

Copper(II) fluorophosphates– Supplementary information

Edward R. Williams and Mark T. Weller

Neutron powder diffraction structural refinement

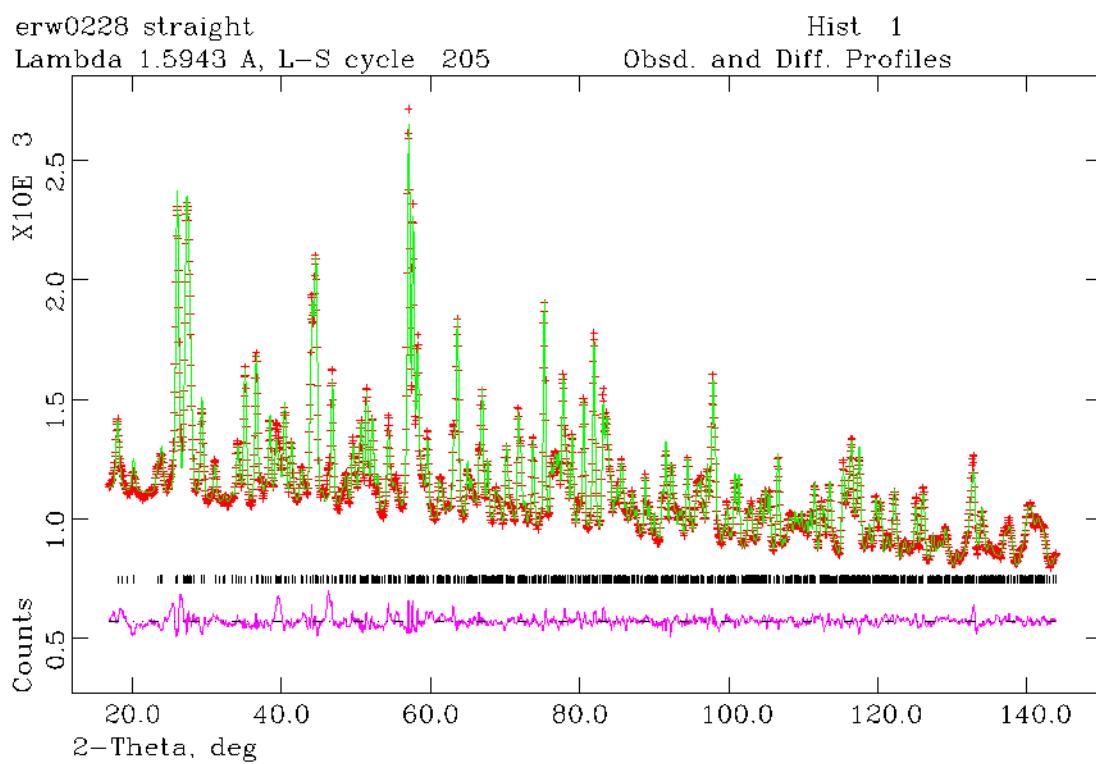


Fig. SI1 Profile fit achieved for the neutron diffraction powder pattern collected from $\text{KCu}_3(\text{PO}_3\text{F})_2(\text{PO}_2(\text{OH})_2)\text{F}_2$ at 120 K. Crosses represent the observed data, the upper green curve the calculated profile, the lower black curve the difference and the tick marks in-between the allowed reflection positions

Table SI2 Crystallographic data for $\text{KCu}_3(\text{PO}_3\text{F})_2(\text{PO}_2(\text{OH})_2)\text{F}_2$ at 120 K. Space group Cc. Lattice parameters $a=18.9897(6)$ $b=7.5038(2)$ $c=7.7687(2)$ $\beta=103.579(1)$ $^\circ$

Atom	x	y	z	$U_{\text{iso}} (\text{\AA}^2 \times 100)$
K1	0.5	0.1506(15)	0.25	1.31(24)
Cu1	0.1560(1)	0.0306(4)	0.8115(4)	0.08(6)
Cu2	0.25	-0.25	1	0.09(8)
P1	0	-0.1320(9)	0.75	0.15
P2	0.3263(2)	0.1669(6)	0.9070(7)	0.15
O1	0.0600(3)	-0.0208(5)	0.7079(6)	0.66(9)
O2	0.2625(2)	0.0583(5)	0.9343(6)	0.25
O3	0.3679(2)	0.2610(6)	1.0754(6)	0.21(8)
O4	0.3070(2)	0.2871(6)	0.7502(6)	0.48(9)
O14	-0.0335(3)	-0.2662(7)	0.5952(6)	1.31(11)
H13	0.0834(5)	0.2325(12)	0.4668(12)	3.56(20)

