

Structure and properties of $\text{SrCu}(\text{OH})_4 \cdot \text{H}_2\text{O}$

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The structure of $\text{SrCu}(\text{OH})_4 \cdot \text{H}_2\text{O}$ has been determined from a single-crystal X-ray refinement and shown to contain isolated square-planar $[\text{Cu}(\text{OH})_4]^{2-}$ groups separated by strontium ions and hydrogen bonded to water molecules. ESR, IR and UV/VIS spectra are also reported for this compound and are consistent with the presence of discrete $[\text{Cu}(\text{OH})_4]^{2-}$ square planes. Thermal decomposition of this material proceeded by a complex multistage process via $\text{Sr}_2(\text{OH})_2\text{Cu}(\text{OH})_4$, through CuO and $\text{Sr}(\text{OH})_2$, to Sr_2CuO_3 and CuO . Consideration of the structure of $\text{SrCu}(\text{OH})_4 \cdot \text{H}_2\text{O}$ shows that the relative orientation of the $[\text{Cu}(\text{OH})_4]^{2-}$ units is such that they do not crosslink to form infinite CuO_2 sheets.

The structures of high-temperature superconducting oxides are based on infinite CuO_2 sheets formed from linked CuO_4 square planes.¹ These layers may be separated by a variety of cations, the simplest involving solely Ca^{2+} or Sr^{2+} ions as in the phases of the stoichiometry MCuO_2 ^{2,3} and $\text{Sr}_2\text{CuO}_{3+x}$.⁴ The discovery of superconducting oxide materials containing only strontium and copper as the cations has recently gained renewed interest following the synthesis of one member of the $\text{Sr}_{n+1}\text{Cu}_n\text{O}_{2n+1}$ series via a novel route involving thermal decomposition of a copper hydroxometalate.^{5,6} Formerly, preparation of the superconducting strontium cuprates has involved annealing the material at high temperatures (typically 900 °C) under elevated pressures, in the case of SrCuO_2 60 kbar (6×10^9 Pa). Mitchell *et al.*⁵ have studied the ambient-pressure synthesis of tetragonal $\text{Sr}_2\text{CuO}_{3+x}$ from strontium hexahydroxocuprate(II), $\text{Sr}_2[\text{Cu}(\text{OH})_6]$, a single-source precursor. Dehydration of $\text{Sr}_2[\text{Cu}(\text{OH})_6]$ below 400 °C in pure oxygen produces tetragonal $\text{Sr}_2\text{CuO}_{3+x}$ directly, probably due to their structural similarity. These two materials are stoichiometrically related by the removal of three H_2O units from $\text{Sr}_2[\text{Cu}(\text{OH})_6]$ to give Sr_2CuO_3 ; elimination of these water molecules by condensation of two hydroxide groups from two different $[\text{Cu}(\text{OH})_6]^{4-}$ octahedra links them together to form the cuprate layers characteristic of high-temperature superconductors.

Another high-temperature cuprate superconductor requiring synthesis under high pressure is the infinite layer $\text{Sr}_{1-x}\text{CuO}_2$ compound. Zhou *et al.*⁷ discovered that application of high pressure to orthorhombic SrCuO_2 prepared at ambient pressure transformed the material into a tetragonal infinite-layer phase consisting of parallel CuO_2 layers separated by Sr^{2+} ions.

A second strontium copper hydroxometalate of the stoichiometry $\text{SrCu}(\text{OH})_4 \cdot \text{H}_2\text{O}$ was reported by Scholder *et al.*⁸ alongside $\text{Sr}_2[\text{Cu}(\text{OH})_6]$ and its thermal decomposition has since been briefly reported,⁹ however, no structure has been described for this material. Of interest is whether the structure of $\text{SrCu}(\text{OH})_4 \cdot \text{H}_2\text{O}$ has the correct features for thermal dehydrative crosslinking to form an infinite CuO_2 sheet. Given that the stoichiometry of this material following dehydration reflects that of SrCuO_2 plus the likelihood that it contains square-planar $[\text{Cu}(\text{OH})_4]^{2-}$ groups, which could link together to form an infinite layered structure, the synthesis and chemistry of $\text{SrCu}(\text{OH})_4 \cdot \text{H}_2\text{O}$ has been studied in this work. This compound has been characterised using both single-crystal and powder diffraction, ESR, IR and UV/VIS spectroscopy. Its thermal decomposition, as studied using thermogravimetric analysis in combination with powder X-ray diffraction, is also discussed.

