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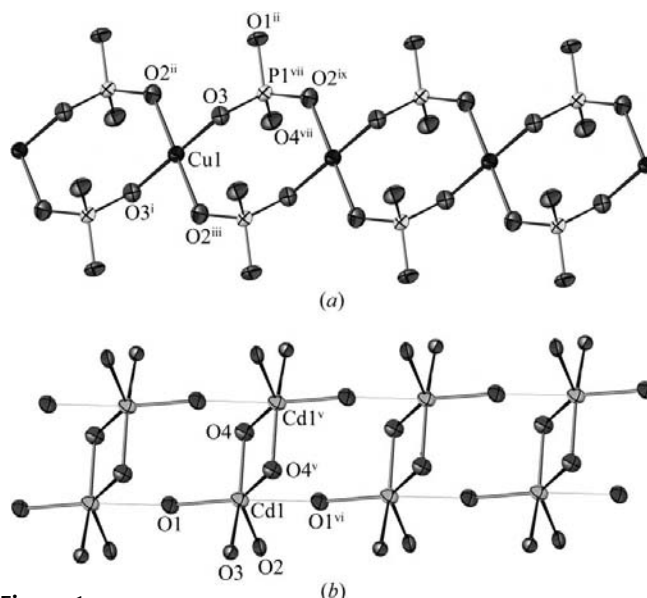
During an investigation of the insufficiently known system $M1O-M2O-X_2O_5-H_2O$ ($M1 = Cd^{2+}$, Sr^{2+} and Ba^{2+} ; $M2 = Cu^{2+}$, Ni^{2+} , Co^{2+} , Zn^{2+} and Mg^{2+} ; $X = P^{5+}$, As^{5+} and V^{5+}), single crystals of the novel compound dicadmium copper(II) bis[phosphate(V)], $Cd_2Cu(PO_4)_2$, were obtained. This compound belongs to a small group of compounds adopting a $Cu_3(PO_4)_2$ -type structure and having the general formula $M1_2M2(XO_4)_2$ ($M1/M2 = Cd^{2+}$, Cu^{2+} , Mg^{2+} and Zn^{2+} ; $X = As^{5+}$, P^{5+} and V^{5+}). The crystal structure is characterized by the interconnection of infinite $[Cu(PO_4)_2]_n$ chains and $[Cd_2O_{10}]_n$ double chains, both extending along the a axis. Exceptional characteristics of this structure are its novel chemical composition and the occurrence of double chains of CdO_6 polyhedra that were not found in related structures. In contrast to the isomorphous compounds, where the $M1$ cations are coordinated by five O atoms, the Cd atom is coordinated by six. The dissimilarity in the geometry of $M1$ coordination between $Cd_2Cu(PO_4)_2$ and the isomorphous compounds is mostly due to the larger ionic radius of the Cd cation in comparison with the Cu, Mg and Zn cations. Sharing a common edge, two CdO_6 polyhedra form Cd_2O_{10} dimers. Each such dimer is bonded to another dimer sharing common vertices, forming $[Cd_2O_{10}]_n$ double chains in the $[100]$ direction. The Cu atoms, located on an inversion centre (site symmetry $\bar{1}$), form isolated CuO_4 squares interconnected by PO_4 tetrahedra, forming $[Cu(PO_4)_2]_n$ chains similar to those found in related structures. Conversely, the $[Cd_2O_{10}]_n$ double chains, which were not found in related structures, are an exclusive feature of this structure.

Comment

Natural and synthetic metal phosphates, arsenates and vanadates often form tetrahedral–octahedral framework structures with potentially interesting properties (e.g. ion conductivity, ion exchange and catalytic activities). An ongoing compre-