Final for parameters: $R(F^2)=0.0328$, $wR_p=0.0189$, $R_p=0.0140$, $\chi^2=8.114$

Additional crystal structure images. Compounds I-X1

Compound I - $M_2Cu_3(PO_3F)_4$

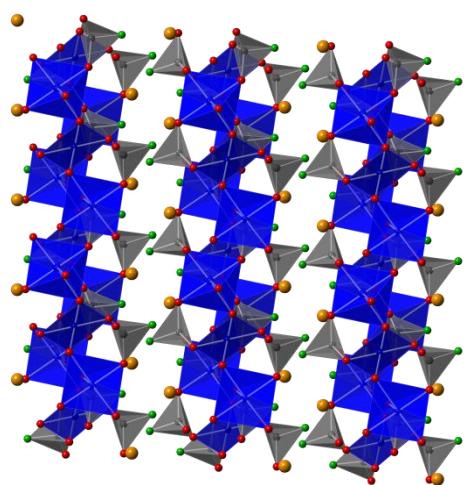


Fig. SI2 View along the *b*-axis for $M_2Cu_3(PO_3F)_4$. Key: blue polyhedra – Cu, grey tetrahedra – P, red sphere – O, green sphere – F, orange sphere – M^+ cation.

Compound II - $K_2Cu_3(PO_3F)_4$

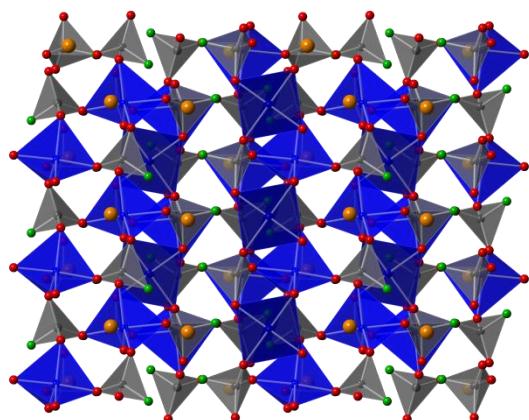


Fig. SI3 View along the c -axis for $K_2Cu_3(PO_3F)_4$. Key: blue polyhedra – Cu, grey tetrahedra – P, red sphere – O, green sphere – F, orange sphere – K⁺ cation.

Compound III - $Cs_2Cu_3(PO_3F)_4$

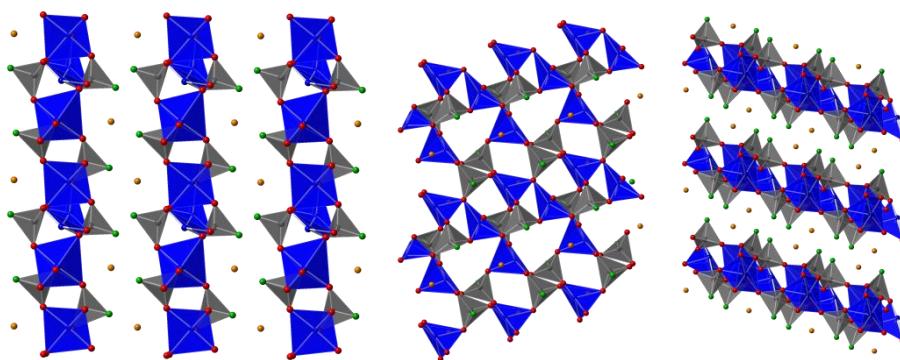


Fig. SI4 View along the a -axis (left), b -axis (middle) and c -axis (right) for $Cs_2Cu_3(PO_3F)_4$. Key: blue polyhedra – Cu, grey tetrahedra – P, red sphere – O, green sphere – F, orange sphere – Cs⁺ cation.

