Preparation and Crystal Structure of the New Quaternary Europium-Polysulfide $KCuEu_2S_6$☆

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The new quaternary europium polysulfide $KCuEu_2S_6$ was obtained using the reactive flux method at an intermediate temperature of 380 °C by reacting K_2S_3 with elemental Cu, EuS and an excess of sulfur. The Eu^{3+} ions exhibit a bicapped trigonal prismatic coordination and the Cu^+ ions are in a tetrahedral environment. The crystal structure is characterized by anionic layers of interconnected Eu and Cu polyhedra with K^+ ions residing between the anionic sheets $[CuEu_2S_6]_n^{n-}$. The Cu^+ ions occupy one half of the tetrahedral sites in an ordered fashion.

Binary and ternary transition-metal chalcogenides have technological interest as they exhibit physical properties which make them usable, for example, for applications as infrared lenses[1], lasers[2], or color phosphors[3].

The usual way for preparing lanthanoid chalcogenides is the high-temperature route which often leads to mixtures of phases or compounds with defect structures. Another way is the metathesis between alkali chalcogenides and lanthanoid halides.

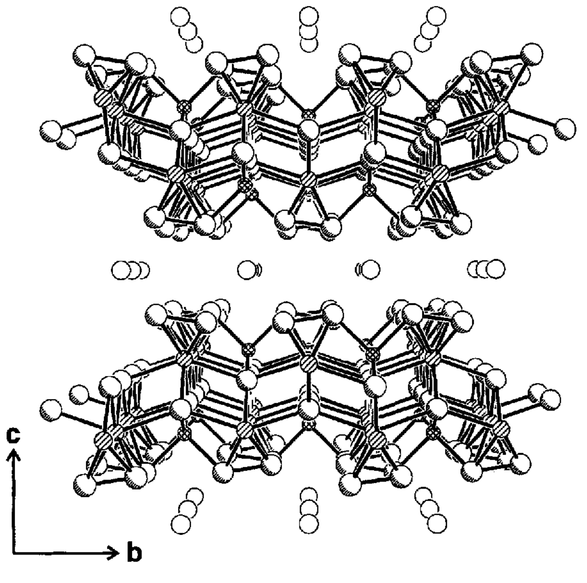
Two known structure types in the alkali metal (A)/lanthanoid (Ln)/chalcogenide (Q) system have the composition $ALnQ_2$[4]. One of these structure types is a simple NaCl structure with statistically distributed A^+ and Ln^{3+} cations. The other $ALnQ_2$ compounds crystallize in the α-$NaFeO_2$ structure type. A third type is represented by the compounds $KLnMQ_4$ (Ln = La, Nd, Gd, Y; M = Si, Ge; Q = S, Se)[5].

A new method for preparing ternary and higher order transition-metal chalcogenides and also rare-earth metal chalcogenides at intermediate temperatures between 270 °C and 500 °C was reported by Ibers and co-workers[6]. Since then a large number of new transition-metal chalcogenides were prepared[7], but only a few lanthanoid compounds. These include the compounds $KCeQ_4$ (Q = Se, Te)[8], ACu-Ce_2Q_6 (A = K, Cs; Q = S, Se)[9,10] and $K_2Cu_2CeS_4$[10] which all represent new structure types of multinary alkali lanthanide chalcogenides. In this paper we report on the structure and synthesis of the first quaternary alkali europium chalcogenide according to the low-temperature route. In $KCuCe_2Se_6$ the Cu centers are statistically distributed over the tetrahedral sites, whereas the Cu^+ ions in the title compound occupy these sites in an ordered way leading to the formation of a superstructure of the $KCuCe_2Se_6$ structure type with all lattice parameters doubled.

Results and Discussion

The crystal structure of $KCuEu_2S_6$ is displayed in Figure 1. Figure 2 shows the numbering scheme as well as the environment of the different atoms. Double layers of Eu^{3+} and Cu^+ centered polyhedra are within the *ab* plane. Every layer consists of interconnected EuS_8 and CuS_4 polyhedra. The K^+ ions are located in the gaps between the layers and connect these layers parallel to [001].

