Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

$RbGd_2CuS_4$

Jiyong Yao and James A. Ibers*

Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208-3113, USA

Correspondence e-mail: ibers@chem.northwestern.edu

Key indicators

Single-crystal X-ray study
T = 153 K
Mean σ(Cu–S) = 0.001 Å
R factor = 0.020
wR factor = 0.058
Data-to-parameter ratio = 18.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 28 June 2004
Accepted 6 July 2004
Online 17 July 2004

Rubidium digadolinium copper tetrasulfide, $RbGd_2CuS_4$, crystallizes in the orthorhombic space group *Cmcm* and is isostructural with KGd_2CuS_4. The structure has a three-dimensional tunnel framework, with tunnels built from GdS_6 octahedra and CuS_4 tetrahedra. These tunnels are filled with Rb atoms.

Comment

Ternary and quaternary rare-earth chalcogenides containing a combination of *d* and *f* elements have been reviewed recently (Mitchell & Ibers, 2002). We report here the structure of $RbGd_2CuS_4$, a new member of this large family.

$RbGd_2CuS_4$, which has the KGd_2CuS_4 structure type (Stoll *et al.*, 1998), crystallizes in space group *Cmcm* of the orthorhombic system. The site symmetries of the atoms in the asymmetric unit (Fig. 1) are: S3 (2/*m*); Rb, Cu and S1 (*mm*); Gd and S2 (*m*). The structure of $RbGd_2CuS_4$ is shown in Fig. 2. It has a three-dimensional tunnel framework built from GdS_6 octahedra and CuS_4 tetrahedra. The tunnel, comprising a ten-membered ring of four Cu—S bonds and six Gd—S bonds, is only large enough in cross section to accommodate one Rb atom. Each Rb atom is coordinated to a bicapped trigonal prism of eight S atoms, with Rb—S distances ranging from 3.193 (1) to 3.7557 (4) Å, comparable to those of 3.247 (2) to 3.7951 (4) Å in $RbNd_2CuS_4$ (Huang & Ibers, 2000). The Gd—S distances range from 2.7259 (6) to 2.8500 (2) Å, consistent with those of 2.697 (1) to 2.8437 (2) Å in $Rb_2Gd_4Cu_4S_9$ (Huang & Ibers, 2000), and the Cu—S distances are 2.346 (1) and 2.361 (1) Å, comparable to those of 2.3530 (9) and 2.4025 (8) Å in KNd_2CuS_4 (Yao *et al.*, 2003).

Experimental

$RbGd_2CuS_4$ was obtained as red blocks from a solid-state reaction of Rb_2S_3 (1.2 mmol), Gd (1.0 mmol, Aldrich, 99%), Cu (0.5 mmol,

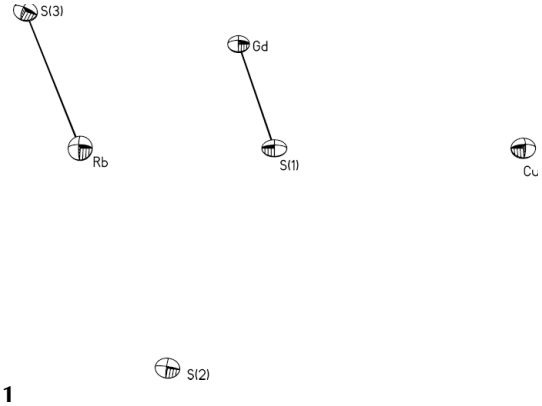

Figure 1
The atoms in the asymmetric unit of $RbGd_2CuS_4$, with displacement ellipsoids shown at the 90% probability level.

Aldrich, 99.999%) and S (2.0 mmol, Aldrich, 99.5%). The Rb_2S_3 reactive flux (Sunshine *et al.*, 1987) was prepared by the stoichiometric reaction of Rb (Aldrich, 98+%) and S in liquid NH_3. The reactants were loaded into a fused-silica tube under an Ar atmosphere in a glove box. The tube was sealed under a 10^{-4} Torr atmosphere and then placed in a computer-controlled furnace. The sample was heated to 1173 K over a period of 25 h, kept at 1173 K for 3 d, slowly cooled at 10 K h^{-1} to 473 K and then cooled to room temperature.

