

Copper(II) manganese(II) ortho-  
phosphate,  $\text{Cu}_{0.5}\text{Mn}_{2.5}(\text{PO}_4)_2$ Andrew D. Bond,<sup>a</sup> Søren P. V. Foghmoes<sup>b</sup> and Terence E. Warner<sup>b\*</sup><sup>a</sup>University of Southern Denmark, Department of Physics and Chemistry, Campusvej 55, 5230 Odense, Denmark, and <sup>b</sup>University of Southern Denmark, Institute of Chemical Engineering, Biotechnology and Environmental Technology, Niels Bohrs Allé, 5230 Odense, Denmark  
Correspondence e-mail: tew@kbn.sdu.dk

Received 3 December 2010

Accepted 24 December 2010

Online 22 February 2011

The title compound,  $\text{Cu}_{0.5}\text{Mn}_{2.5}(\text{PO}_4)_2$ , is a copper–manganese phosphate solid solution with the graftonite-type structure, *viz.*  $(\text{Mn},\text{Fe},\text{Ca},\text{Mg})_3(\text{PO}_4)_2$ . The structure has three distinct metal cation sites, two of which are occupied by  $\text{Mn}^{\text{II}}$  and one of which accommodates  $\text{Cu}^{\text{II}}$ . Incorporation of  $\text{Cu}^{\text{II}}$  into the structure distorts the coordination geometry of the metal cation site from five-coordinate square-pyramidal towards four-coordinate flattened tetrahedral, and serves to contract the structure principally along the *c* axis.

## Comment

The copper–manganese phosphate solid solution  $\text{Cu}_{0.15}\text{Mn}_{2.85}(\text{PO}_4)_2$ , with the graftonite-type structure, *viz.*  $(\text{Mn},\text{Fe},\text{Ca},\text{Mg})_3(\text{PO}_4)_2$  (Calvo, 1968), was first prepared by Nord (1982) *via* a reaction between the end members,  $\text{Cu}_3(\text{PO}_4)_2$  and  $\text{Mn}_3(\text{PO}_4)_2$ , at 1073 K for one month in an evacuated silica-glass ampoule. The product material was analysed using powder X-ray diffraction, and the monoclinic unit-cell parameters at 298 K were reported as  $a = 8.803$  (6) Å,  $b = 11.454$  (9) Å and  $c = 6.267$  (5) Å,  $\beta = 99.00$  (6)° and  $V = 624.1$  (12) Å<sup>3</sup>. No information was obtained concerning the location of  $\text{Cu}^{\text{II}}$  within the structure. Apparently, Nord was unable to increase the solubility of  $\text{Cu}_3(\text{PO}_4)_2$  within  $\text{Mn}_3(\text{PO}_4)_2$  beyond 5 mol% under these preparative conditions, and he noted that ‘the low solubility of  $\text{Cu}^{\text{II}}$  in Mn/Cu orthophosphate is curious, considering this ion’s large tendency to enter into very distorted environments’. We have been able to prepare a significantly more copper-rich composition, the title compound,  $\text{Cu}_{0.5}\text{Mn}_{2.5}(\text{PO}_4)_2$ , corresponding to approximately 17 mol%  $\text{Cu}^{\text{II}}$  (in terms of the metal content), *via* a reaction between the constituent oxides at 1223 K under argon.

Since Fe and Mn are known to substitute for one another within the alluaudite family of minerals, represented by the general formula  $(\text{Na},\text{Ca},\square)_2(\text{Fe},\text{Mn})_3(\text{PO}_4)_3$  (Moore & Ito,

1979), it seemed reasonable to attempt preparation of the Mn analogue of the known Cu-containing alluaudite-type phase,  $\text{Cu}_{1.35}\text{Fe}_3(\text{PO}_4)_3$  (Warner *et al.*, 1993). However, attempts to prepare the composition  $\text{Cu}_{1.5}\text{Mn}_3(\text{PO}_4)_3$  yielded a material for which the powder X-ray diffraction pattern showed no resemblance to that of the alluaudite structure, and instead indicated the presence of a major phase with the graftonite-type structure. Consequently, a single crystal was selected for further analysis.