hensive study of the hydrothermal synthesis, crystallography and properties of phosphate(V), arsenate(V) and vanadate(V) compounds in the insufficiently known system $M1O-M2O-X_2O_5-H_2O$ ($M1 = Sr^{2+}$, Cd^{2+} and Ba^{2+} ; $M2 = Mg^{2+}$, Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} ; $X = P^{5+}$, As^{5+} and V^{5+}) yielded a large number of new $M1^{2+}$, $M2^{2+}$ and $M1-M2-(H-)$ phosphates, arsenates and vanadates (Mihajlović & Effenberger, 2004, 2006; Mihajlović, Libowitzky & Effenberger, 2004; Mihajlović, Kolitsch & Effenberger, 2004; Đorđević, Štović *et al.*, 2008; Đorđević, Karanović & Tillmanns, 2008; Đorđević & Karanović, 2008; Đorđević, 2008a,b), which were characterized structurally and also, in part, by spectroscopic techniques. The present contribution reports the hydrothermal synthesis and crystal structure of the novel compound dicadmium copper(II) bis[phosphate(V)], $Cd_2Cu(PO_4)_2$.

$Cd_2Cu(PO_4)_2$ is isomorphous with only five compounds, namely two phosphates, two arsenates and one vanadate [structure prototype $Cu_3(PO_4)_2$ (Forsyth *et al.*, 1990; Shoemaker *et al.*, 1977), $(Mg_{0.21}, Cu_{0.79})_3(PO_4)_2$ (Moqine *et al.*, 1994), $Cu_3(AsO_4)_2$ (Effenberger, 1988), $Zn_2Cu(AsO_4)_2$ (mineral stranskiite; Plieth & Sängler, 1967; Calvo & Leung, 1969; Keller *et al.*, 1979) and $Cu_3(VO_4)_2$ (mineral mcbirneyite; Coing-Boyat, 1982)]. All compounds crystallize in the space group $P\bar{1}$ and have the general formula $M1_2M2(XO_4)_2$ ($M1/M2 = Cd^{2+}$, Cu^{2+} , Mg^{2+} and Zn^{2+} ; $X = As^{5+}$, P^{5+} and V^{5+} ; Table 1). It is interesting that the crystal structure of $Cd_2Cu(PO_4)_2$ is different from that of monoclinic $Cd_{1.35}Cu_{1.65}(PO_4)_2$, which has a very similar chemical composition (Müller-Buschbaum & Münchau, 1996). The crystal structure of $Cd_2Cu(PO_4)_2$ consists of $[Cu(PO_4)_2]_n$ chains, running along the $[100]$ direction, interconnected by double chains of CdO_6 polyhedra extending in the same direction (Fig. 1). Very

**Figure 1**

(a) The infinite $[Cu(PO_4)_2]_n$ chain and (b) the double $[Cd_2O_{10}]_n$ chain with the atomic numbering scheme (displacement ellipsoids are shown at the 91% probability level). The longest $Cd1-O1$ bond distance is shown as a fine line. [Symmetry codes: (i) $-x, -y, -z$; (ii) $-x, -y + 1, -z$; (iii) $x, y - 1, z$; (iv) $-x + 1, -y, -z + 1$; (v) $x + 1, y, z$; (vi) $x, y, z - 1$; (vii) $-x + 1, -y + 1, -z$.]

similar $[\text{Cu}(\text{PO}_4)_2]_n$ chains have been described in the crystal structures of $\text{Ba}_2\text{Cu}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ (Effenberger, 1999), $\text{Ba}_2\text{Cu}(\text{PO}_4)_2$ (Etheredge & Hwu, 1996) and $\text{Sr}_2\text{Cu}(\text{PO}_4)_2$ (Johannes *et al.*, 2006).

The Cu atom, located on an inversion centre ($M2$ position), is coordinated by four O atoms with an average Cu1—O bond distance of 1.941 (3) Å, forming a slightly distorted square-planar coordination [the $\text{O}2^{\text{ii}}-\text{Cu}1-\text{O}3$ and $\text{O}2^{\text{ii}}-\text{Cu}1-\text{O}3^{\text{i}}$ bond angles are 88.42 (10) and 91.58 (10)°; symmetry codes: (i) $-x, -y, -z$; (ii) $-x, -y + 1, -z$]. All four O atoms ($\text{O}2 \times 2$ and $\text{O}3 \times 2$) of the CuO_4 squares are triply coordinated, bridging Cd1, Cu1 and P1 atoms. The P atom exhibits the usual tetrahedral coordination, with a mean P1—O distance of 1.541 (3) Å. The CuO_4 squares and PO_4 tetrahedra generate $[\text{Cu}(\text{PO}_4)_2]_n$ chains along the a axis (Fig. 1*a*).

