

SUPPLEMENTARY MATERIAL

Fig S1. Observed (crosses), calculated (solid line), and difference (at the bottom) neutron diffraction (D1A, D2B, ILL) profiles of (a) $\text{Cr}(\text{PO}_3)_3$ and (b) $\text{Cr}_2\text{P}_6\text{O}_{18}$, at room temperature. Vertical marks correspond to the position of the allowed reflections for the crystallographic structures.

Table S1. Final refined positional and thermal parameters from neutron diffraction patterns (D1A, D2B) at room temperature for (a) $\text{Cr}(\text{PO}_3)_3$ and (b) $\text{Cr}_2\text{P}_6\text{O}_{18}$.

Table S2. Main interatomic distances (\AA) and angles ($^\circ$) for (a) $\text{Cr}(\text{PO}_3)_3$ and (b) $\text{Cr}_2\text{P}_6\text{O}_{18}$ at room temperature.

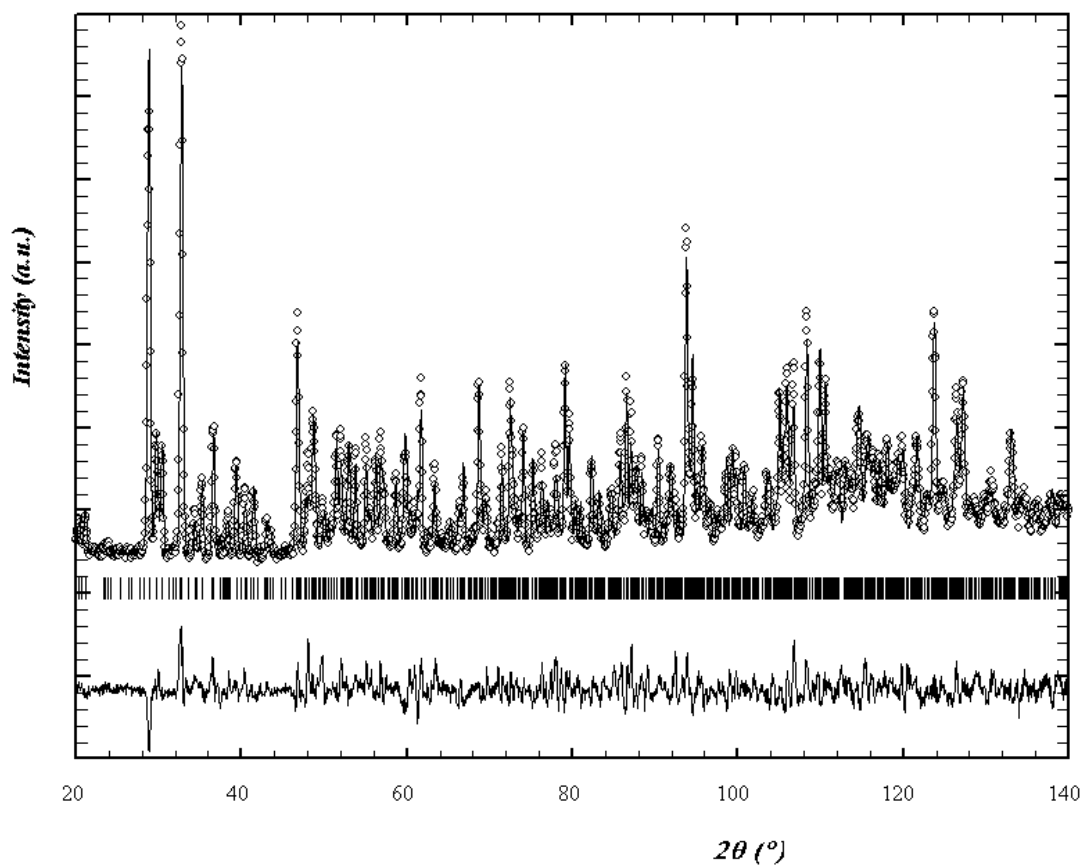


Fig S1(a)

