—P1—O1	110.70 (11)	Cu1^{xi}—O1—Ni1^{xi}	108.98 (8)
O3—P1—O1	105.95 (11)		

(II)			
Cu1—O2^{xii}	1.925 (2)	Mn1—O3^{xv}	2.152 (3)
Cu1—O2	1.925 (2)	Mn1—O1^{xiii}	2.164 (3)
Cu1—O1^{xiii}	1.975 (3)	Mn1—O2^{x}	2.186 (2)
Cu1—O1^{xiv}	1.975 (3)	Mn1—O4^{xii}	2.848 (3)
Cu1—O3^{xi}	3.039 (3)	P—O4	1.514 (3)
Cu1—O3	3.039 (3)	P—O3	1.543 (3)
Mn1—O4	2.113 (3)	P—O2	1.550 (2)
Mn1—O3^{v}	2.134 (2)	P—O1	1.555 (3)
O4—P—O3	111.58 (15)	O2—P—O1	108.75 (14)
O4—P—O2	110.45 (14)	Cu1^{vi}—O1—Mn1^{vi}	125.43 (12)
O3—P—O2	108.03 (15)	Cu1—O2—Mn1^{x}	111.23 (11)
O4—P—O1	107.78 (15)	Mn1^{v}—O3—Mn1^{xvi}	100.25 (11)
O3—P—O1	110.22 (15)		

Symmetry code(s): (i) −*x*+2, −*y*+1, −*z*+1; (ii) *x*+1/2, −*y*+1/2, *z*+1/2; (iii) −*x*+3/2, *y*+1/2, −*z*+1/2; (iv) −*x*+2, −*y*+1, −*z*; (v) −*x*+1, −*y*+1, −*z*; (vi) *x*+1, *y*, *z*; (vii) *x*+1/2, −*y*+1/2, *z*−1/2; (viii) *x*, *y*, *z*+1; (ix) *x*−1/2, −*y*+1/2, *z*+1/2; (x) −*x*+1, −*y*+1, −*z*+1; (xi) −*x*+3/2, *y*−1/2, −*z*+1/2; (xii) −*x*+1, −*y*, −*z*+1; (xiii) *x*−1, *y*, *z*; (xiv) −*x*+2, −*y*, −*z*+1; (xv) *x*−1, *y*+1, *z*; (xvi) *x*+1, *y*−1, *z*.