inorganic compounds

Reinvestigation of Sr₂[Cu(OH)₆]

Sabina Šutović,[a]* Ljiljana Karanović[a] and Dejan Poleti[b]

[a]Laboratory of Crystallography, Faculty of Mining and Geology, University of Belgrade, Đušina 7, 11000 Belgrade, Serbia, and [b]Department of General and Inorganic Chemistry, Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11000 Belgrade, Serbia
Correspondence e-mail: sabinakovac@yahoo.com

During an investigation of the SrO–CuO–P_2O_5–H_2O system, single crystals of distrontium hexahydroxidocuprate(II), Sr_2[Cu(OH)$_6$], were obtained by the hydrothermal method. The blue prismatic crystals of Sr_2[Cu(OH)$_6$] adopt the same structure type as Ba_2[Cu(OH)$_6$], Sr_2[Zn(OH)$_6$] and Ba_2[Zn(OH)$_6$]. The Cu atoms, located at $(0, 0, \frac{1}{2})$ (site symmetry $\bar{1}$), form mutually isolated and highly elongated Cu(OH)$_6$ octahedra, which are interconnected to slightly distorted Sr(OH)$_6$ trigonal prisms, forming a layered structure. The location of H atoms from difference Fourier maps and their refinement allowed the precise determination of a three-dimensional hydrogen-bonding network in which all hydroxide O atoms are involved. In addition, the hydrogen-bonding topologies in Sr_2[Cu(OH)$_6$] and other similar hexahydroxido-metallates with the general formulae $M1[M2(OH)_6]$, $M1_2[M2(OH)_6]$ and $M1_3[M2(OH)_6]$ were analysed in detail.

Comment

This work is part of our ongoing investigations regarding tetrahedral–octahedral framework structures with potentially interesting properties (Đorević et al., 2008; Đorević & Karanović, 2008; Stojanović et al., 2008). The aim of the current study was the synthesis and characterization of new compounds in the insufficiently known SrO–CuO–P_2O_5–H_2O system. The hydrothermal synthesis and crystal structure of distrontium hexahydroxidocuprate(II), Sr_2[Cu(OH)$_6$], are reported here.

Sr_2[Cu(OH)$_6$] belongs to a small family of inorganic compounds having the same structure type and general formula $M1_2[M2(OH)_6]$ ($M1 = Ba^{2+}$ and Sr^{2+}, and $M2 = Cu^{2+}$ and Zn^{2+}). All compounds crystallize in the space group $P2_1/c$ (No. 14) with $Z = 2$, but they were described in different settings. A study by Dubler et al. (1973) reported the space group as $P2_1/c$ (unique axis b) for both Ba_2[Cu(OH)$_6$] and Sr_2[Cu(OH)$_6$]. The crystal structure of Sr_2[Cu(OH)$_6$] was investigated later (Nadezhina et al., 1980a,b) in the same space group but in the $P2_1/b$ setting (unique axis c). The analogous

Zn compounds Sr_2[Zn(OH)$_6$] and Ba_2[Zn(OH)$_6$] were described in $P2_1/n$ (Stahl & Jacobs, 1998), and they have the same features as our data. In the present study, the previously reported structural model was confirmed, although with much improved precision for the atomic coordinates and inter-atomic distances. In addition, the first reliable location of H atoms allowed detailed insight into the network of hydrogen bonds.

