inorganic papers

Reinvestigation of CuSe$_2$O$_5$

Richard Becker[a]* and Helmuth Berger[b]

[a]Inorganic Chemistry, Stockholm University, S-106 91 Stockholm, Sweden, and [b]Institut de Physique de la Matière Complexe, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

Correspondence e-mail: richard@inorg.su.se

The crystal structure of the title compound, copper(II) diselenium(IV) pentoxide [Meunier, Svensson & Carpy, (1976). *Acta Cryst.* B**32**, 2664–2667], has been reinvestigated and confirmed to much higher precision, and anisotropic displacement parameters has been refined. The structure consists of CuO$_4$ planar squares and Se$_2$O$_5$E$_2$ (E = lone pair) dimers. The Cu atom has site symmetry $\bar{1}$ and one O atom has site symmetry 2.

Comment

The crystal structure of CuSe$_2$O$_5$, (I), was determined by Meunier *et al.* (1976). The structure has been reinvestigated and here we report a redetermination with improved precision and anisotropic displacement parameters. The $R(F)$ residual has decreased from 0.06 (Meunier *et al.*, 1976; Meunier & Bertaud, 1976) to 0.028 for the present study.

The structure consists of CuO$_4$ planar squares (Cu site symmetry $\bar{1}$) with normal Cu—O distances (Table 1). Two additional O atoms at 2.730 (3) Å from Cu would complete a distorted octahedral CuO$_6$ coordination, but these two O atoms are positioned outside the primary coordination sphere (Fig. 1). The Se atom coordinates to three O atoms and the stereochemically active lone pair, E, completes an SeO$_3$E tetrahedron (Fig. 1). Two SeO$_3$E tetrahedra are connected *via* corner-sharing at O1 (site symmetry 2) to form Se$_2$O$_5$E$_2$ dimers (or Se$_2$O$_5{}^{2-}$ diselenite groups). The CuO$_4$ squares are connected to the Se$_2$O$_5$E$_2$ dimers *via* corner-sharing to form chains along the c axis. The chains are arranged to form layers parallel to the bc plane, and the longer Cu···O octahedral 'bond' connects the chains. The layers are, in turn, separated by the stereochemically active lone pair on Se^{IV} (Fig. 2).
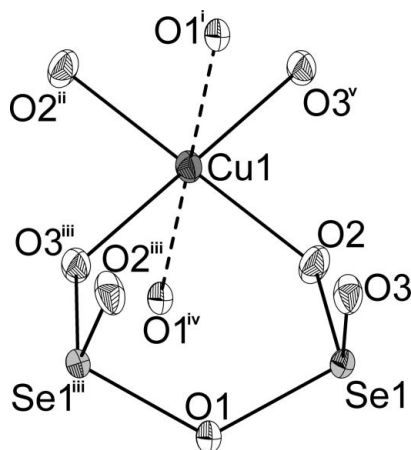

Figure 1
Local coordination around Cu1 and the diselenite group. Symmetry codes: (i) x, $1 + y$, z; (ii) $-x$, $1 - y$, $1 - z$; (iii) $-x$, y, $\frac{3}{2} - z$; (iv) $-x$, $-y$, $1 - z$; (v) x, $1 - y$, $-\frac{1}{2} + z$.
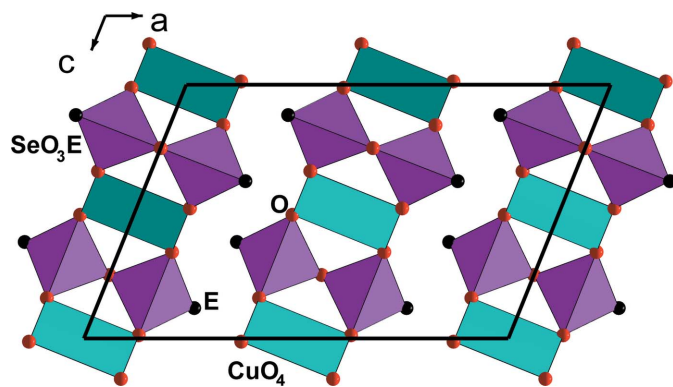
Figure 2
Structure of (I), viewed down [010].

The diselenite Se$_2$O$_5$E$_2$ dimer is a common building block in selenites and exists in *e.g.* orthorhombic ZnSe$_2$O$_5$ (Meunier & Bertaud, 1974) and CoSe$_2$O$_5$ (Harrison *et al.*, 1992). The Se$_2$O$_5$ dimer can take different arrangements, *e.g.* with the two lone pairs being positioned either *cis* or *trans*, but the Se—O bonds are often similar in distance. The bridging Se—O bond is usually around 1.8 Å and the terminal bonds are usually much shorter (around 1.65 Å). For the transition metal diselenites noted above, the complete Se$_2$O$_5$ group is generated by twofold symmetry, but for some of the alkaline earth diselenites, *e.g.* BaSe$_2$O$_5$ (Giester & Lengauer, 1992) and CaSe$_2$O$_5$ (Delage *et al.*, 1982), two crystallographically different Se^{IV} atoms are present, which allows for more variations in the geometry of the anion.

Table 1
Selected bond lengths (Å).

Se—O2	1.662 (3)	Cu—O2	1.938 (3)
Se—O3	1.673 (3)	Cu—O3^i	1.949 (3)
Se—O1	1.837 (2)	Cu—O1^{ii}	2.730 (3)

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

The maximum difference peak is located 0.80 Å from Cu1; the deepest difference hole is located 0.91 Å from Se1.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2005); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2005); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXL97*.

Experimental

The starting materials used were CuO (99.7%, Alfa Aesar), SeO$_2$ (99.4% Alfa Aesar), CuBr$_2$ (99% Alfa Aesar) and HBr (electronic grade Carba-Gas). The single crystals used in this study were grown from the approximately stoichiometric molar ratios CuO:SeO$_2$:CuBr$_2$ = 1:1:1. The starting materials, in powder form, were placed in one end of the reaction tube, which was then evacuated to 10^{-5} Torr. HBr electronic grade gas at room temperature was subsequently introduced into this tube and the tube was then sealed off. For crystallization of green CuSe$_2$O$_5$, the ampoule was subjected to a chemical vapour transport reaction in a temperature gradient from 753 K to 573 K.

Crystal data

CuO$_5$Se$_2$	$Z = 4$
$M_r = 301.46$	$D_x = 4.478$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 12.3869$ (19) Å	$\mu = 21.08$ mm^{-1}
$b = 4.8699$ (7) Å	$T = 292$ (3) K
$c = 7.9917$ (13) Å	Needle, green
$\beta = 111.953$ (15)°	$0.32 \times 0.08 \times 0.04$ mm
$V = 447.13$ (12) Å^3	

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