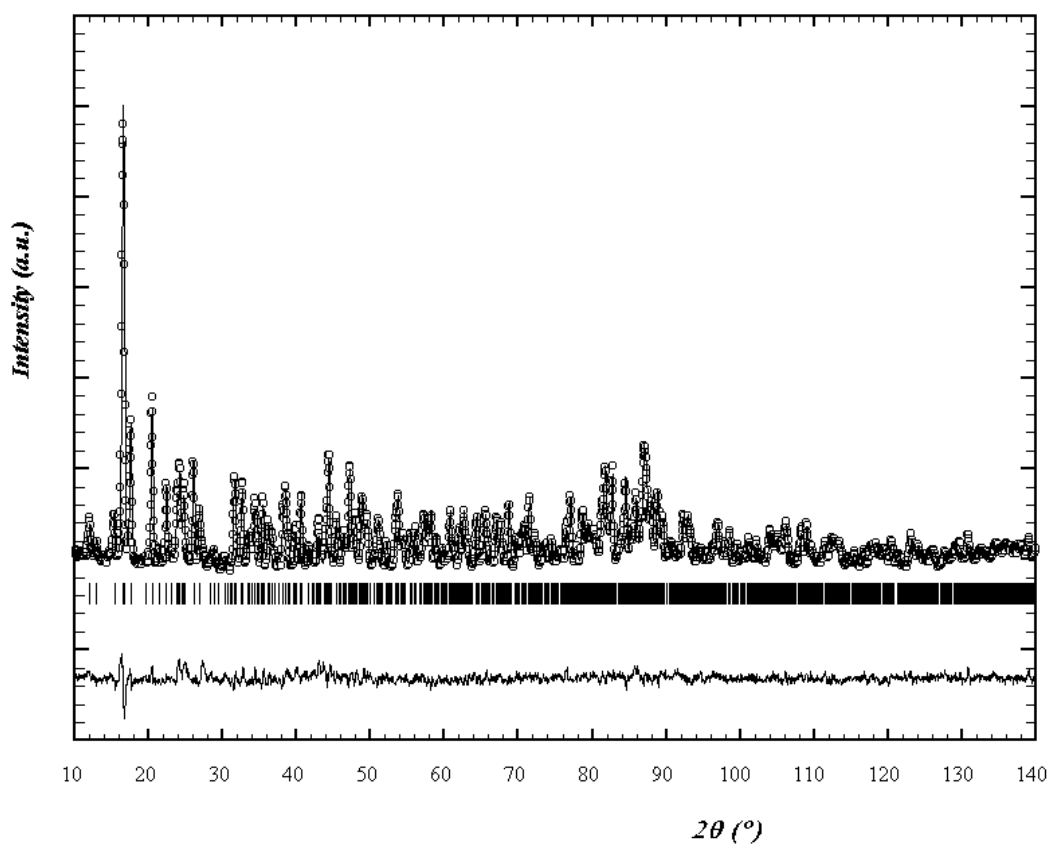


Fig S1(b)

Table S1

Cr(PO₃)₃				
Atom	x	y	z	B(Å²)
Cr(1)	0.933(1)	0.0814(7)	0.226(2)	0.68(5)
Cr(2)	0.909(1)	0.2455(7)	-0.307(2)	0.68(5)
Cr(3)	0.442(1)	0.0841(8)	-0.279(2)	0.68(5)
P(1)	0.802(1)	-0.0289(8)	-0.102(2)	0.68(5)
P(2)	0.790(1)	0.3027(8)	-0.121(2)	0.68(5)
P(3)	0.789(1)	0.3638(8)	0.375(2)	0.68(5)
P(4)	0.195(1)	0.0166(8)	-0.017(2)	0.68(5)
P(5)	0.692(1)	0.1912(8)	-0.019(2)	0.68(5)
P(6)	0.577(1)	0.0285(7)	-0.457(2)	0.68(5)
P(7)	0.658(1)	0.1436(8)	-0.574(2)	0.68(5)
P(8)	0.567(1)	0.3025(8)	0.032(2)	0.68(5)
P(9)	1.069(1)	0.1350(8)	0.036(2)	0.68(5)
O(1)	0.740(2)	0.100(1)	0.391(3)	0.68(5)
O(2)	0.777(2)	0.138(1)	1.107(3)	0.68(5)
O(3)	0.965(2)	0.111(1)	1.050(3)	0.68(5)
O(4)	0.766(2)	0.177(1)	0.588(3)	0.68(5)
O(5)	0.403(2)	0.207(1)	0.374(3)	0.68(5)
O(6)	0.493(2)	0.023(1)	0.601(3)	0.68(5)
O(7)	0.632(2)	0.101(1)	0.546(3)	0.68(5)
O(8)	0.927(2)	0.049(1)	0.428(2)	0.68(5)
O(9)	0.547(2)	0.186(1)	0.270(3)	0.68(5)
O(10)	0.785(2)	0.230(1)	0.954(3)	0.68(5)
O(11)	0.404(2)	0.130(1)	0.875(3)	0.68(5)
O(12)	0.303(2)	0.020(1)	0.654(3)	0.68(5)
O(13)	0.705(2)	0.019(1)	0.741(2)	0.68(5)
O(14)	0.574(2)	0.158(1)	0.818(3)	0.68(5)
O(15)	0.662(2)	0.240(1)	1.084(3)	0.68(5)
O(16)	0.155(2)	0.146(1)	0.691(2)	0.68(5)
O(17)	0.154(2)	0.188(1)	0.192(2)	0.68(5)
O(18)	0.309(2)	0.138(1)	0.499(2)	0.68(5)
O(19)	0.568(2)	0.046(1)	0.976(2)	0.68(5)
O(20)	0.959(2)	0.211(1)	0.542(3)	0.68(5)
O(21)	0.837(3)	-0.001(1)	1.077(3)	0.68(5)
O(22)	1.021(2)	0.171(1)	0.348(2)	0.68(5)
O(23)	1.035(2)	0.181(1)	0.882(2)	0.68(5)
O(24)	0.309(2)	0.181(1)	1.019(2)	0.68(5)
O(25)	0.280(2)	0.065(1)	0.956(3)	0.68(5)
O(26)	0.155(2)	0.071(1)	1.067(3)	0.68(5)
O(27)	0.087(2)	0.024(1)	0.325(3)	0.68(5)