Figure 1. A perspective view of the layer structure of $KCuEu_2S_6$ showing the connection of the EuS_8 bicapped trigonal prisms and CuS_4 tetrahedra; the polyhedra around the K^+ ions are omitted for clarity; atom types: cross-hatched circles: Cu; striped circles: Eu; light shaded circles: S; open circles: K



The Eu^{3+} ions are in a distorted bicapped trigonal prismatic environment with the short basal edges of the triangular faces being $(S_2)^{2-}$ units and the rest of the sites

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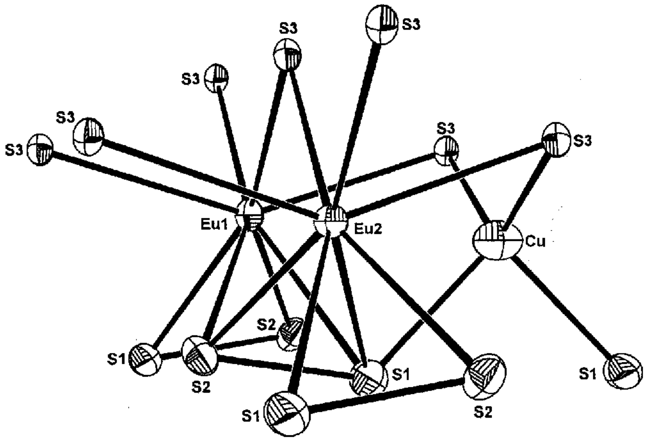
Figure 2. The coordination of the different atoms in $KCuEu_2S_6$ together with the numbering scheme; the ellipsoids are drawn at the 70% probability level



occupied by S^{2-}. Two S^{2-} are located above two of the three rectangular faces of the prism.

The trigonal prisms are connected via the two triangular faces forming rods parallel [100]. These rods are interconnected parallel [010] such that each capping atom of one prism is the third S atom of the triangular faces of a neighbouring EuS_8 polyhedra.

The Eu/S part of the structure is also found in the compounds $ACuCe_2Q_6$[9,10], $ZrSe_3$[11], $CsTh_2Te_6$[12], and the $[CeS_3]_n^{n-}$ framework of $NaCeS_3$[7]. In $ZrSe_3$ the Zr–Se distances to the two capping Se atoms are significantly longer than the other 6 Zr–Se bond lengths within the trigonal prism. The grooves between the interconnected Eu polyhedra possess tetrahedral sites which accommodate the Cu^+ ions (see Figure 1). Every second tetrahedral site is occupied by a Cu^+ ion in an ordered fashion.

According to the crystal structure analysis reported in ref.[9] the two compounds $CsCuCe_2S_6$ and $KCuCe_2Se_6$ crystallize in the orthorhombic space group *Immm*. In these compounds the tetrahedral sites are only half occupied by the copper ions. The authors suggested that the Cu centers are either mobile or statistically distributed over the two possible sites. In the former case the compounds should be good ionic conductors. Unfortunately, no experimental details were reported which would support this assumption.

If the reflections defining the superstructure of $KCuEu_2S_6$ are neglected it is also possible to solve the structure in space group *Immm* leading to the same model with disordered Cu centers. In space group *Fddd*, however, the tetrahedral sites split into two alternating independent sites of which only one is occupied by Cu. As a result of this ordered arrangement all crystallographic axes are doubled.

The Eu–S distances range from 2.817(5) to 3.032(5) Å for Eu(1) and from 2.822(1) to 2.965(5) Å for Eu(2) with an average of 2.873 Å and 2.865 Å respectively and are within the range found for other europium sulfide compounds containing Eu^{3+}. In Eu_2CuS_3[13] for instance Eu^{III} is in a distorted octahedral environment of six S atoms and the average ⟨Eu–S⟩ distance amounts to 2.774 Å. In Eu_2BiS_4[14] Eu^{III} is coordinated by 7 S atoms in an octahedral-like fashion with one corner being split into two S atoms and ⟨Eu–S⟩ amounts to 2.86 Å. In $Eu_5Sn_3S_{12}$[15] the two Eu^{III} species have coordination numbers 8 (bicapped trigonal prism with ⟨Eu–S⟩ = 2.94 Å) and 7 (monocapped trigonal prism with ⟨Eu–S⟩ = 2.82 Å). The Eu–S interatomic distances to the capping atoms are significantly longer than the Eu–S separations within the prism. In the $KCuEu_2S_6$ the Eu–S distances to the atoms in the prism (⟨Eu1–S⟩ = 2.89 Å; ⟨Eu2–S⟩ = 2.87 Å) and to the two capping atoms (⟨Eu1–S⟩ = 2.818 Å; ⟨Eu2–S⟩ = 2.850 Å) are nearly identical, as a consequence of the uneven S–S distances within the triangular faces.