The single-crystal analysis confirmed the graftonite-type structure of the title compound,  $\text{Cu}_{0.5}\text{Mn}_{2.5}(\text{PO}_4)_2$ . It consists of three different cation polyhedra linked through edge- and corner-sharing of O atoms from the  $\text{PO}_4^{3-}$  groups (Figs. 1 and 2). The  $\text{Cu}^{\text{II}}$  content is accommodated at the Mn2/Cu2 site. Atom Mn1 occupies an essentially six-coordinate distorted octahedral environment, with Mn1–O bond distances in the range 2.0923 (16)–2.4125 (17) Å (Table 1). A further contact of 2.7617 (17) Å is made to atom O3, which led Calvo (1968) to describe the coordination geometry of Mn1 as an ‘irregular pentagonal bipyramid’. Atom Mn3 occupies a five-coordinate environment with a geometry that approximates square-pyramidal (Addison parameter  $\tau = 0.38$ ; Addison *et al.*, 1984), with atom O2<sup>vi</sup> at the apical position [symmetry code: (vi)  $1 + x, y, z$ ]. The Mn3–O bond distances are in the range 2.0359 (16)–2.1892 (16) Å (Table 1). For the mixed cation site, Mn2/Cu2, atom Mn2 has a distorted square-pyramidal geometry ( $\tau = 0.18$ ) made up of atoms O3, O4, O6<sup>iv</sup>, O7<sup>ii</sup> and O8<sup>v</sup> [symmetry codes: (ii)  $1 - x, -y, 1 - z$ ; (iv)  $x, y, -1 + z$ ; (v)  $-x, -y, 1 - z$ ], with O7<sup>ii</sup> at the apical position. The Mn2–O distances are in the range 1.885 (3)–2.491 (2) Å (Table 1). The Cu2 site lies close to that of Mn2, but shifted away from atom O3 to give a Cu2–O3 distance of 2.913 (2) Å. Thus, the coordination environment of Cu2 resembles more closely a

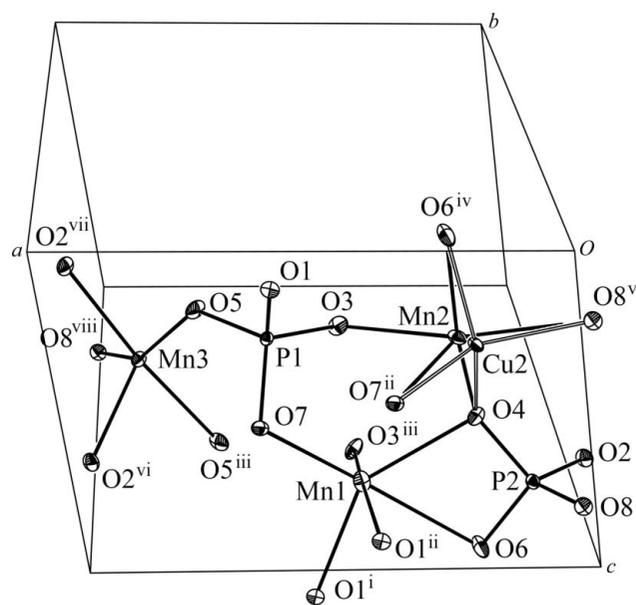
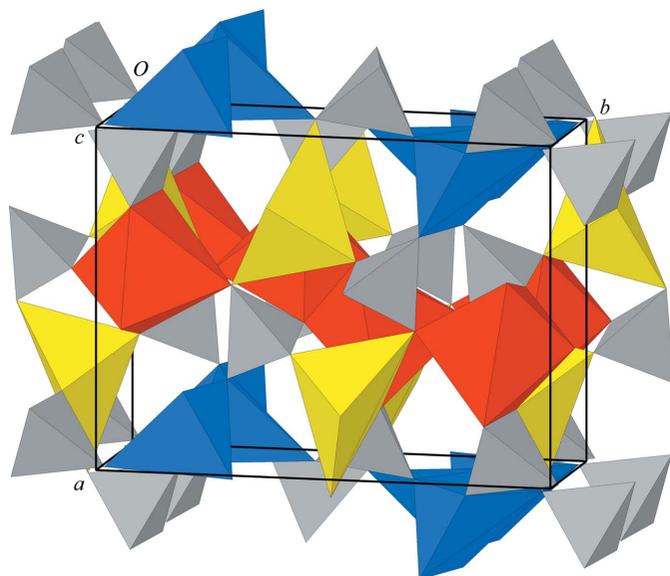