Cr₂P₆O₁₈				
Atom	x	y	z	B(Å²)
Cr	0.381(1)	0.1378(7)	0.118(2)	0.73(7)
P(1)	0.0143(9)	0.1616(5)	0.209(1)	0.73(7)
P(2)	0.2909(9)	0.1128(5)	0.585(1)	0.73(7)
P(3)	0.2783(9)	-0.0445(4)	0.853(1)	0.73(7)
O(1)	0.1101(9)	0.1500(4)	0.462(1)	0.99(4)
O(2)	-0.0949(8)	0.0764(4)	0.161(1)	0.99(4)
O(3)	0.2485(9)	0.0123(4)	0.632(1)	0.99(4)
O(4)	-0.0928(9)	0.2402(4)	0.182(1)	0.99(4)
O(5)	0.1342(8)	0.1546(4)	0.068(1)	0.99(4)
O(6)	0.3530(8)	0.1617(5)	0.800(1)	0.99(4)
O(7)	0.4009(8)	0.1142(4)	0.424(1)	0.99(4)
O(8)	0.3410(8)	0.0110(4)	0.058(1)	0.99(4)
O(9)	0.3852(8)	-0.1230(4)	0.826(1)	0.99(4)

Table S2(a)

Cr(PO₃)₃					
Bond Distances Cr-O (Å)					
Cr(1)-(O2)	1.95(3)	Cr(2)-(O4)	1.98(3)	Cr(3)-(O6)	1.97(3)
Cr(1)-(O3)	2.00(3)	Cr(2)-(O5)	1.96(3)	Cr(3)-(O11)	1.98(3)
Cr(1)-(O8)	2.02(3)	Cr(2)-(O9)	1.97(3)	Cr(3)-(O12)	1.95(3)
Cr(1)-(O21)	1.95(2)	Cr(2)-(O20)	1.97(3)	Cr(3)-(O14)	1.96(3)
Cr(1)-(O22)	1.98(2)	Cr(2)-(O23)	1.95(3)	Cr(3)-(O18)	2.00(2)
Cr(1)-(O27)	1.96(3)	Cr(2)-(O24)	1.92(2)	Cr(3)-(O19)	2.04(2)
Bond Angles O-Cr-O (°)					
O(2)-Cr(1)-(O3)	92.1(3)	O(4)-Cr(2)-(O5)	102.1(2)	O(6)-Cr(3)-(O11)	168.5(2)
O(2)-Cr(1)-(O8)	94.9(2)	O(4)-Cr(2)-(O9)	173.5(2)	O(6)-Cr(3)-(O12)	91.0(2)
O(2)-Cr(1)-(O21)	91.6(2)	O(4)-Cr(2)-(O20)	92.7(2)	O(6)-Cr(3)-(O14)	99.4(2)
O(2)-Cr(1)-(O22)	84.5(2)	O(4)-Cr(2)-(O23)	93.8(2)	O(6)-Cr(3)-(O18)	95.5(2)
O(2)-Cr(1)-(O27)	174.7(2)	O(4)-Cr(2)-(O24)	95.5(2)	O(6)-Cr(3)-(O19)	98.2(2)
O(3)-Cr(1)-(O8)	172.2(2)	O(5)-Cr(2)-(O9)	83.4(2)	O(11)-Cr(3)-(O12)	84.6(2)
O(3)-Cr(1)-(O21)	89.9(2)	O(5)-Cr(2)-(O20)	165.0(2)	O(11)-Cr(3)-(O14)	85.1(2)
O(3)-Cr(1)-(O22)	84.2(2)	O(5)-Cr(2)-(O23)	87.3(2)	O(11)-Cr(3)-(O18)	94.7(2)
O(3)-Cr(1)-(O27)	83.1(2)	O(5)-Cr(2)-(O24)	92.1(2)	O(11)-Cr(3)-(O19)	71.7(2)
O(8)-Cr(1)-(O21)	93.2(2)	O(9)-Cr(2)-(O20)	81.9(2)	O(12)-Cr(3)-(O14)	169.6(2)
O(8)-Cr(1)-(O22)	93.2(2)	O(9)-Cr(2)-(O23)	89.8(2)	O(12)-Cr(3)-(O18)	85.3(2)
O(8)-Cr(1)-(O27)	89.9(2)	O(9)-Cr(2)-(O24)	80.8(2)	O(12)-Cr(3)-(O19)	95.3(2)
O(21)-Cr(1)-(O22)	172.8(2)	O(20)-Cr(2)-(O23)	89.3(2)	O(14)-Cr(3)-(O18)	94.4(2)
O(21)-Cr(1)-(O27)	86.1(2)	O(20)-Cr(2)-(O24)	88.9(2)	O(14)-Cr(3)-(O19)	82.6(2)
O(22)-Cr(1)-(O27)	97.3(2)	O(23)-Cr(2)-(O24)	107.6(2)	O(18)-Cr(3)-(O19)	166.3(2)