Similar to other isomorphous compounds, the $M1$ cation ($M1 = \text{Cd}$) is situated in a general position. However, it is surrounded by six not five O atoms, forming a (5+1)-coordination polyhedron, which can be described as an extremely distorted octahedron. Pairs of CdO_6 polyhedra sharing an $\text{O}4-\text{O}4^{\text{i}}$ edge form Cd_2O_{10} dimers (Fig. 1*b*) similar to the isolated $M1\text{O}_8$ dimers in related structures. The exceptional characteristic of this structure is that the Cd_2O_{10} dimers are further polymerized, sharing common vertices ($\text{O}1$ and its symmetry equivalents) in double chains $[\text{Cd}_2\text{O}_{10}]_n$ running along the a axis. In this way, every Cd polyhedron shares additionally two vertices with neighbouring polyhedra. The neighbouring $[\text{Cd}_2\text{O}_{10}]_n$ double chains are interconnected by PO_4 tetrahedra, which are linked to both CdO_6 and CuO_4 polyhedra. In addition to atom P1, atoms $\text{O}1$ and $\text{O}4$ are bonded to two Cd1 atoms, and $\text{O}2$ and $\text{O}3$ to one Cd1 and one Cu1 atoms (Fig. 2).

Excluding the sixth O atom [$\text{O}1^{\text{vi}}$; symmetry code: (vi) $x + 1, y, z$] of the CdO_6 polyhedron, the average Cd1—O bond length is 2.259 (2) Å. The sixth O atom, located at a Cd1— $\text{O}1^{\text{vi}}$ distance of 2.716 (2) Å, contributes to the bond valence by approximately 5.5%. Taking into account the contribution of the five O atoms only, atom Cd1 is undersaturated, *i.e.* $v_{ij}(\text{Cd}1)$ is 1.92 valence units (v.u.). Including the sixth O atom, $\text{O}1^{\text{vi}}$, $v_{ij}(\text{Cd}1)$ increases to 2.02 v.u. The bond valence calculated according to the formula suggested by Brown & Altermatt (1985) for $\text{O}1$ shows that $\text{O}1$ is also undersaturated, *i.e.* $v_{ij}(\text{O}1)$ is 1.80 v.u. This could indicate that vacancies exist at the $\text{O}1$ position, but the refinement showed that no such significant vacancies are present at this site [the refined occupancy was 1.05 (1)]. Therefore, the refinement was completed with a fixed atom site-occupancy value of 1. Very probably, the undersaturation of $\text{O}1$ is due to the unusually long Cd—O distance. Hypothetically, if it is assumed that both the Cd1— $\text{O}1$ and the Cd1— $\text{O}1^{\text{vi}}$ distances are equal to 2.242 (2) Å, the calculated $v_{ij}(\text{O}1)$ becomes 2.09 v.u.

The dissimilarity in the geometry of $M1$ coordination between $\text{Cd}_2\text{Cu}(\text{PO}_4)_2$ and the other isomorphous compounds is mostly due to the larger ionic radius of the Cd cation in comparison with that of Cu, Mg and Zn. The increase in the polymerization of the CdO_6 polyhedra is accompanied by a decrease of the $M1 \cdots M1$ distances along the a axis. The Cd1—Cd1 distance along the chain extension is 4.7982 (3) Å,

which is identical to the unit-cell parameter a and is shorter than the Cu \cdots Cu distances in $\text{Cu}_3(\text{PO}_4)_2$, $\text{Cu}(\text{AsO}_4)_2$ and $\text{Cu}_3(\text{VO}_4)_2$, as well as the Zn \cdots Zn distance in $\text{Zn}_2\text{Cu}(\text{AsO}_4)_2$. Therefore, the unit-cell parameter a in $\text{Cd}_2\text{Cu}(\text{PO}_4)_2$ achieves the shortest value amongst the isomorphous compounds,