Compound IV - $\text{MCu}_3(\text{PO}_3\text{F})_2(\text{PO}_2(\text{OH})_2)\text{F}_2$ ($\text{M}=\text{NH}_4, \text{K}, \text{Rb}$)

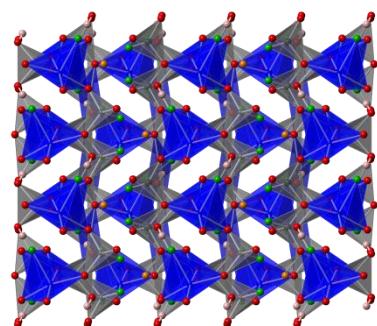


Fig. SI5 View along the a -axis for $\text{MCu}_3(\text{PO}_3\text{F})_2(\text{PO}_2(\text{OH})_2)\text{F}_2$ ($\text{M}=\text{NH}_4, \text{K}, \text{Rb}$). Key: blue polyhedra – Cu, grey tetrahedra – P, red sphere – O, green sphere – F, orange sphere – M^+ cation, pink sphere – H.

Compound V - $[\text{H}_2\text{-piperazine}]\text{Cu}_2(\text{PO}_3\text{F})_2(\text{PO}_2\text{F}_2)\text{F}$

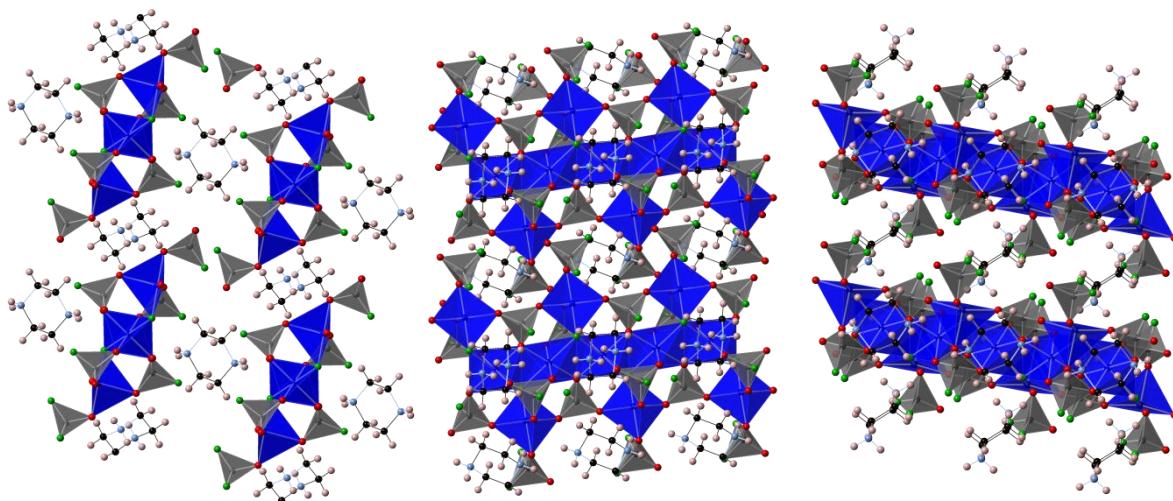


Fig. SI6 View along the a -axis (left), b -axis (middle) and c -axis (right) for $[\text{H}_2\text{-piperazine}]\text{Cu}_2(\text{PO}_3\text{F})_2(\text{PO}_2\text{F}_2)\text{F}$. Key: blue polyhedra – Cu, grey tetrahedra – P, red sphere – O, green sphere – F, black sphere – C, pale blue sphere – N, pink sphere – H.