Bond Distances P-O (Å)					
P(1)-O(1)	1.55(3)	P(2)-O(5)	1.50(3)	P(3)-O(11)	1.51(3)
P(1)-O(8)	1.52(3)	P(2)-O(10)	1.57(2)	P(3)-O(16)	1.55(3)
P(1)-O(13)	1.53(3)	P(2)-O(17)	1.58(3)	P(3)-O(24)	1.47(3)
P(1)-O(21)	1.55(3)	P(2)-O(18)	1.50(2)	P(3)-O(25)	1.58(3)
P(4)-O(12)	1.51(2)	P(5)-O(2)	1.43(3)	P(6)-O(6)	1.49(3)
P(4)-O(25)	1.57(3)	P(5)-O(10)	1.56(3)	P(6)-O(7)	1.55(3)
P(4)-O(26)	1.57(3)	P(5)-O(14)	1.53(3)	P(6)-O(13)	1.59(3)
P(4)-O(27)	1.50(3)	P(5)-O(15)	1.53(2)	P(6)-O(19)	1.51(2)
P(7)-O(1)	1.53(4)	P(8)-O(15)	1.57(3)	P(9)-O(3)	1.51(4)
P(7)-O(4)	1.45(3)	P(8)-O(16)	1.55(2)	P(9)-O(17)	1.55(2)
P(7)-O(7)	1.57(3)	P(8)-O(20)	1.49(4)	P(9)-O(23)	1.50(3)
P(7)-O(9)	1.52(3)	P(8)-O(22)	1.52(2)	P(9)-O(26)	1.55(3)
Bond Angles O-P-O (°)					
O(1)-P(1)-O(8)	105.2(3)	O(5)-P(2)-O(10)	102.5(3)	O(11)-P(3)-O(16)	117.7(3)
O(1)-P(1)-O(13)	111.2(2)	O(5)-P(2)-O(17)	116.5(3)	O(11)-P(3)-O(24)	114.3(3)
O(1)-P(1)-O(21)	98.3(2)	O(5)-P(2)-O(18)	113.2(3)	O(11)-P(3)-O(25)	106.7(3)
O(8)-P(1)-O(13)	120.5(3)	O(10)-P(2)-O(17)	105.5(2)	O(16)-P(3)-O(24)	113.9(2)
O(8)-P(1)-O(21)	107.8(3)	O(10)-P(2)-O(18)	111.0(2)	O(16)-P(3)-O(25)	106.1(2)
O(13)-P(1)-O(21)	111.4(2)	O(17)-P(2)-O(18)	107.8(2)	O(24)-P(3)-O(25)	94.5(2)
O(12)-P(4)-O(25)	98.3(2)	O(2)-P(5)-O(10)	99.6(2)	O(6)-P(6)-O(7)	119.4(3)
O(12)-P(4)-O(26)	98.8(3)	O(2)-P(5)-O(14)	110.7(3)	O(6)-P(6)-O(13)	93.4(3)
O(12)-P(4)-O(27)	121.7(2)	O(2)-P(5)-O(15)	105.9(3)	O(6)-P(6)-O(19)	101.7(3)
O(25)-P(4)-O(26)	99.7(3)	O(10)-P(5)-O(14)	114.6(3)	O(7)-P(6)-O(13)	85.6(2)
O(25)-P(4)-O(27)	118.4(3)	O(10)-P(5)-O(15)	109.5(3)	O(7)-P(6)-O(19)	138.5(2)
O(26)-P(4)-O(27)	115.8(2)	O(14)-P(5)-O(15)	115.0(2)	O(13)-P(6)-O(19)	97.9(2)
O(1)-P(7)-O(4)	95.6(2)	O(15)-P(8)-O(16)	100.4(2)	O(3)-P(9)-O(17)	106.7(3)
O(1)-P(7)-O(7)	110.7(3)	O(15)-P(8)-O(20)	116.7(3)	O(3)-P(9)-O(23)	119.7(3)
O(1)-P(7)-O(9)	117.3(3)	O(15)-P(8)-O(22)	107.3(2)	O(3)-P(9)-O(26)	109.7(3)
O(4)-P(7)-O(7)	88.5(2)	O(16)-P(8)-O(20)	103.7(3)	O(17)-P(9)-O(23)	98.7(2)
O(4)-P(7)-O(9)	122.3(2)	O(16)-P(8)-O(22)	115.4(2)	O(17)-P(9)-O(26)	106.9(2)
O(7)-P(7)-O(9)	117.4(2)	O(20)-P(8)-O(22)	112.8(3)	O(23)-P(9)-O(26)	113.6(2)