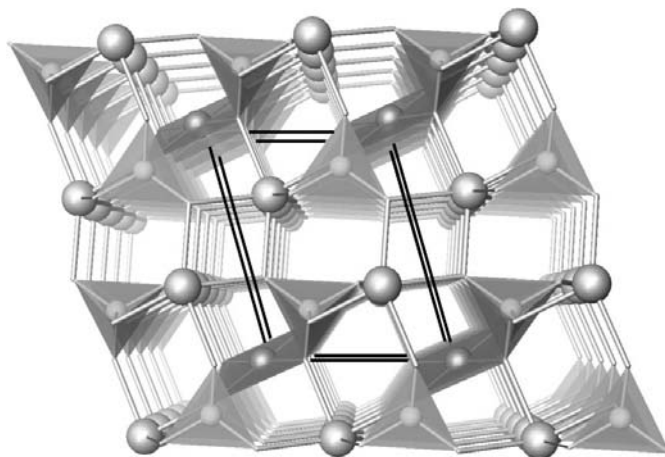


Figure 2

A perspective view of the crystal structure of $\text{Cd}_2\text{Cu}(\text{PO}_4)_2$, projected along $[100]$ (b axis horizontal). Large grey spheres represent Cd1 and smaller spheres represent Cu1 atoms. PO_4 tetrahedra and CuO_4 coordination squares are shaded.

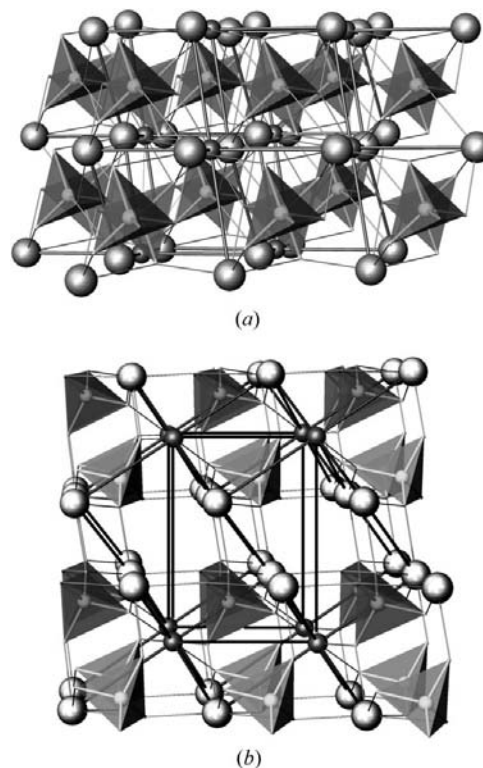


Figure 3

Perspective views of the crystal structure of $\text{Cd}_2\text{Cu}(\text{PO}_4)_2$, projected approximately along (a) $[111]$ and (b) $[010]$, showing PO_4 tetrahedra sandwiched between metal layers situated near the $(10\bar{1})$ plane. Larger grey spheres represent Cd1 and smaller spheres represent Cu1 atoms. PO_4 tetrahedra are shaded.

although it has the largest $M1$ cation and unit-cell volume (Table 1). In contrast, the b parameter has the largest value, while c is longer than those obtained for $\text{Cu}_3(\text{PO}_4)_2$, $\text{Cu}_3(\text{AsO}_4)_2$ and $\text{Cu}_3(\text{VO}_4)_2$, but similar to c in $\text{Zn}_2\text{Cu}(\text{AsO}_4)_2$.