The Cu atom, situated at an inversion centre (special position 2b in $P2_1/n$), is coordinated by four closer O atoms (two O1 and two O2) and two O3 atoms at much longer distances (Fig. 1 and Table 1), forming very elongated Cu(OH)$_6$ octahedra that are isolated from one another. The six nearest O atoms (two symmetry equivalents of O1, O2 and O3) define a somewhat distorted trigonal prismatic geometry around the Sr ions, which are displaced toward one of the bases. Each Sr(OH)$_6$ prism shares two edges from its basal plane with two neighbouring prisms, forming zigzag chains parallel to the [010] direction. The remaining two O atoms bridge the chains, producing slightly corrugated layers of Sr prisms (which lie on their rectangular sides, i.e. parallel to the layer) parallel to (110). In this way, the whole structure contains alternate layers of Sr and Cu polyhedra (Fig. 2). Alternatively, if the second-sphere Sr neighbours are accounted for, the Sr coordination can be described as a distorted tricapped trigonal prism (Fig. 1), similar to that found for the $M1$ site in the apatite structure (Đorević et al., 2008). Three capping O atoms (O1, O2 and O3) at longer distances are located near the equatorial plane of the trigonal prism. The longest is the Sr1—O1^{vi} bond distance [3.384 (3) Å; symmetry code: (vi) $x - 1$, y, z] and it contributes to the bond-valence sum by only 3.3%.
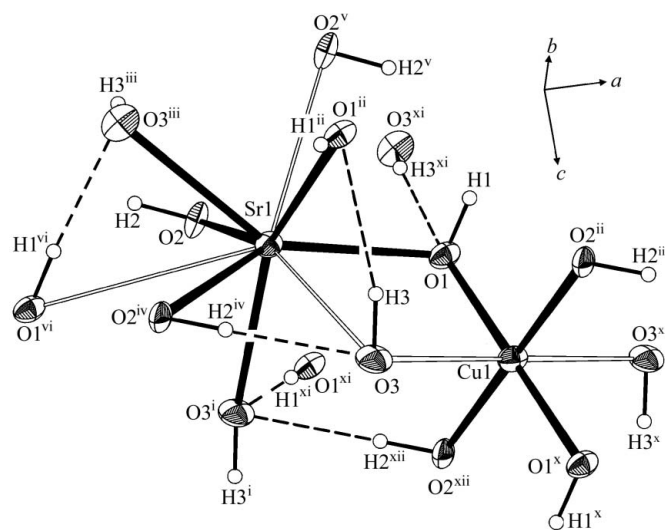

Figure 1
The coordination environment of the Sr and Cu sites, showing the hydrogen bonding. Displacement ellipsoids are drawn at the 70% probability level. The shorter Sr—O and Cu—O bonds are shown in black, the longer bonds are unfilled and hydrogen bonds are dashed lines. [Symmetry codes: (i) $-x + 1$, $-y$, $-z + 1$; (ii) $-x + \frac{3}{2}$, $y + \frac{1}{2}$, $-z + \frac{1}{2}$; (iii) $x - \frac{1}{2}$, $-y + \frac{1}{2}$, $z - \frac{1}{2}$; (iv) $-x + \frac{1}{2}$, $y + \frac{1}{2}$, $-z + \frac{1}{2}$; (v) $-x + 1$, $-y$, $-z$; (vi) $x - 1$, y, z; (x) $-x + 2$, $-y$, $-z + 1$; (xi) $-x + \frac{3}{2}$, $y - \frac{1}{2}$, $-z + \frac{1}{2}$; (xii) $x + \frac{1}{2}$, $-y - \frac{1}{2}$, $z + \frac{1}{2}$.]

As expected, H atoms fill the spaces between Sr and Cu polyhedra. The O1—H1 and O2—H2 groups are both hydrogen bonded to O3 atoms [O3[vii] and O3[viii], respectively; symmetry codes: (vii) $x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (viii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$], while the O3—H3 group is hydrogen bonded to atom O1[ii] [symmetry code: (ii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; Table 2].

Considering the contribution of non-H atoms only, the bond-valence calculation (Wills, 2009) is satisfied by the described geometry: $\sum v_{ij}(Sr1) = 2.01$ valence units (v.u.) for coordination number (CN) = 9 (and 1.70 v.u. for CN = 6), $\sum v_{ij}(Cu1) = 2.00$ v.u. for CN = 6 (1.84 v.u. for CN = 4), $\sum v_{ij}(O1) = 1.09$ v.u., $\sum v_{ij}(O2) = 1.10$ v.u. and $\sum v_{ij}(O3) = 0.82$ v.u. The bond-valence calculations show that the Sr—O and Cu—O bond lengths are consistent with the presence of divalent strontium and divalent copper. As expected, the bond-valence sums for the O atoms are undersaturated. Taking into account that all O atoms act as single hydrogen-bond donors and atom O1 acts as a single hydrogen-bond acceptor, while atom O3 is a double hydrogen-bond acceptor, the bond valences are well balanced (Brown, 1992; Wills, 2009). The fact that the bond valences for atoms O1 and O2 are the same indicates that O2 could also be a single hydrogen-bond acceptor. This could be explained by a possible different orientation of atom H3, which would be associated with two acceptors, viz. O1 and O2. Nevertheless, the two O···O distances are different; O3···O1[ii] [3.048 (5) Å; symmetry code: (ii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$] is shorter than O3···O2[i] [3.128 (5) Å; symmetry code: (i) $-x + 1, -y, -z + 1$], and in the structure refinement it was assumed that hydroxy group O3—H3 was completely in one orientation.