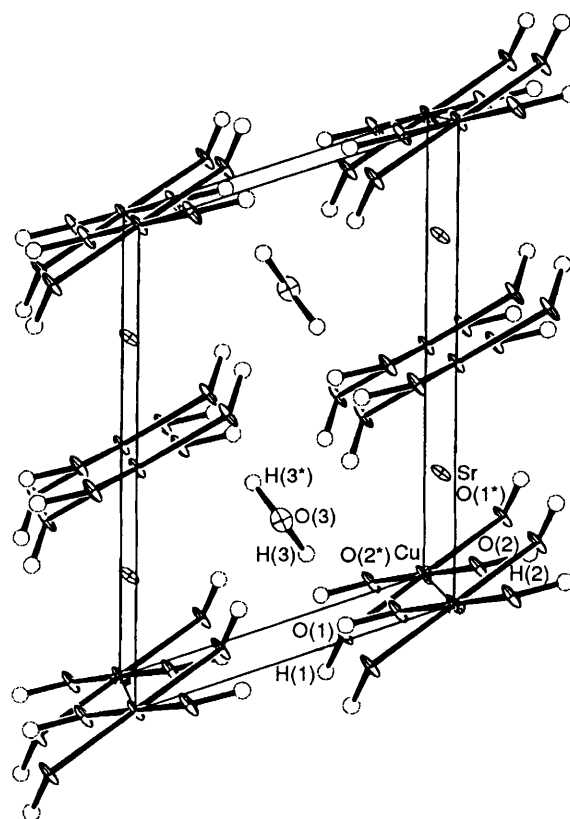


Fig. 1 The structure of $\text{SrCu}(\text{OH})_4 \cdot \text{H}_2\text{O}$ viewed down the b axis. Thermal ellipsoids are shown at 90% probability

Discussion

Final refined atomic coordinates for $\text{SrCu}(\text{OH})_4 \cdot \text{H}_2\text{O}$ are given in Table 1 and derived bond lengths and angles of importance summarised in Table 2. The crystal structure of $\text{SrCu}(\text{OH})_4 \cdot \text{H}_2\text{O}$ consists of square-planar $[\text{Cu}(\text{OH})_4]^{2-}$ units stacked along the c axis with the strontium atoms positioned midway between the four-co-ordinate units, Fig. 1. This contrasts with the Jahn-Teller distorted $[\text{Cu}(\text{OH})_6]^{4-}$ octahedron contained in $\text{Sr}_2[\text{Cu}(\text{OH})_6]$ (and the barium analogue), where the coordination polyhedron of the Cu^{II} ion is formed from four equatorial and two very distant axial oxygen atoms. The coordination of the copper atom in $\text{Na}_2\text{Cu}(\text{OH})_4$ ¹⁰ is four-fold square-planar to hydroxide, however, two more distant oxygen atoms again complete a very distorted octahedron. Therefore,

Table 1 Refined atomic coordinates for SrCu(OH)₄·H₂O

Atom	x	y	z
Sr	0.0000	-0.4501(2)	0.2500
Cu	0.0000	0.0000	0.0000
O(1)	0.2758(9)	0.1520(8)	-0.0569(7)
O(2)	-0.1504(10)	0.2791(8)	-0.0005(8)
O(3)	0.5000	0.388(1)	0.2500
H(1)	0.3254	0.0549	-0.1341
H(2)	-0.3181	0.2620	-0.0096
H(3)	0.41(2)	0.32(1)	0.15(1)

Table 2 Selected bond lengths (Å) and angles (°) for SrCu(OH)₄·H₂O with estimated standard deviations in parentheses

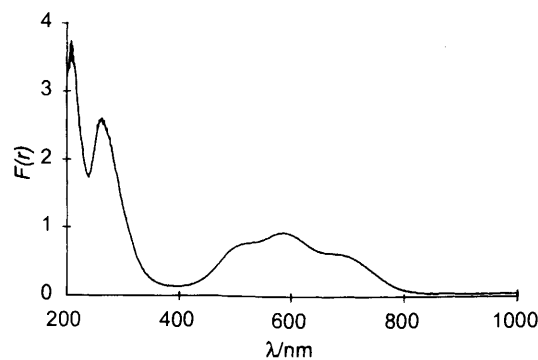
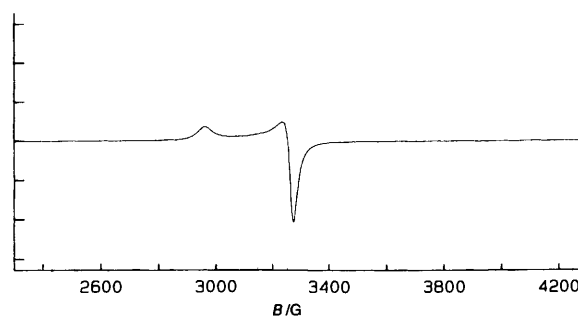
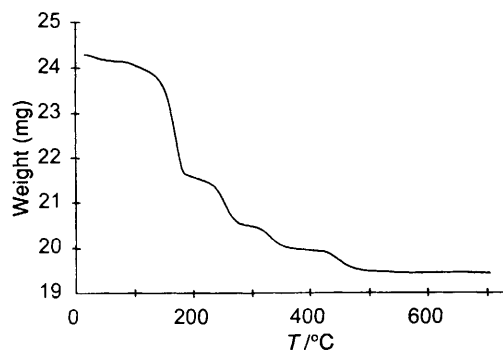
Sr-O(2)	2.534(5)	O(1)-H(1)	0.96
Cu-O(1)	1.948(5)	O(3)-H(3)	0.88
Cu-O(2)	1.929(5)	O(2)-H(2)	0.90
O(1)-Cu-O(2)	85.2(2)	H(3)-O(3)-H(3)	118(11)