Crystal data

$RbGd_2CuS_4$
M_r = 591.75
Orthorhombic, *Cmcm*
a = 4.0030 (3) Å
b = 13.7095 (10) Å
c = 13.8146 (10) Å
V = 758.13 (10) Å^3
Z = 4
D_x = 5.184 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4160 reflections
θ = 3.0–28.3°
μ = 27.44 mm^{-1}
T = 153 (2) K
Block, red
0.25 × 0.16 × 0.12 mm

Data collection

Bruker SMART 1000 CCD diffractometer
ω scans
Absorption correction: numerical face-indexed (*SHELXTL*; Sheldrick, 2003)
T_{min} = 0.012, T_{max} = 0.122
4276 measured reflections
546 independent reflections
542 reflections with $I > 2\sigma(I)$
R_{int} = 0.048
θ_{max} = 28.3°
$h = -5 \rightarrow 5$
$k = -17 \rightarrow 18$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.020
$wR(F^2)$ = 0.058
S = 1.40
546 reflections
30 parameters
$w = 1/[\sigma^2(F_o^2) + (0.03P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.40 e Å^{-3}
$\Delta\rho_{min}$ = −1.20 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0049 (3)

Table 1
Selected geometric parameters (Å, °).

Gd—S1	2.7259 (6)	Rb—S2^{v}	3.3160 (9)
Gd—S2^{i}	2.7348 (8)	Rb—S3	3.7557 (4)
Gd—S2^{ii}	2.7688 (11)	Cu—S2^{vi}	2.3460 (11)
Gd—S3^{iii}	2.8500 (2)	Cu—S1^{iii}	2.3612 (11)
Rb—S1^{iv}	3.1928 (14)		
S1—Gd—S2^{i}	87.98 (3)	S1—Gd—S3^{viii}	95.19 (3)
S2^{i}—Gd—S2^{vii}	94.09 (3)	S2^{i}—Gd—S3^{viii}	88.267 (18)
S1—Gd—S2^{ii}	166.52 (4)	S3^{iii}—Gd—S3^{viii}	89.221 (8)
S2^{i}—Gd—S2^{ii}	82.86 (3)	S2^{vi}—Cu—S2^{ix}	111.60 (6)
S2^{i}—Gd—S3^{iii}	176.13 (2)	S2^{vi}—Cu—S1^{iii}	107.35 (2)
S2^{ii}—Gd—S3^{iii}	94.396 (18)	S1^{iii}—Cu—S1^{viii}	115.92 (8)

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

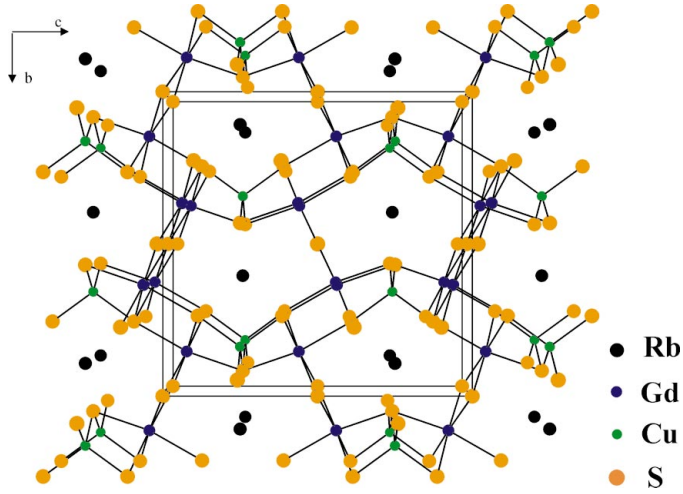

Figure 2
Structure of $RbGd_2CuS_4$, viewed down [100].

The maximim and minimum residual electron densities are located 0.96 and 1.27 Å from atoms Gd and Cu, respectively.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2003); program(s) used to refine structure: *SHELXTL*; molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

This research was supported by the MRSEC program of the National Science Foundation (DMR00-76097) at the Materials Research Center of Northwestern University.

References

Bruker (2003). *SMART* (Version 5.054) and *SAINT-Plus* (Version 6.45). Bruker AXS Inc., Madison, Wisconsin, USA.
Huang, F. Q. & Ibers, J. A. (2000). *J. Solid State Chem.* **151**, 317–322.
Mitchell, K. & Ibers, J. A. (2002). *Chem. Rev.* **102**, 1929–1952.
Sheldrick, G. M. (2003). *SHELXTL* DOS/Windows/NT. Version 6.14. Bruker AXS Inc., Madison, Wisconsin, USA.
Stoll, P., Dürichen, P., Näther, C. & Bensch, W. (1998). *Z. Anorg. Allg. Chem.* **624**, 1807–1810.
Sunshine, S. A., Kang, D. & Ibers, J. A. (1987). *J. Am. Chem. Soc.* **109**, 6202–6204.
Yao, J., Deng, B., Ellis, D. E. & Ibers, J. A. (2003). *J. Solid State Chem.* **176**, 5–12.