Ca$_2$CuO$_2$Cl$_2$, a redetermination from single-crystal X-ray diffraction data

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The crystal structure of Ca$_2$CuO$_2$Cl$_2$, dicalcium oxidocuprate(II) dichloride, was redetermined on the basis of single-crystal X-ray diffraction data using a laboratory Mo anode. Previous structure determinations based on single-crystal X-ray data [Grande & Müller-Buschbaum (1977). *Z. Anorg. Allg. Chem.* **429**, 88–90], powder X-ray diffraction data [Yamada *et al.* (2005). *Phys. Rev. B*, **72**, 224503–1–5] or neutron diffraction data [Argyriou *et al.* (1995). *Phys. Rev. B*, **51**, 8434–8437] were confirmed. The present study allowed the refinement of anisotropic displacement parameters for all crystallographic sites, accompanied with higher accuracy and precision for bond lengths and angles. The layered title compound comprises of [CuO$_4$] square-planar and [CaO$_4$Cl$_4$] square-antiprismatic coordination polyhedra, and is the undoped parent compound of a high-temperature superconducting cuprate.

3D view
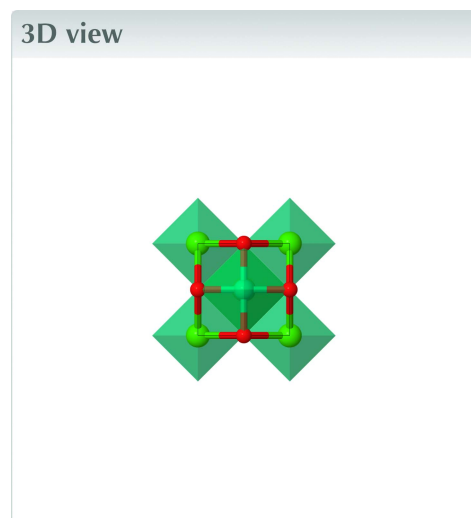
Structure description

The layered crystal structure of Ca$_2$CuO$_2$Cl$_2$ (Fig. 1) has tetragonal symmetry (space group *I*4/*mmm*), and is the undoped parent compound of a high-temperature super-conducting cuprate (Hiroi *et al.*, 1994; Kohsaka *et al.*, 2002; Yamada *et al.*, 2005).

The principal building blocks in the structure are square-planar [CuO$_4$] and square-antiprismatic [CaO$_4$Cl$_4$] polyhedra, both with point group symmetry 4/*mmm*. Relevant bond lengths are listed in Table 1. The building units are fused together by sharing O and Cl atoms into layers extending parallel to (001). Square-planar [CuO$_4$] polyhedra are typical of oxocuprates(II) (Müller-Buschbaum, 1977), and are found in other high-temperature superconducting cuprates (Raveau *et al.*, 1991). However, here the [CuO$_4$]

Table 1
Selected bond lengths (Å).

Cu1—Cl1	2.7452 (14)	Ca1—Cl1^{i}	2.9775 (7)
Cu1—O1	1.9340 (1)	Ca1—O1^{ii}	2.4900 (7)

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

units are complemented to elongated [CuO$_4$Cl$_2$] octahedra with the Cl atoms at the axial sites.

Previous structure determinations of Ca$_2$CuO$_2$Cl$_2$ based on single-crystal X-ray data (Grande & Müller-Buschbaum, 1977), powder X-ray diffraction data (Yamada *et al.*, 2005) or neutron diffraction data (Argyriou *et al.*, 1995) are confirmed by the current study. The first determination of the crystal structure of Ca$_2$CuO$_2$Cl$_2$ converged with rather high residuals (R_1 = 0.105; Grande & Müller-Buschbaum, 1977). Another previous attempt to determine anisotropic displacement parameters for all crystallographic sites has been made on basis of neutron powder diffraction data (Argyriou *et al.*, 1995). We note that most of the refined values are compatible with our refinement within uncertainty, with the notable exception of U_{33} for the chlorine and oxygen sites, which have larger values in our refinement. Although a direct comparison between the results of the two techniques is difficult, we note that neutrons are more sensitive to oxygen but the number of measured reflections is much smaller in powder diffraction. The much higher redundancy resulting from single-crystal X-ray data collection allows a better data-to-parameter ratio and hence a more reliable refinement. We also estimate that our model shows a lower correlation between fitted parameters.