the presence of four coplanar bonds alone forming [Cu(OH)₄]²⁻ units in SrCu(OH)₄·H₂O is unique. Interatomic distances and bond angles of the [Cu(OH)₄]²⁻ unit match closely those of crystalline CuO; the simplest example of Cu^{II} forming four coplanar bonds. Other compounds containing discrete [M(OH)₄]²⁻ species are rare: the tetrahedral [Zn(OH)₄]²⁻ ion has been isolated in the stoichiometrically equivalent SrZn(OH)₄·H₂O¹¹ and a compound of the stoichiometry K₂Pd(OH)₄ is described by the same authors.¹² The square-planar tetrahydroxyaurate(III) ion, Au(OH)₄⁻, is well known and the strontium salt Sr[Au(OH)₄]₂ has a similar structure to SrCu(OH)₄·H₂O with layers of discrete [Au(OH)₄]⁻ ions separated by strontium.¹³ Powder X-ray diffraction data collected from polycrystalline SrCu(OH)₄·H₂O were in good agreement with the expected pattern as calculated from the refined structure.

The UV/VIS spectrum shown in Fig. 2, obtained from SrCu(OH)₄·H₂O, is consistent with the square-planar geometry around copper showing three broad features at 14 800, 17 100 and 19 400 cm⁻¹ corresponding to transition to the d_{x²-y²} orbital from the d_{z²}, d_{xy} and d_{yz}. No data has been reported previously for this ion but the planar CuO₄ chromophore has been extensively studied as the [Cu(acac)₂] (acac = acetylacetonate) species and substituted versions thereof.¹⁴ For [Cu(acac)₂] the three characteristic transitions are seen at 14 500, 15 600 and 18 000 cm⁻¹; for SrCu(OH)₄·H₂O these transitions move to 14 800, 17 100 and 19 400 cm⁻¹ indicative of a slightly stronger ligand field. In CaCuSi₄O₁₀ where the copper geometry is also strictly square planar with respect to oxygen, the three transitions are centred at 12 900, 15 800 and 18 800 cm⁻¹.¹⁵

The ESR spectrum of SrCu(OH)₄·H₂O is typical of square-planar copper showing resonances with g_{||} = 2.26 and g_⊥ = 2.06, Fig. 3. Similar values are again found for copper in true square-planar co-ordination of oxygen to copper in CaCuSi₄O₁₀ (2.054 and 2.326).¹⁵ The IR spectra show broad features at 3400 and 1500 cm⁻¹ characteristic of water; absorptions at 1024 and 850 cm⁻¹ probably derive from MO-H deformations. A series of bands observed below 600 cm⁻¹ are typical of metal-oxygen stretching modes, in SrZn(OH)₄·H₂O with a tetrahedral anion the zinc-oxygen stretches are seen at 415 and 445 cm⁻¹.¹¹

The thermogravimetric trace for the thermal decomposition of SrCu(OH)₄·H₂O in air over the temperature range room temperature to 700 °C is depicted in Fig. 4. The decomposition proceeds by a complex route with several stages, which were not seen to be reversible. In order to determine the nature of the products formed at each stage powder X-ray diffraction