Compound VI - [H₂-1,4-diaminobutane]Cu₃(PO₃F)₄

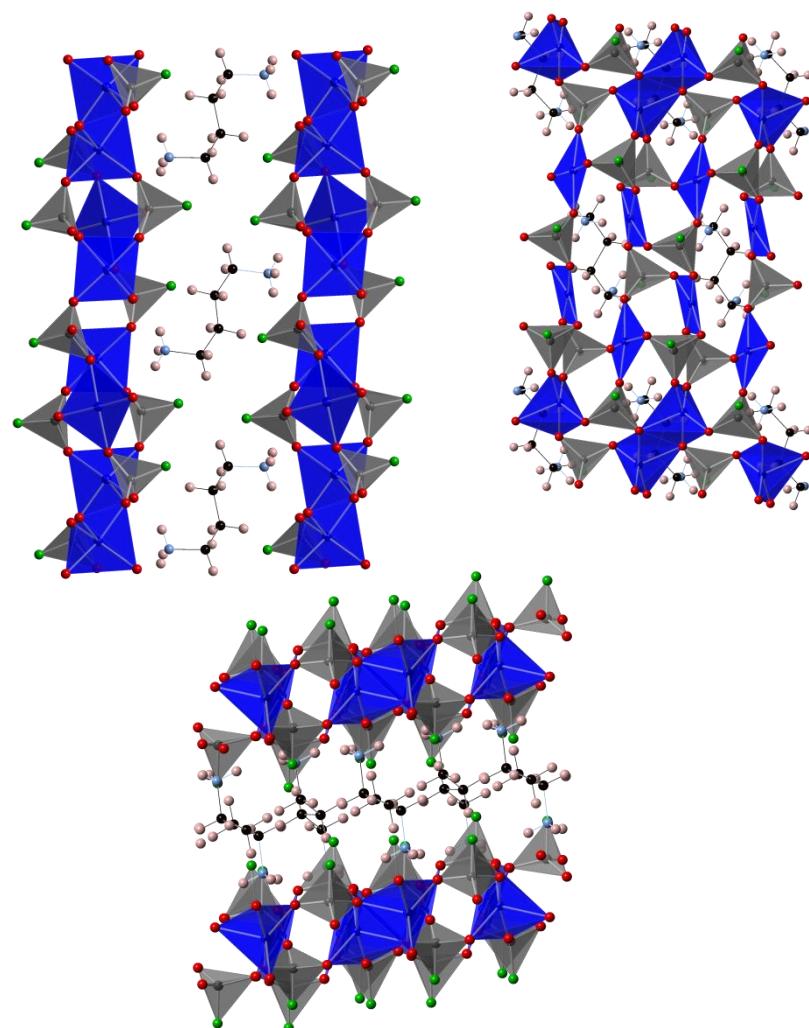


Fig. SI7 View along the *a*-axis (left), *b*-axis (middle) and *c*-axis (right) for [H₂-1,4-diaminobutane]Cu₃(PO₃F)₄. Key: blue polyhedra – Cu, grey tetrahedra – P, red sphere – O, green sphere – F, black sphere – C, pale blue sphere – N, pink sphere – H.

Compound VII - [H₂-trans-1,4-diaminocyclohexane]Cu₂(PO₃F)₂F₂

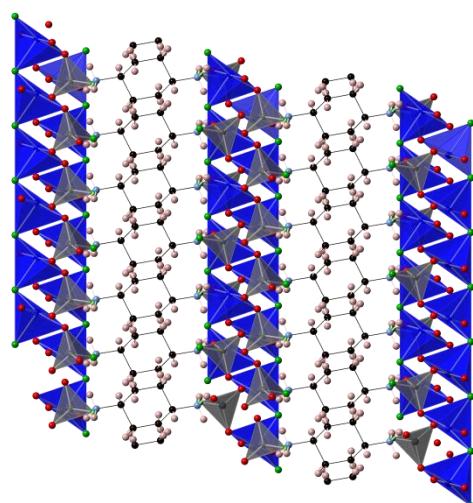


Fig. SI8 View along the *b*-axis (right) [H₂-trans-1,4-diaminocyclohexane]Cu₂(PO₃F)₂F₂.
Key: blue polyhedra – Cu, grey tetrahedra – P, red sphere – O, green sphere – F, black sphere
– C, pale blue sphere – N, pink sphere – H.