Between every two Cu(OH)$_6$ octahedra from the same layer there are two O2—H2···O3 bonds, forming eight-membered pseudo-rings and pseudo-chains of Cu octahedra parallel to [100]. The Cu···Cu distance along the pseudo-chain extension is shorter [5.7924 (4) Å] than that perpendicular to it [6.1663 (4) Å]. The other two pairs of hydrogen bonds, viz. O1—H1···O3[vii] and O3—H3···O1[ii], form additional eight-membered pseudo-rings around an empty site at (0, 0, 0) (special position 2a in $P2_1/n$), linking Cu(OH)$_6$ octahedra
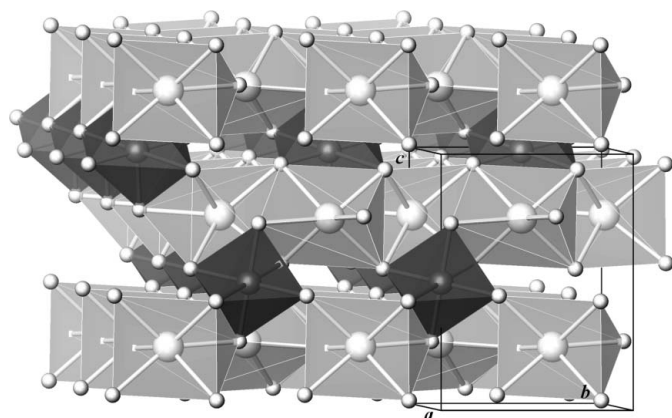

Figure 2
The packing of Cu (dark) and Sr (light) polyhedra (H atoms have been omitted for clarity).

from different layers so an infinite three-dimensional network of hydrogen bonds exists.

Although the H-atom positions and O—H distances were mostly unrealistic, a similar network of three hydrogen bonds connecting the Zn(OH)$_6$ octahedra was observed in Sr$_2$[Zn(OH)$_6$] and Ba$_2$[Zn(OH)$_6$] (Stahl & Jacobs, 1998). The shortest O···O distances are comparable to those in Sr$_2$[Cu(OH)$_6$] and are in the ranges 2.89–3.05, 3.02–3.10 and 3.11–3.15 Å for Sr$_2$[Cu(OH)$_6$], Sr$_2$[Zn(OH)$_6$] and Ba$_2$[Zn(OH)$_6$], respectively. The increasing O···O distances can be attributed to the incorporation of larger cations. Consequently, the strongest hydrogen bonding is expected in Sr$_2$[Cu(OH)$_6$].

Depending on the cation valences, hexahydroxido-metallates can be classified in three main groups with general formulae $M1[M2(OH)_6]$, $M1_2[M2(OH)_6]$ and $M1_3[M2(OH)_6]$.

In addition to the above-discussed cuprates and zincates, in the $M1_2[M2(OH)_6]$ group there are three complexes with $M2^{IV}$ and $M2^{IV}$ cations. Two of them, Li$_2$[Pt(OH)$_6$] (Troemel & Lupprich, 1975a) and Na$_2$[Hf(OH)$_6$] (Troyanov et al., 1999), are rather similar layered compounds with the H atoms directed toward the interlayer space and weak hydrogen bonding between layers. The third complex, K$_2$[Pb(OH)$_6$] (Jacobs & Stahl, 2000), shows some similarities with Sr$_2$[Cu(OH)$_6$], because between every two neighbouring Pb(OH)$_6$ octahedra there are two hydrogen bonds forming eight-membered pseudo-rings. Together with two K atoms below and above the pseudo-rings, empty octahedral sites around special position 9d in $R\bar{3}$ are created. Edge-sharing Pb(OH)$_6$ and □K$_2$(OH)$_4$ (□ is a vacancy) octahedra form pseudo-chains, which are further interconnected by hydrogen bonds only.

A large series of cubic or tetragonal minerals and synthetic compounds make up the $M1[M2(OH)_6]$ group of hydroxido-metallates ($M1$= Na, Ca, Cd, Co, Cu, Fe, Mg, Mn and Zn, and $M2$ = Ge, Pb, Sn and Sb). Structurally, all complexes from this group are very similar (Welch & Crichton, 2002, and references therein; Asai, 1975; Levy-Clement & Billiet, 1976; Morgenstern Badarau, 1976; Morgenstern Badarau & Michel, 1976; Troemel & Lupprich, 1975b). They can be easily compared with Sr$_2$[Cu(OH)$_6$] and isotypic compounds from the $M1_2[M2(OH)_6]$ group if all compounds are considered as derived from the perovskite ABO_3-type structure consisting of vertex-sharing BO_6 octahedra and A cations situated in cuboctahedral positions.