Synthesis and crystallization

Powders of CaO and CuCl$_2$ were mixed in a molar ratio of 2:1 and put into an alumina crucible. The mixed powder was heated at 1053 K for 24 h with intermediate grindings.
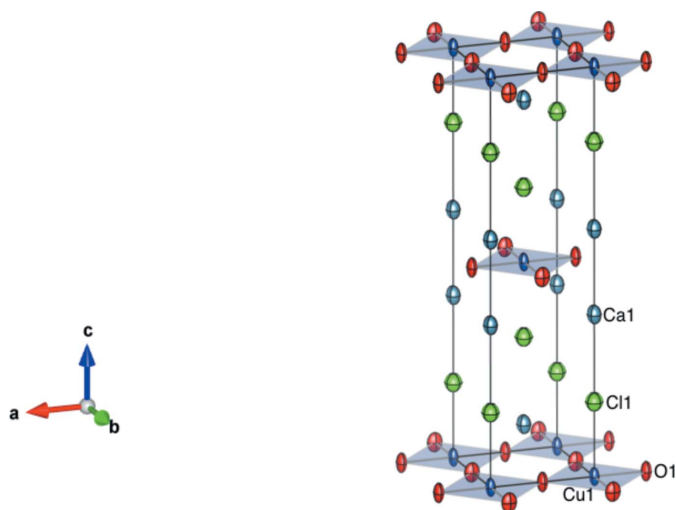

Figure 1
The crystal structure of Ca$_2$CuO$_2$Cl$_2$, showing displacement ellipsoids drawn at the 90% probability level.

Table 2
Experimental details.

Crystal data	
Chemical formula	Ca$_2$CuO$_2$Cl$_2$
M_r	246.60
Crystal system, space group	Tetragonal, $I4/mmm$
Temperature (K)	293
a, c (Å)	3.8680 (2), 15.0321 (15)
V (Å^3)	224.90 (3)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	8.16
Crystal size (mm)	0.80 × 0.40 × 0.16
Data collection	
Diffractometer	Agilent Xcalibur, Sapphire3
Absorption correction	Analytical [*CrysAlis PRO* (Agilent, 2013), using a multi-faceted crystal model based on expressions derived by Clark & Reid (1995)]
T_{min}, T_{max}	0.056, 0.287
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	634, 101, 101
R_{int}	0.019
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.652
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.018, 0.047, 1.24
No. of reflections	101
No. of parameters	12
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.51, −0.43

Computer programs: *CrysAlis PRO* (Agilent, 2013), *OLEX2* (Dolomanov *et al.*, 2009), *VESTA* (Momma & Izumi, 2011) and *publCIF* (Westrip, 2010).

Subsequently, the as-obtained Ca$_2$CuO$_2$Cl$_2$ material was again heated to 1053 K at a ramp rate of 60 K h^{-1} and kept at this temperature for 5 h. It was then heated to 1203 K at a ramp rate of 60 K h^{-1} and kept at that temperature for 10 h. Finally, it was cooled down to room temperature at a ramp rate of 60 K h^{-1}. Single crystals with a size up to 2 mm × 2 mm × 0.1 mm could be harvested by cleaving the as-grown bulks.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Coordinates from an isotypic compound were used in the structure solution.

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full crystallographic data

Ca$_2$CuO$_2$Cl$_2$, a redetermination from single-crystal X-ray diffraction data

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Dicalcium oxidocuprate(II) dichloride

Crystal data

Ca$_2$CuO$_2$Cl$_2$	$D_x = 3.641$ Mg m^{-3}
$M_r = 246.60$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Tetragonal, $I4/mmm$	Cell parameters from 440 reflections
$a = 3.8680$ (2) Å	$\theta = 5.4–27.4°$
$c = 15.0321$ (15) Å	$\mu = 8.16$ mm^{-1}
$V = 224.90$ (3) Å^3	$T = 293$ K
$Z = 2$	Block, black
$F(000) = 238$	$0.80 \times 0.4 \times 0.16$ mm

Data collection

Agilent Xcalibur, Sapphire3 diffractometer	$T_{min} = 0.056$, $T_{max} = 0.287$
Radiation source: Enhance (Mo) X-ray Source	634 measured reflections
Graphite monochromator	101 independent reflections
Detector resolution: 16.0318 pixels mm^{-1}	101 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.019$
Absorption correction: analytical	$\theta_{max} = 27.6°$, $\theta_{min} = 5.4°$
[CrysAlis PRO (Agilent, 2013), using a multi-faceted crystal model based on expressions derived by Clark & Reid (1995)]	$h = -4 \rightarrow 4$
	$k = -4 \rightarrow 4$
	$l = -18 \rightarrow 18$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.018$	
$wR(F^2) = 0.047$	$w = 1/[\sigma^2(F_o^2) + (0.0248P)^2 + 0.4487P]$
$S = 1.24$	where $P = (F_o^2 + 2F_c^2)/3$
101 reflections	$(\Delta/\sigma)_{max} < 0.001$
12 parameters	$\Delta\rho_{max} = 0.51$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.43$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
Cu1	0.0000	0.0000	0.5000	0.0090 (3)
Cl1	0.0000	0.0000	0.31738 (9)	0.0158 (4)
Ca1	0.0000	0.0000	0.10434 (7)	0.0128 (3)
O1	0.5000	0.0000	0.5000	0.0120 (7)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0049 (4)	0.0049 (4)	0.0171 (5)	0.000	0.000	0.000
Cl1	0.0152 (5)	0.0152 (5)	0.0171 (6)	0.000	0.000	0.000
Ca1	0.0101 (4)	0.0101 (4)	0.0183 (6)	0.000	0.000	0.000
O1	0.0049 (16)	0.0114 (17)	0.0198 (16)	0.000	0.000	0.000