Table S2(b)

Cr₂P₆O₁₈					
Bond Distances Cr-O (Å) and Angles O-Cr-O (°)					
Cr-(O4)	1.89(1)	O(4)-Cr-(O5)	87.6(6)	O(5)-Cr-(O9)	178.4(7)
Cr-(O5)	2.00(1)	O(4)-Cr-(O6)	90.2(6)	O(6)-Cr-(O7)	177.9(7)
Cr-(O6)	1.95(1)	O(4)-Cr-(O7)	90.1(6)	O(6)-Cr-(O8)	91.3(6)
Cr-(O7)	1.88(1)	O(4)-Cr-(O8)	176.1(7)	O(6)-Cr-(O9)	92.4(6)
Cr-(O8)	1.97(1)	O(4)-Cr-(O9)	91.5(6)	O(7)-Cr-(O8)	88.1(6)
Cr-(O9)	1.88(1)	O(5)-Cr-(O6)	88.9(6)	O(7)-Cr-(O9)	89.5(6)
		O(5)-Cr-(O7)	89.0(6)	O(8)-Cr-(O9)	91.8(6)
		O(5)-Cr-(O8)	88.8(6)		
Bond Distances P-O (Å)					
P(1)-O(1)	1.559(9)	P(2)-O(1)	1.59(1)	P(3)-O(2)	1.57(1)
P(1)-O(2)	1.560(9)	P(2)-O(3)	1.60(1)	P(3)-O(3)	1.581(9)
P(1)-O(4)	1.46(1)	P(2)-O(6)	1.486(9)	P(3)-O(8)	1.494(9)
P(1)-O(5)	1.49(1)	P(2)-O(7)	1.52(1)	P(3)-O(9)	1.522(9)
Bond Angles O-P-O (°)					
O(1)-P(1)-O(2)	102.1(7)	O(1)-P(2)-O(3)	101.5(7)	O(2)-P(3)-O(3)	101.3(7)
O(1)-P(1)-O(4)	109.4(7)	O(1)-P(2)-O(6)	107.7(7)	O(2)-P(3)-O(8)	109.3(7)
O(1)-P(1)-O(5)	109.8(7)	O(1)-P(2)-O(7)	109.3(8)	O(2)-P(3)-O(9)	109.5(7)
O(2)-P(1)-O(4)	110.4(7)	O(3)-P(2)-O(6)	110.6(7)	O(3)-P(3)-O(8)	111.3(7)
O(2)-P(1)-O(5)	105.8(7)	O(3)-P(2)-O(7)	109.2(7)	O(3)-P(3)-O(9)	106.8(7)
O(4)-P(1)-O(5)	117.8(8)	O(6)-P(2)-O(7)	117.1(8)	O(8)-P(3)-O(9)	117.2(7)