In Sr$_2$[Cu(OH)$_6$], around an empty site at special position 2a, (0, 0, 0), two O2—H2···O3 hydrogen bonds with neighbouring pairs of O1—H1···O3 and O3—H3···O1 hydrogen bonds (see Fig. 3 for the acceptor-atom symmetry codes) form six edges of a very distorted □(OH)$_6$ octahedron, which shares vertices with Cu(OH)$_6$ octahedra. These two types of octahedra further form an octahedral framework similar to that found in perovskites. The Sr atoms are situated between two vacant special positions [2c, ($\frac{1}{2}$, 0, $\frac{1}{2}$), and 2d, ($\frac{1}{2}$, 0, 0)] along the zigzag central line of the channel running along the c axis. A very similar framework of alternating $M1$ and $M2$ vertex-linked octahedra exists in the $M1[M2(OH)_6]$ compounds, but with different hydrogen-bonding topology. While in Sr$_2$[Cu-
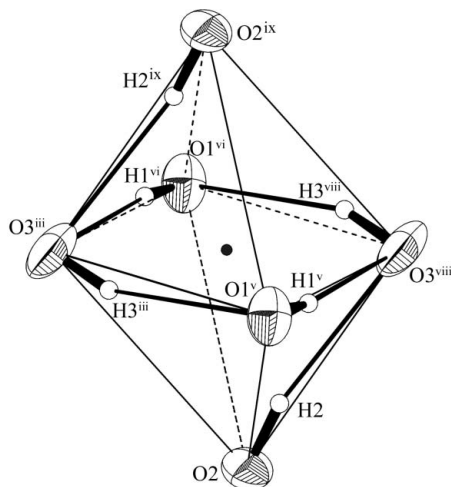
inorganic compounds

Figure 3
The network of hydrogen bonds around the empty (0, 0, 0) site (black circle) in $Sr_2[Cu(OH)_6]$. Full and dashed thin lines emphasize the deformed octahedral geometry of the empty site. H atoms are shown as small circles of arbitrary radii. [Symmetry codes: (iii) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (v) $-x + 1, -y, -z$; (vi) $x - 1, y, z$; (viii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (ix) $-x, -y, -z$.]

$(OH)_6]$ and isotypic compounds hydrogen bonds are concentrated around an empty octahedral site, in the $M1[M2(OH)_6]$ structures all octahedral sites are occupied and hydrogen bonds are concentrated around an empty cuboctahedral site. In $M1[M2(OH)_6]$, all O atoms act as single donors and acceptors of hydrogen bonds and help to bind the octahedra into a three-dimensional framework. It was concluded that the absence of cuboctahedral cations and hydrogen-bonding topology affect the compressibility of the protonated octahedral framework in $M1[M2(OH)_6]$ (Welch & Crichton, 2002; Ross *et al.*, 2002). Therefore, it seems worthwhile to study the compressibility of $Sr_2[Cu(OH)_6]$ and similar compounds given the absence of some octahedral cations and the different hydrogen-bonding topology.

Finally, the $M1_3[M2(OH)_6]$ group comprises three very similar and specific complexes, namely $K_3[Sc(OH)_6]$, $Rb_3[Sc(OH)_6]$ and $Rb_3[Cr(OH)_6]$ (Hennig & Jacobs, 1992). They contain mutually isolated face-to-face-oriented $M2(OH)_6$ octahedra that are hydrogen bonded in infinite chains. Very weak hydrogen bonds with O···O distances longer than 3 Å form trigonal pyramids between $M2(OH)_6$ octahedra. However, the H atoms are oriented almost directly toward each other and their positions are doubtful.

Experimental

$Sr_2[Cu(OH)_6]$ was synthesized hydrothermally from a mixture of $Sr(OH)_2 \cdot 8H_2O$ (Merck, >97%), $Cu(OH)_2 \cdot 2H_2O$ (Merck, >99%) and $(NH_4)_2HPO_4$ (Loba Chemie, >99%). The solid mixture was transferred into a Teflon vessel filled to approximately 70% of its volume with distilled water. The initial pH of the mixture was 8. The Teflon vessel was enclosed in a stainless steel autoclave, which was heated under autogenous pressure to 373 K, held at this temperature for 72 h and cooled to room temperature over a period of 96 h. The pH of the supernatant solution was 10. The resulting products were filtered off,

washed thoroughly with distilled water and dried in air at room temperature. The title compound crystallized as prismatic blue transparent crystals (yield *ca* 5%) together with a light-blue powder.

Table 1
Selected geometric parameters (Å, °).