**Fig. 2** UV/VIS spectrum of SrCu(OH)₄·H₂O**Fig. 3** ESR spectrum of SrCu(OH)₄·H₂O showing resonances typical of square-planar copper**Fig. 4** Thermogravimetric trace for the decomposition of SrCu(OH)₄·H₂O in static air between room temperature and 700 °C

patterns were taken once the sample had been equilibrated at that temperature, typically for 8 h. Products equilibrated under these conditions were characterised by powder X-ray diffraction as identical to those formed during heating on the thermobalance but larger quantities were available from this process. As the material is extremely difficult to dry completely a small initial weight loss between 25 and 100 °C results from the loss of surface water. The second weight loss between 120 and 180 °C represents the decomposition to a phase of stoichiometry Sr₂(OH)₂Cu(OH)₄ as identified by powder X-ray diffraction; this phase was first reported by Nadezhina *et al.*¹⁶ and prepared in that work under hydrothermal conditions. During this process one and a half water molecules are lost per SrCu(OH)₄·H₂O unit, as shown by the weight change and CuO is also formed; no evidence for CuO was seen in the powder diffraction pattern, however CuO formed at such low temperatures is likely to be amorphous.

The next stage in decomposition is more complex and occurs near 250 °C. The weight loss corresponds to the loss of one half of a water molecule per SrCu(OH)₄·H₂O and the formation of a product of stoichiometry ½Sr₂Cu₂O₅H₄ [*i.e.*, Sr(OH)₂ + CuO]. Powder X-ray diffraction data of the product at this stage shows total decomposition to Sr(OH)₂ and CuO. The

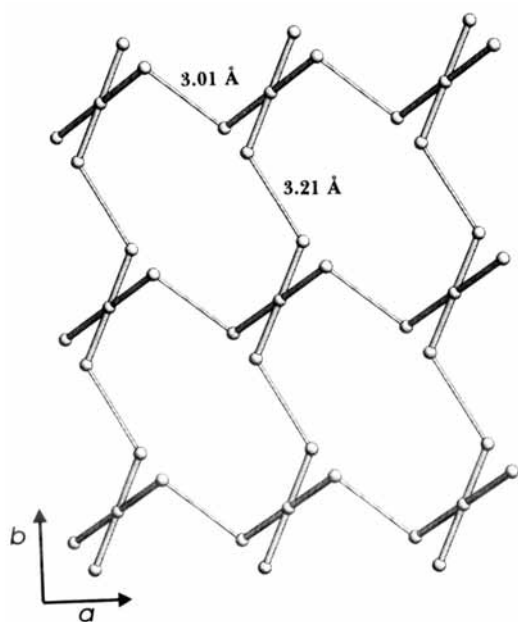


Fig. 5 Relative positions of the CuO_4 units in the ab plane with the shortest interunit distances shown

final weight losses occurring between 300 and 470 °C involves the partial back reaction of strontium hydroxide and copper oxide to yield Sr_2CuO_3 though this reaction is incomplete in air where reaction of some of the hydroxide with carbon dioxide produces small amounts of unreactive SrCO_3 and leaving residual CuO in the product. The solid-state mechanism of the observed changes is unclear however, as the dehydration was irreversible, the process is unlikely to be topotactic.

The decomposition of the complex hydroxide to copper oxide and alkali-metal hydroxide parallels the behaviour seen for $\text{NaCu}(\text{OH})_4$ where NaOH and CuO are formed in the decomposition process before reacting back together to produce NaCuO_2 at a higher temperature.¹⁰

The structure of $\text{SrCu}(\text{OH})_4 \cdot \text{H}_2\text{O}$, Fig. 1, shows that the relative positions of the $\text{Cu}(\text{OH})_4$ units are such that the formation of CuO_2 layers by loss of H_2O could be easily visualised. However, consideration of the closest contacts between the OH groups, Fig. 5, shows that the linking between $\text{Cu}(\text{OH})_4$ units is unlikely to take place in a single plane in the structure. Indeed a probable route leads to chains of edge-shared CuO_4 square planes as found in CuO .

Conclusion

A material containing the discrete square-planar $[\text{Cu}(\text{OH})_4]^{2-}$ ion has been prepared and structurally characterised for the first time. Spectroscopic data are consistent with the presence of this anion which has copper in a four-co-ordinate environment rather than the elongated octahedral co-ordination found in other complex copper hydroxides. Thermal decomposition of $\text{SrCu}(\text{OH})_4 \cdot \text{H}_2\text{O}$ results ultimately in the formation of Sr_2CuO_3 and CuO via CuO and $\text{Sr}(\text{OH})_2$ as crosslinking of the $\text{Cu}(\text{OH})_4$ units on thermolysis leads to chain-like units rather than the infinite planes of SrCuO_2 .