An interesting aspect of the crystal structure is that it can also be described as PO_4 tetrahedra sandwiched between two metal layers, which are situated near the $(10\bar{1})$ plane (Fig. 3). The two $\text{Cd}1$ cations in the dimer are located in the same $(10\bar{1})$ plane and separated from each other by 3.5198 (8) Å, and the $\text{Cd}1-\text{O}4-\text{Cd}1^{\text{v}}$ [symmetry code: (v) $-x + 1, -y, -z + 1$] angle is 102.33 (10)°. As mentioned above, the $\text{Cd}1 \cdots \text{Cd}1$ distances between neighbours along the chain direction are 4.7982 (3) Å, and the shortest $\text{Cd}1 \cdots \text{Cd}1$ distance between neighbouring dimers positioned in the adjacent $(10\bar{1})$ plane is 4.2599 (5) Å. The shortest $\text{Cu}1 \cdots \text{Cd}1$ distances in the $(10\bar{1})$ plane are 3.5270 (3) and 3.7977 (4), and the separation between two $(10\bar{1})$ planes is 3.9408 (4) Å. Because the $\text{Cu}1$ atoms are situated at the origin of the unit cell, the $\text{Cu}1 \cdots \text{Cu}1$ distances are equal to the lengths of unit-cell parameters a , b and c . All metal–metal distances are longer than the sum of the van der Waals radii [3.16 Å ($2 \times r_{\text{Cd}}$), 2.98 Å ($r_{\text{Cd}} + r_{\text{Cu}}$) = 1.58 + 1.40 = 2.98 Å] and 2.80 Å ($2 \times r_{\text{Cu}}$) (Bondi, 1964)].

Experimental

A mixture of $\text{Cd}(\text{OH})_2$ (Alfa Products, >99%), $(\text{NH}_4)_2\text{HPO}_4$ (Loba Chemie, >99%) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Merck, >99%) was transferred into Teflon vessels and filled to approximately 70% of the inner volume with distilled water (quantitative ratio of reagents = 2:1:2). The pH of the mixture was 5. The vessel was enclosed in a stainless steel autoclave and heated from room temperature to 493 K (over a period of 4 h), held at 493 K for 192 h, and finally spontaneously cooled to room temperature. At the end of the reaction the pH of the mixture was 6. The title compound crystallized as blue prismatic crystals (yield ca 55%) of up to 100 µm in length, together with green prismatic crystals of $\text{Cu}_2(\text{PO}_4)\text{OH}$ (yield ca 35%) and colourless crystals of NH_4Cl (yield ca 10%). All the reaction products were filtered off, washed thoroughly with distilled water and dried in air at room temperature.

Crystal data

$\text{Cd}_2\text{Cu}(\text{PO}_4)_2$	$\gamma = 69.924 (3)^\circ$
$M_r = 478.31$	$V = 162.62 (2) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 1$
$a = 4.7982 (3) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 5.5801 (3) \text{ \AA}$	$\mu = 10.22 \text{ mm}^{-1}$
$c = 6.7217 (3) \text{ \AA}$	$T = 295 (2) \text{ K}$
$\alpha = 74.266 (3)^\circ$	$0.09 \times 0.04 \times 0.02 \text{ mm}$
$\beta = 86.330 (3)^\circ$	

Data collection

Nonius KappaCCD diffractometer	1596 measured reflections
Absorption correction: multi-scan (Otwinowski & Minor, 1997)	805 independent reflections
$T_{\text{min}} = 0.460$, $T_{\text{max}} = 0.822$	747 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.016$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.018$	63 parameters
$wR(F^2) = 0.043$	$\Delta\rho_{\text{max}} = 0.79 \text{ e \AA}^{-3}$
$S = 1.09$	$\Delta\rho_{\text{min}} = -0.59 \text{ e \AA}^{-3}$
805 reflections	

Table 1

Selected geometric parameters (Å, °).