Figure 1

The coordination environments of the three metal cation sites, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Atoms Mn2 and Cu2 have a site-occupancy factor of 0.5. (Symmetry codes correspond to those in Table 1.)



**Figure 2**  
A polyhedral representation of the structure, viewed approximately along the *c* axis. (In the electronic version of the paper, Mn1 polyhedra are red, Mn2/Cu2 polyhedra are yellow, Mn3 polyhedra are blue and PO<sub>4</sub> polyhedra are grey.)

flattened tetrahedron, with the bond distances to O4, O6<sup>iv</sup>, O7<sup>ii</sup> and O8<sup>v</sup> in the range 1.955 (2)–1.993 (2) Å. The incorporation of Cu<sup>II</sup> at the Mn2 site is consistent with the statement made by Calvo (1968) that ‘the coordination number of site II can be changed homogeneously from four to five by altering the chemical composition’.

The graftonite-type crystal structure of the end member manganese orthophosphate, Mn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, has not been published to date, although two other crystal modifications have been described for this compound (Stephens & Calvo, 1969; El Bali *et al.*, 2000; Massa *et al.*, 2005). The unit-cell parameters for graftonite-type Mn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> have been reported by Calvo (1968) to be *a* = 8.80 (1) Å, *b* = 11.45 (2) Å and *c* = 6.25 (5) Å, β = 98.3 (2)° and *V* = 623 (1) Å<sup>3</sup>. Thus, the incorporation of 17 mol% Cu<sup>II</sup> into Mn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> in the title compound reduces the unit-cell volume by approximately 13 Å<sup>3</sup> compared with Mn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, which is slightly more than the reductions observed on the incorporation of an equivalent mole fraction of Co<sup>II</sup> (approximately 10 Å<sup>3</sup>) or Fe<sup>II</sup> (approximately 8 Å<sup>3</sup>) (Nord, 1982), consistent with the expected cation sizes. The largest change in the unit-cell parameters compared with Mn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> is observed for the *c* axis, which lies approximately parallel to the O4–Cu2/Mn2–O6<sup>iv</sup> bonds (Fig. 1). This indicates that the change in coordination geometry from five-coordinate for Mn<sup>II</sup> towards four-coordinate for Cu<sup>II</sup> serves to pull together the O4 and O6 corners of neighbouring Mn1 polyhedra, thereby contracting the structure along this direction.

It is interesting to note that it has not been possible, so far, to prepare a copper–manganese phosphate with the alluaudite-type structure, nor indeed a copper–iron phosphate with the graftonite-type structure. It seems likely that the relative stability of Mn<sup>II</sup> over Mn<sup>III</sup> favours the co-existence of Cu<sup>II</sup> and Mn<sup>II</sup> in the title compound, compared with the require-

ment for mixed valency (Mn<sup>II</sup>/Mn<sup>III</sup>) within an alluaudite-type phase.