Experimental

The hydroxide, $\text{SrCu}(\text{OH})_4 \cdot \text{H}_2\text{O}$, was synthesised following the method described by Scholder *et al.*⁸ All solutions were handled in polymethylpropylene containers to prevent silicate contamination. Copper(II) bromide (7.5 g) in H_2O (20 cm^3) was gradually added to a cold solution (< 5 °C) of NaOH (60 g) in H_2O (120 cm^3) with cooling in an ice-bath. The solution was then warmed to 65 °C and filtered, the filtrate being cooled to 10 °C and diluted with H_2O (ca. 40 cm^3). An ice-cold

solution of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ (3.5 g) in H_2O (40 cm^3) was added and the solution warmed to 25–30 °C. The violet precipitate produced was filtered.

Crystals of $\text{SrCu}(\text{OH})_4 \cdot \text{H}_2\text{O}$ suitable for single-crystal X-ray structure determination were obtained by a similar method to the bulk precipitate used for powder X-ray diffraction, however, the volume of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ solution was reduced by half and added gradually over a 30 min period. Well formed violet needle-shaped crystals were formed over a period of 30 min. The crystals could not be isolated from the mother liquor and washed due to their instability. Therefore, for crystallographic studies, a small single crystal coated in the mother liquor was quickly sealed inside a glass capillary.

Powder X-ray diffraction data were collected using $\text{Cu-K}\alpha_1$ ($\lambda = 1.5406 \text{ \AA}$) radiation over the 2θ range 20–120° with a step size of 0.02° over a period of 15 h on a Siemens D5000 diffractometer. ESR spectra were recorded from a powdered sample at room temperature on a Bruker ECS106 spectrometer referenced to diphenylpicrylhydrazyl, UV/VIS spectra on a Perkin-Elmer Lambda 19 spectrophotometer and IR spectra, both as KBr and CsI discs, on a Perkin-Elmer 983G spectrometer in the range 4000–200 cm^{-1} . Thermal decomposition was investigated *via* thermogravimetric and differential thermal analysis using a Stanton Redcroft STA 1500H simultaneous thermal analyser in static air.

Crystal-structure determinations

A crystal of $\text{SrCu}(\text{OH})_4 \cdot \text{H}_2\text{O}$ having approximate dimensions 0.05 × 0.03 × 0.3 mm was mounted in a quartz capillary. All measurements were made on a Rigaku AFC7S diffractometer with graphite-monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$).

Crystal data. $\text{H}_6\text{CuO}_5\text{Sr}$, $M = 237.21$, primitive monoclinic, $a = 5.458(2)$, $b = 6.257(3)$, $c = 7.879(2) \text{ \AA}$, $\beta = 108.28(2)^\circ$, $U = 255.5(1) \text{ \AA}^3$, space group $P2_1/c$ (no. 13), $Z = 2$, $D_c = 3.08 \text{ g cm}^{-3}$, $F(000) = 226.00$, $\mu(\text{Mo-K}\alpha) = 145.0 \text{ cm}^{-1}$.

Data collection and processing. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 18 carefully centred reflections in the range $20.51 < 2\theta < 27.19^\circ$. Data were collected at $22 \pm 1 \text{ }^\circ\text{C}$, using the ω - 2θ scan technique to a maximum 2θ value of 50.0°. Omega scans of several intense reflections, made prior to data collection, had an average width at a half-height of 0.19° with a take-off angle of 6.0°; ω -scan width = $0.84 + 0.35 \tan\theta$, ω -scan speed $16.0^\circ \text{ min}^{-1}$. 552 Reflections measured, 499 were unique ($R_{\text{int}} = 0.232$). An empirical absorption correction using the program DIFABS¹⁷ was applied which resulted in transmission factors ranging from 0.69 to 1.00. The data were corrected for Lorentz polarisation effects and changes in standard intensities (1.42% increase).

Structure analysis and refinement. The structure was solved by heavy-atom Patterson methods¹⁸ and expanded using Fourier techniques.¹⁹ The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located from the Fourier-difference maps. Positional and thermal parameters were fixed for H(1) and H(2). The positional parameters of H(3) were varied but its thermal parameter was fixed. Function minimised = $\sum w(|F_o| - |F_c|)^2$. The final cycle of full-matrix least-squares refinement was based on 371 observed reflections [$I > 3.00\sigma(I)$] and 38 variable parameters and converged with R and R' values of 0.032 and 0.036 respectively.

Neutral-atom scattering factors were taken from Cromer and Waber.²⁰ Anomalous dispersion effects were included in F_c ,²¹ the values for the mass-attenuation coefficients are those of Creagh and Hubbel.²² All calculations were performed using the TEXSAN²³ crystallographic software package.

Complete atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.* 1996, Issue 1.

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