$\text{Cu}1-\text{O}3$	1.928 (2)	$\text{Cd}1-\text{O}1$	2.242 (2)
$\text{Cu}1-\text{O}3^{\text{i}}$	1.928 (2)	$\text{Cd}1-\text{O}4^{\text{v}}$	2.263 (3)
$\text{Cu}1-\text{O}2^{\text{ii}}$	1.952 (3)	$\text{Cd}1-\text{O}2$	2.271 (2)
$\text{Cu}1-\text{O}2^{\text{iii}}$	1.952 (3)	$\text{Cd}1-\text{O}3$	2.288 (2)
$\text{Cu}1-\text{Cd}1^{\text{i}}$	3.5270 (3)	$\text{Cd}1-\text{O}1^{\text{vi}}$	2.716 (2)
$\text{Cu}1-\text{Cd}1^{\text{ii}}$	3.7977 (4)	$\text{Cd}1-\text{Cd}1^{\text{v}}$	3.5019 (8)
$\text{Cu}1-\text{Cd}1^{\text{iv}}$	3.9408 (4)	$\text{Cd}1-\text{Cd}1^{\text{vii}}$	4.2599 (5)
$\text{Cd}1-\text{O}4$	2.232 (3)	$\text{Cd}1-\text{Cd}1^{\text{ii}}$	4.7525 (5)
$\text{O}3-\text{Cu}1-\text{O}2^{\text{ii}}$	88.42 (10)	$\text{O}3^{\text{i}}-\text{Cu}1-\text{O}2^{\text{ii}}$	91.58 (10)

Symmetry codes: (i) $-x, -y, -z$; (ii) $-x, -y + 1, -z$; (iii) $x, y - 1, z$; (iv) $-x + 1, -y, -z$; (v) $-x + 1, -y, -z + 1$; (vi) $x + 1, y, z$; (vii) $-x, -y + 1, -z + 1$.

Table 2

Unit-cell parameters (Å, °, Å³) of the $M1_2M2(\text{XO}_4)_2$ ($M1/M2 = \text{Cd}^{2+}$, Cu^{2+} , Mg^{2+} and Zn^{2+} ; $X = \text{As}^{5+}$, P^{5+} and V^{5+}) family of compounds.

Compound	a	b	c	α	β	γ	V
$\text{Cu}_3(\text{PO}_4)_2^1$	4.855 (1)	5.288 (1)	6.184 (1)	72.34 (1)	86.99 (1)	68.54 (1)	140.49
$\text{Cu}_3(\text{PO}_4)_2^1$	4.848 (1)	5.280 (1)	6.183 (1)	72.30 (1)	86.90 (1)	68.59 (1)	140.08
$\text{Cu}_3(\text{PO}_4)_2^2$	4.8537 (7)	5.2855 (6)	6.1821 (8)	72.35 (1)	86.99 (1)	68.54 (1)	140.35
$\text{Mg}_{0.63}\text{Cu}_{2.37}(\text{PO}_4)_2^3$	4.845 (3)	5.265 (3)	6.246 (2)	71.98 (4)	93.04 (4)	111.42 (4)	140.72
Red. cell ^a	4.845 (3)	5.265 (3)	6.246 (2)	71.98 (4)	86.959	68.579	
$\text{Cd}_2\text{Cu}(\text{PO}_4)_2^4$	4.7982 (3)	5.5801 (3)	6.7217 (3)	74.266 (3)	86.330 (3)	69.924 (3)	162.62
$\text{Cu}_3(\text{VO}_4)_2^5$	5.196 (4)	5.355 (1)	6.505 (4)	69.22 (3)	88.69 (4)	68.08 (3)	155.73
$\text{Cu}_3(\text{AsO}_4)_2^6$	5.046 (2)	5.417 (2)	6.354 (2)	70.61 (2)	86.52 (2)	68.43 (2)	151.98
$\text{Zn}_2\text{Cu}(\text{AsO}_4)_2^7$	5.092 (2)	6.695 (2)	5.304 (2)	110.16 (2)	112.09 (2)	86.74 (2)	156.73
Red. cell ^b	5.092 (2)	5.304 (2)	6.695 (2)	69.84	86.74	67.91	
$\text{Zn}_2\text{Cu}(\text{AsO}_4)_2^8$	5.094 (1)	6.752 (1)	5.304 (1)	111.0 (1)	112.5 (1)	86.0 (1)	156.87
Red. cell ^b	5.094 (1)	5.304 (1)	6.752 (1)	69	86	67.5	
$\text{Zn}_2\text{Cu}(\text{AsO}_4)_2^9$	5.094 (5)	6.752 (5)	5.304 (5)	111	112	86	157.47
Red. cell ^b	5.094 (5)	5.304 (5)	6.752 (5)	69	86	68	