Compound VIII - Na₂Cu₂(P₂O₇)F

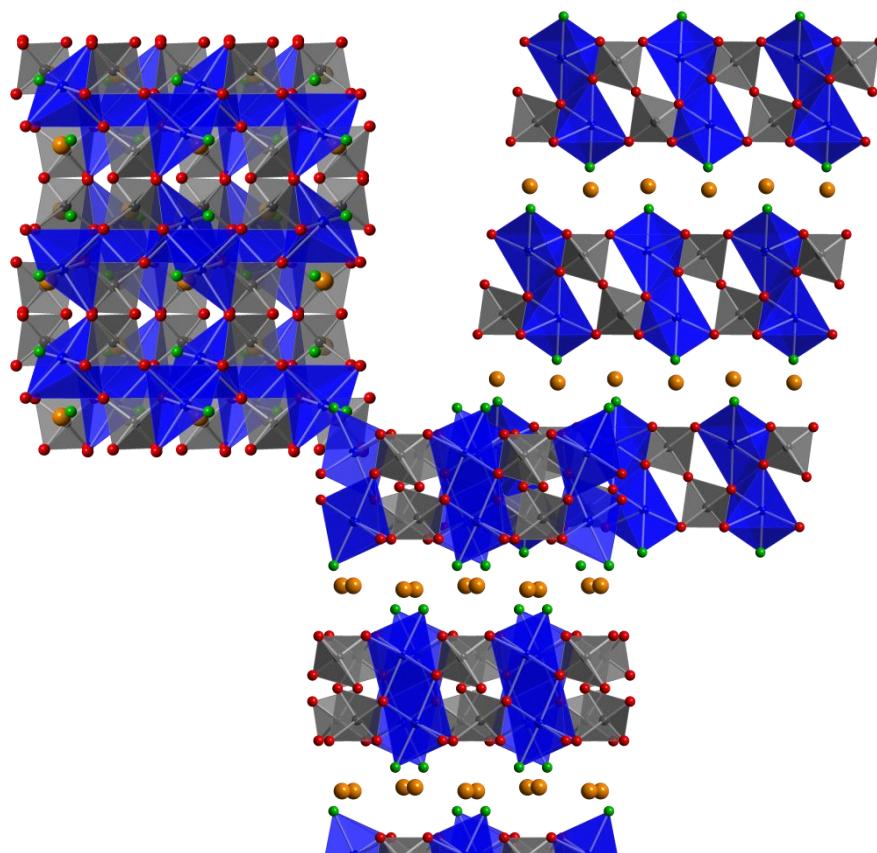


Fig. SI9 View along the *a*-axis (left), *b*-axis (middle) and *c*-axis (right) for Na₂Cu₂(P₂O₇)F.
Key: blue polyhedra – Cu, grey tetrahedra – P, red sphere – O, green sphere – F, orange
sphere – Na⁺ cation.

Compound IX - $\text{Cs}_2\text{Cu}_2(\text{PO}_3\text{F})_2\text{F}_{0.5}[\text{P(O,OH,F)}_4]_x$