## Experimental

An attempt was made to prepare a 10 g specimen of the hypothetical copper–manganese orthophosphate Cu<sub>1.5</sub>Mn<sub>3</sub>(PO<sub>4</sub>)<sub>3</sub> using a method similar to that described by Warner *et al.* (1993) for preparation of the analogous alluaudite-type phase Cu<sub>1.35</sub>Fe<sub>3</sub>(PO<sub>4</sub>)<sub>3</sub>. It was considered plausible that the following reaction might occur at high temperature: 0.75Cu<sub>2</sub>O + 1.5Mn<sub>2</sub>O<sub>3</sub> + 1.5P<sub>2</sub>O<sub>5</sub> → Cu<sub>1.5</sub>Mn<sub>3</sub>(PO<sub>4</sub>)<sub>3</sub> + 0.5O<sub>2</sub>(g).

The chemical reagents were purchased from Sigma–Aldrich. Appropriate amounts of Cu<sub>2</sub>O (97%), Mn<sub>2</sub>O<sub>3</sub> (99%) and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> (99.99+%), corresponding to the composition Cu<sub>1.5</sub>Mn<sub>3</sub>(PO<sub>4</sub>)<sub>3</sub>, were ground together in an agate pestle and mortar. This mixture was placed in an alumina boat (SRX61, Almath Ltd), which was contained within a larger alumina boat (SRX110, Almath Ltd) in order to reduce the risk of spillage, and then heated under a flowing atmosphere of argon (99.99%, 0.5 l min<sup>−1</sup>) in a Lenton LTF16/50/180 tube furnace (with appropriate gas-flow attachments) to 673 K at a rate of 300 K h<sup>−1</sup>. After 5 h at 673 K, the furnace was heated further to 1223 K at a rate of 300 K h<sup>−1</sup>. After 7 h at 1223 K, the furnace was cooled to ambient temperature at a rate of 300 K h<sup>−1</sup>. The powder X-ray diffraction pattern of the bulk product was consistent with that of the title compound, with no indication of any other crystalline phase.

### Crystal data

Cu <sub>0.5</sub> Mn <sub>2.5</sub> (PO <sub>4</sub> ) <sub>2</sub>	<i>V</i> = 610.28 (4) Å <sup>3</sup>
<i>M<sub>r</sub></i> = 359.06	<i>Z</i> = 4
Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>c</i>	Mo <i>K</i> α radiation
<i>a</i> = 8.8428 (3) Å	<i>μ</i> = 7.35 mm <sup>−1</sup>
<i>b</i> = 11.5331 (4) Å	<i>T</i> = 298 K
<i>c</i> = 6.0539 (2) Å	0.15 × 0.10 × 0.05 mm
β = 98.712 (2)°	

### Data collection

Bruker–Nonius X8 APEXII CCD area-detector diffractometer	11353 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	1519 independent reflections
<i>T</i> <sub>min</sub> = 0.467, <i>T</i> <sub>max</sub> = 0.696	1429 reflections with <i>I</i> > 2σ( <i>I</i> )
	<i>R</i> <sub>int</sub> = 0.026

### Refinement

<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )] = 0.019	127 parameters
<i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.050	Δρ <sub>max</sub> = 0.47 e Å <sup>−3</sup>
<i>S</i> = 1.09	Δρ <sub>min</sub> = −0.63 e Å <sup>−3</sup>
1519 reflections	

Refinement of the structure with all metal sites assigned as Cu produces unreasonably small displacement ellipsoids for all P and O atoms. Refinement with all metal sites assigned as Mn provides an acceptable result for all P and O atoms and for atoms Mn1 and Mn3. For the Mn2 site, however, isotropic refinement as a single Mn atom leaves two peaks of *ca* 14 e Å<sup>−3</sup> in the difference electron density either side of the atom. Anisotropic refinement gives a prolate ellipsoid for Mn2 that appears significantly smaller than those of Mn1 and Mn3, and peaks of *ca* 2 e Å<sup>−3</sup> remain in the difference electron density. Refinement of the site as a single Cu atom is not possible, since it results in several nonpositive definite atoms and a dramatic increase in *R* factors. Refinement as a mixed Mn/Cu site, with the two atoms constrained to lie at the same position, does not provide any significant improvement over refinement solely as Mn, and the best