Geometric parameters (Å, º)

Cu1—Cl1^{i}	2.7451 (14)	Ca1—Cl1^{vi}	2.9775 (7)
Cu1—Cl1	2.7452 (14)	Ca1—Cl1^{vii}	2.9775 (7)
Cu1—O1^{ii}	1.9340 (1)	Ca1—Cl1^{viii}	2.9775 (7)
Cu1—O1^{iii}	1.9340 (1)	Ca1—O1^{ix}	2.4900 (7)
Cu1—O1^{iv}	1.9340 (1)	Ca1—O1^{x}	2.4900 (7)
Cu1—O1	1.9340 (1)	Ca1—O1^{xi}	2.4900 (7)
Ca1—Cl1^{v}	2.9775 (7)	Ca1—O1^{xii}	2.4900 (7)
Cl1^{i}—Cu1—Cl1	180.0	Ca1^{vii}—Cl1—Ca1^{viii}	133.44 (6)
O1^{ii}—Cu1—Cl1	90.0	Ca1^{viii}—Cl1—Ca1^{vi}	81.01 (2)
O1^{iii}—Cu1—Cl1	90.0	Ca1^{vii}—Cl1—Ca1^{v}	81.01 (2)
O1—Cu1—Cl1	90.0	Ca1^{viii}—Cl1—Ca1^{v}	81.01 (2)
O1^{iv}—Cu1—Cl1	90.0	O1^{ix}—Ca1—O1^{xi}	66.63 (2)
O1^{iv}—Cu1—Cl1^{i}	90.0	O1^{x}—Ca1—O1^{xi}	101.92 (4)
O1—Cu1—Cl1^{i}	90.0	O1^{x}—Ca1—O1^{ix}	66.63 (2)
O1^{ii}—Cu1—Cl1^{i}	90.0	O1^{xi}—Ca1—O1^{xii}	66.63 (2)
O1^{iii}—Cu1—Cl1^{i}	90.0	O1^{ix}—Ca1—O1^{xii}	101.92 (4)
O1^{ii}—Cu1—O1	90.0	O1^{x}—Ca1—O1^{xii}	66.63 (2)
O1^{iii}—Cu1—O1	90.0	Cu1^{xiii}—O1—Cu1	180.0
O1^{iii}—Cu1—O1^{ii}	180.0	Cu1^{xiii}—O1—Ca1^{vii}	90.0
O1—Cu1—O1^{iv}	180.0	Cu1—O1—Ca1^{vii}	90.0
O1^{ii}—Cu1—O1^{iv}	90.0	Cu1—O1—Ca1^{xiv}	90.0
O1^{iii}—Cu1—O1^{iv}	90.0	Cu1^{xiii}—O1—Ca1^{xiv}	90.0
Cu1—Cl1—Ca1^{vi}	66.72 (3)	Cu1—O1—Ca1^{v}	90.0
Cu1—Cl1—Ca1^{v}	66.72 (3)	Cu1^{xiii}—O1—Ca1^{xv}	90.0

Cu1—Cl1—Ca1	180.0	Cu1^{xiii}—O1—Ca1^v	90.0
Cu1—Cl1—Ca1^{viii}	66.72 (3)	Cu1—O1—Ca1^{xv}	90.0
Cu1—Cl1—Ca1^{vii}	66.72 (3)	Ca1^v—O1—Ca1^{xiv}	78.08 (4)
Ca1^v—Cl1—Ca1	113.28 (3)	Ca1^{xv}—O1—Ca1^{xiv}	101.92 (4)
Ca1^{vii}—Cl1—Ca1	113.28 (3)	Ca1^{vii}—O1—Ca1^{xiv}	180.0
Ca1^{vi}—Cl1—Ca1	113.28 (3)	Ca1^v—O1—Ca1^{xv}	180.0
Ca1^{vi}—Cl1—Ca1^v	133.44 (6)	Ca1^v—O1—Ca1^{vii}	101.92 (4)
Ca1^{viii}—Cl1—Ca1	113.28 (3)	Ca1^{xv}—O1—Ca1^{vii}	78.08 (4)
Ca1^{vii}—Cl1—Ca1^{vi}	81.01 (2)		

Symmetry codes: (i) $-x, -y, -z+1$; (ii) $-y, x-1, z$; (iii) $-y, x, z$; (iv) $x-1, y, z$; (v) $-x+1/2, -y-1/2, -z+1/2$; (vi) $-x-1/2, -y+1/2, -z+1/2$; (vii) $-x+1/2, -y+1/2, -z+1/2$; (viii) $-x-1/2, -y-1/2, -z+1/2$; (ix) $x-1/2, y-1/2, z-1/2$; (x) $-y-1/2, x-1/2, z-1/2$; (xi) $-y+1/2, x-1/2, z-1/2$; (xii) $x-1/2, y+1/2, z-1/2$; (xiii) $x+1, y, z$; (xiv) $x+1/2, y-1/2, z+1/2$; (xv) $x+1/2, y+1/2, z+1/2$.