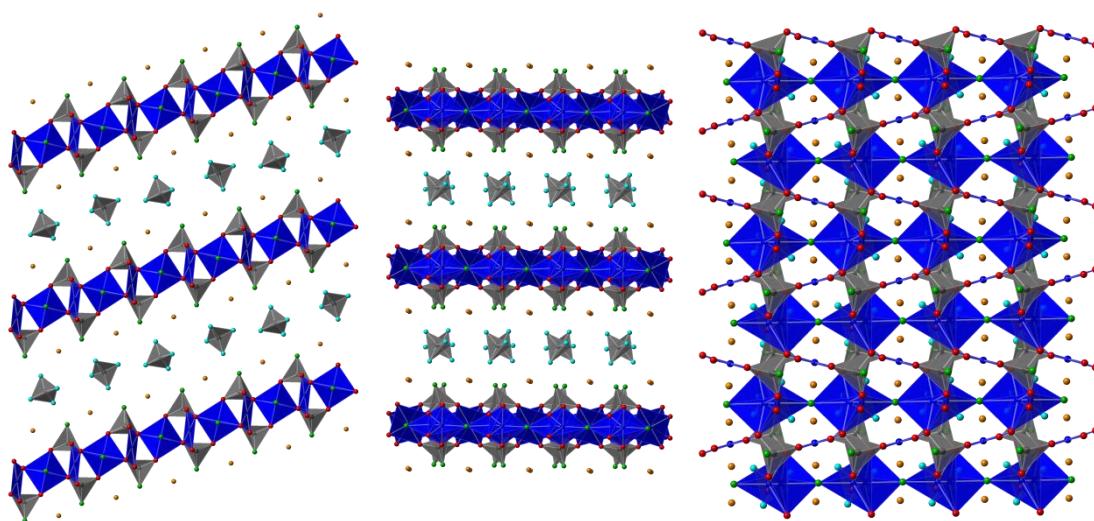


Fig. SI10 View along the *a*-axis (left), *b*-axis (middle) and *c*-axis (right) for $\text{Cs}_2\text{Cu}_2(\text{PO}_3\text{F})_2\text{F}_{0.5}[\text{P(O,OH,F)}_4]_x$. Key: blue polyhedra – Cu, grey tetrahedra – P, red sphere – O, green sphere – F, orange sphere – Cs^+ cation, turquoise sphere – mixed O/OH/F.

Compound X - $[\text{Triethylamine}]_x\text{Cu}_3(\text{PO}_3\text{F})_3$

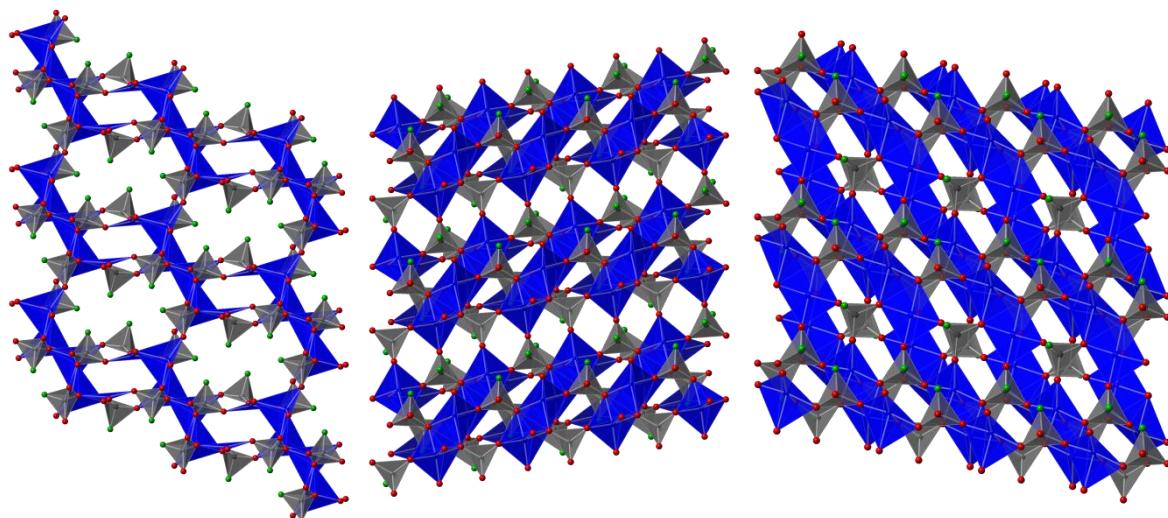


Fig. SI11 View along the *a*-axis (left), *b*-axis (middle) and *c*-axis (right) for $[\text{Triethylamine}]_x\text{Cu}_3(\text{PO}_3\text{F})_3$. Key: blue polyhedra – Cu, grey tetrahedra – P, red sphere – O, green sphere – F.

Compound XI - $\text{CsCu}_2(\text{PO}_3\text{F})_2\text{F}$

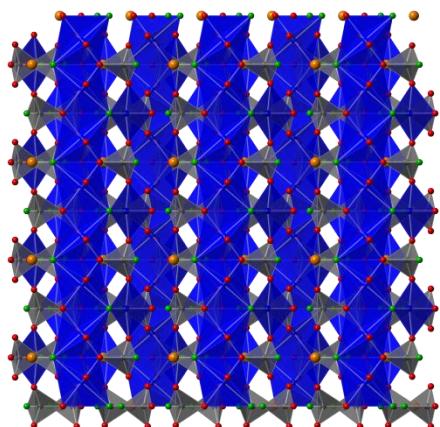


Fig. SI11 View along the *c*-axis for $\text{CsCu}_2(\text{PO}_3\text{F})_2\text{F}$. Key: blue polyhedra – Cu, grey tetrahedra – P, red sphere – O, green sphere – F, orange sphere – Cs^+ cation.