**Table 1**  
Selected bond lengths (Å).

Mn1—O1 <sup>i</sup>	2.2425 (15)	Mn2—O8 <sup>v</sup>	2.301 (2)
Mn1—O1 <sup>ii</sup>	2.1226 (15)	Cu2—O7 <sup>ii</sup>	1.987 (2)
Mn1—O3 <sup>iii</sup>	2.0923 (16)	Cu2—O6 <sup>iv</sup>	1.955 (2)
Mn1—O4	2.3314 (17)	Cu2—O4	1.975 (2)
Mn1—O6	2.4125 (17)	Cu2—O8 <sup>v</sup>	1.993 (2)
Mn1—O7	2.3861 (15)	Mn3—O2 <sup>vi</sup>	2.1597 (16)
Mn2—O3	2.491 (2)	Mn3—O2 <sup>vii</sup>	2.1892 (16)
Mn2—O4	1.885 (3)	Mn3—O5	2.0359 (16)
Mn2—O6 <sup>iv</sup>	1.891 (3)	Mn3—O5 <sup>iii</sup>	2.1398 (16)
Mn2—O7 <sup>ii</sup>	2.047 (3)	Mn3—O8 <sup>viii</sup>	2.0896 (15)

Symmetry codes: (i)  $x, y, z + 1$ ; (ii)  $-x + 1, -y, -z + 1$ ; (iii)  $x, -y + \frac{1}{2}, z + \frac{1}{2}$ ; (iv)  $x, y, z - 1$ ; (v)  $-x, -y, -z + 1$ ; (vi)  $x + 1, y, z$ ; (vii)  $x + 1, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (viii)  $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$ .

result is obtained by allowing the Mn and Cu atoms to refine freely with site-occupancy factors constrained to sum to unity. The refined site-occupancy factors of 0.489 (9):0.511 (9) for Mn2:Cu2 do not differ significantly from 0.5, and they were therefore constrained to 0.5 for the final cycles of refinement. There is no clear evidence for any Cu content at the Mn1 or Mn3 sites, although trace occupancy cannot be excluded. The labelling scheme chosen for the atoms corresponds to that used by Calvo (1968), although the positions of the atoms within the asymmetric unit have been changed in order to minimize as far as possible the number of symmetry operators required in Fig. 1 and Table 1.

Data collection: *APEX2* (Bruker–Nonius, 2004); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to

refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *ATOMS* (Dowty, 1997).

The authors are grateful to the Danish Natural Sciences Research Council and the Carlsberg Foundation for provision of the X-ray equipment.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3246). Services for accessing these data are described at the back of the journal.

## References

- Addison, A. W., Rao, T. N., Reedijk, J., van Rijn, J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.
- Bruker (2003). *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker–Nonius (2004). *APEX2*. Bruker–Nonius BV, Delft, The Netherlands.
- Calvo, C. (1968). *Am. Mineral.* **53**, 742–750.
- Dowty, E. (1997). *ATOMS for Windows*. Shape Software, Kingsport, Tennessee, USA.
- El Bali, B., Boukhari, A., Glaum, R., Gerck, M. & Maass, K. (2000). *Z. Anorg. Allg. Chem.* **626**, 2557–2562.
- Massa, W., Yakubovich, O. V. & Dimitrova, O. V. (2005). *Solid State Sci.* **7**, 950–956.
- Moore, P. B. & Ito, J. (1979). *Mineral. Mag.* **43**, 227–235.
- Nord, A. G. (1982). *Mater. Res. Bull.* **17**, 1001–1010.
- Sheldrick, G. M. (2003). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Stephens, J. S. & Calvo, C. (1969). *Can. J. Chem.* **47**, 2215–2225.
- Warner, T. E., Milius, M. & Maier, J. (1993). *J. Solid State Chem.* **106**, 301–309.