Notes: (a) reduced cell, transformation matrix 1: (100/0 $\bar{1}$ 0/00 $\bar{1}$); (b) transformation matrix 2: (100/00 $\bar{1}$ 0/10). References: (1) Forsyth *et al.* (1990); (2) Shoemaker *et al.* (1977); (3) Moqine *et al.* (1994); (4) this work; (5) Coing-Boyat (1982); (6) Effenberger (1988); (7) Keller *et al.* (1979); (8) Plieht & Sanger (1967); (9) Calvo & Leung (1969).

Data collection: COLLECT (Nonius, 2002); cell refinement: SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO-SMN (Otwinowski *et al.*, 2003); program(s) used to solve structure: SIR97 (Altomare *et al.*, 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008) and WinGX (Farrugia, 1999); molecular graphics: ATOMS (Dowty, 2000); software used to prepare material for publication: publCIF (Westrip, 2008).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KU3001). Services for accessing these data are described at the back of the journal.

References

- Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
- Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
- Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* **B41**, 244–247.
- Calvo, C. & Leung, K. Y. (1969). *Z. Kristallogr.* **130**, 231–233.
- Coing-Boyat, J. (1982). *Acta Cryst.* **B38**, 1546–1548.
- Dordević, T. (2008a). *Acta Cryst.* **E64**, i57.
- Dordević, T. (2008b). *Acta Cryst.* **E64**, i58–i59.
- Dordević, T. & Karanović, Lj. (2008). *J. Solid State Chem.* doi:10.1016/j.jssc.2008.07.025.
- Dordević, T., Karanović, Lj. & Tillmanns, E. (2008). *Cryst. Res. Technol.* **43**, 1202–1209.
- Dordević, T., Šutović, S., Stojanović, J. & Karanović, Lj. (2008). *Acta Cryst.* **C64**, i82–i86.
- Dowty, E. (2000). *ATOMS for Windows*. Version 5.1. Shape Software, Kingsport, Tennessee, USA.
- Effenberger, H. (1988). *Monatsh. Chem.* **119**, 1103–1112.
- Effenberger, H. (1999). *J. Solid State Chem.* **142**, 6–13.
- Etheredge, K. M. S. & Hwu, S. J. (1996). *Inorg. Chem.* **35**, 1474–1477.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Forsyth, J. B., Wilkinson, C., Paster, S. & Effenberger, H. (1990). *J. Phys. Condens. Matter*, **2**, 1609–1617.
- Johannes, M. D., Richter, J., Drechsler, S. L. & Rosner, H. (2006). *Phys. Rev. B*, **74**, 174435.
- Keller, P., Hess, H. & Dunn, P. J. (1979). *Tschermaks Mineral. Petrogr. Mitt.* **26**, 167–174.
- Mihajlović, T. & Effenberger, H. (2004). *Mineral. Mag.* **68**, 757–767.
- Mihajlović, T. & Effenberger, H. (2006). *Z. Kristallogr.* **221**, 770–781.
- Mihajlović, T., Kolitsch, U. & Effenberger, H. (2004). *J. Alloys Compd.* **379**, 103–109.
- Mihajlović, T., Libowitzky, E. & Effenberger, H. (2004). *J. Solid State Chem.* **177**, 3963–3970.
- Moqine, A., Boukhari, A. & Holt, E. M. (1994). *J. Solid State Chem.* **108**, 193–197.
- Müller-Buschbaum, H. & Münchau, S. (1996). *Z. Naturforsch. Teil B*, **51**, 229–232.
- Nonius (2002). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z., Borek, D., Majewski, W. & Minor, W. (2003). *Acta Cryst.* **A59**, 228–234.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography, Part A*, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Plieth, V. K. & Sängler, G. (1967). *Z. Kristallogr.* **124**, 91–100.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Shoemaker, G. L., Anderson, J. B. & Kostiner, E. (1977). *Acta Cryst.* **B33**, 2969–2972.
- Westrip, S. P. (2008). *pubCIF*. In preparation.