Sr1—O3^i	2.484 (3)	Sr1—O2^v	2.839 (3)
Sr1—O2	2.533 (3)	Sr1—O3	2.856 (3)
Sr1—O1^{ii}	2.565 (3)	Sr1—O1^{vi}	3.384 (3)
Sr1—O1	2.569 (3)	Cu1—O2^{iv}	1.965 (3)
Sr1—O3^{iii}	2.665 (3)	Cu1—O1^{vi}	1.967 (3)
Sr1—O2^{iv}	2.765 (3)	Cu1—O3^{vi}	2.619 (3)
O2^{iv}—Cu1—O1^{vi}	91.83 (13)	O1^{vi}—Cu1—O3^{vi}	90.86 (12)
O2^{iv}—Cu1—O1^i	88.17 (13)	O1^i—Cu1—O3^{vi}	89.14 (12)
O2^{iv}—Cu1—O3^{vi}	86.85 (12)	O2^{iv}—Cu1—O3^i	93.15 (12)

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O3^{vii}	0.79 (4)	2.10 (4)	2.888 (5)	174 (4)
O2—H2···O3^{viii}	0.82 (3)	2.12 (3)	2.909 (5)	162 (3)
O3—H3···O1^{ii}	0.80 (4)	2.32 (4)	3.048 (5)	152 (4)

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

All H atoms were located in difference Fourier maps and their positional parameters were refined with the O—H distances restrained to 0.82 (2) Å; U_{iso}(H) values were fixed at $1.3U_{eq}$(O).

Data collection: *CrysAlisPro* (Oxford Diffraction, 2009); cell refinement: *CrysAlisPro*; data reduction: *CrysAlisPro*; 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, 2009).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3197). 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.

Asai, T. (1975). *Bull. Chem. Soc. Jpn*, **48**, 2677–2679.

Brown, I. D. (1992). *Acta Cryst.* B**48**, 553–572.

Đorević, T. & Karanović, Lj. (2008). *J. Solid State Chem.* **181**, 2889–2898.

Đorević, T., Šutović, S., Stojanović, J. & Karanović, Lj. (2008). *Acta Cryst.* C**64**, i82–i86.

Dowty, E. (2000). *ATOMS for Windows*. Version 5.1. Shape Software, Kingsport, Tennessee, USA.

Dubler, E., Korber, P. & Oswald, H. R. (1973). *Acta Cryst.* B**29**, 1929–1933.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Hennig, T. J. & Jacobs, H. (1992). *Z. Anorg. Allg. Chem.* **616**, 71–78.

Jacobs, H. & Stahl, R. (2000). *Z. Anorg. Allg. Chem.* **626**, 1863–1866.

Levy-Clement, C. & Billiet, Y. (1976). *Bull. Soc. Fr. Miner. Cristallogr.* **99**, 361–372.

Morgenstern Badarau, I. (1976). *J. Solid State Chem.* **17**,399–406.

Morgenstern Badarau, I. & Michel, A. (1976). *J. Inorg. Nucl. Chem.* **38**, 1400–1402.

Nadezhina, T. N., Pobedimskaya, E. A. & Belov, N. V. (1980a). *Dokl. Akad. Nauk SSSR*, **250**, 1126–1130.

Nadezhina, T. N., Pobedimskaya, E. A. & Belov, N. V. (1980b). *Sov. Phys. Dokl.* **25**, 73–75.

Oxford Diffraction (2009). *CrysAlisPro*. Version 1.171.33.31. Oxford Diffraction Ltd, Yarnton, England.

Ross, N. L., Chaplin, T. D. & Welch, M. D. (2002). *Am. Mineral.* **87**, 1410–1414.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Stahl, R. & Jacobs, H. (1998). *Z. Anorg. Allg. Chem.* **624**, 17–20.

Stojanović, J., Đorević, T. & Karanović, Lj. (2008). *Acta Cryst.* C**64**, i91–i94.

Troemel, M. & Lupprich, E. (1975a). *Z. Anorg. Allg. Chem.* **414**, 160–168.

Troemel, M. & Lupprich, E. (1975b). *Z. Anorg. Allg. Chem.* **414**, 169–175.

Troyanov, S. I., Kostrikin, A. V., Linko, I. V., Zaitsev, B. E., Ezhov, A. I. & Spiridonov, F. M. (1999). *Kristallografiya*, **44**, 1054–1058.

Welch, M. D. & Crichton, W. A. (2002). *Mineral. Mag.* **66**, 431–440.

Westrip, S. P. (2009). *publCIF*. In preparation.

Wills, A. S. (2009). *VaList*. http://www.ccp14.ac.uk.