The shortest Eu–Cu separations are 3.1920(9) and 3.3851(2) Å. These distances are too long for significant Eu–Cu interactions [$r(Eu^{3+})$ = 1.066 Å, $r(Cu^+)$ = 0.60 Å][16].

The mean bond length for Cu–S of 2.338 Å is comparable to those found in other CuS_4 tetrahedra containing compounds like NH_4CuS_4[17] (Cu–S = 2.293–2.437 Å), CuAsS[18] (Cu–S = 2.30–2.34 Å) or Eu_2CuS_3[13] (Cu–S = 2.337–2.397 Å). The CuS_4 tetrahedra exhibit a significant distortion from the ideal tetrahedral symmetry as is evidenced by the S–Cu–S angles ranging from 90.35(7) to 118.27(7)°. This distortion is further evidenced by the distortion parameters DP_a = 0.0568 and DP_d = 0.0103 (compare Table 3). The nonbonding S–S separations within the CuS_4 tetrahedra range from 3.351 Å [S(1)–S(1)] to 3.973 Å [S(3)–S(3)].

The S–S interatomic bondlength of 2.104(2) Å is typical for a single bond.

The K^+ ions are in a distorted parallel epiped of 8 sulfur atoms. The KS_8 polyhedra are joined by common faces parallel [100]. The mean K–S distance of 3.32 Å agrees well with the sum of the ionic radii of K^+ [$r(K^+)$ = 1.51 Å] and S^{2-} [$r(S^{2-})$ = 1.84 Å][16].

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Experimental

The quaternary compound $KCuEu_2S_6$ was first prepared by combining K_2S_3 with EuS (99.9% Heraeus), Cu (99.999% Heraeus) and additional sulfur (99.99% Heraeus) in the ratio 2:2:1:6. K_2S_3 was made by the reaction of stoichiometric amounts of K (>98.0% Heraeus) and S in liquid ammonia under argon. In a dry box the starting materials were thoroughly mixed and then loaded into pyrex glass ampoules which were subsequently evacuated ($4 \cdot 10^{-5}$ mbar) and sealed. The ampoule was heated to 653 K within 6 h, held at this temperature for 6 d. After the heat treatment the sample was cooled to room temperature with a rate of 2 K/h. The resulting melt was washed with DMF and ether. The product was microcrystalline with some small dark-bronze plate-like crystals of the title compound. Preparation of $KCuEu_2S_6$ at 573 K led to a completely microcristalline product with a powder pattern which could be fully indexed on the basis of $KCuEu_2S_6$. Crystals suitable for X-ray crystal structure determination were grown at 723 K using the element ratio mentioned above. $KCuEu_2S_6$ is stable to air for a long period.

EDAX investigations on a number of selected crystals yielded a composition of 11% K, 10% Cu, 22% Eu, 56% S (atom percent).

Table 1. Technical details of data acquisition and selected refinement results for $KCuEu_2S_6$

$KCuEu_2S_6$	
a [Å]	8.1077(7)
b [Å]	10.7600(8)
c [Å]	42.191(4)
volume [$Å^3$]	3680.7(5)
crystal system	orthorhombic
space group	Fddd
Z	16
MW	598.92
μ [mm^{-1}]	17.485
ρ[Mg/m^3]	4.323
2 Θ [°]	3.0 - 70.0
Index ranges	$-2 < h < 13$
	$-1 < k < 17$
	$-68 < l < 40$
reflections collected	4736
unique data	2033
absorption correction	numerical
min./max. transmission	0.54285/0.74528
R_{int} [%]	5.16
k[a]	0.00705(1)
x[a]	0.000023(2)
y[b]	0.0134
parameters refined	49
R1 (827 with $I>2\sigma I$) [%]	2.00
wR2 (2030 data) [%]	4.71
R1 (2033 data) [%]	11.32
GOOF	0.908
difference peaks [$eÅ^{-3}$]	1.64 / -1.20
Cell parameter determination	$30.6 \leq 2\Theta \leq 52.6$
reflections	92

[a] Extinction correction: $F^* = F_c \cdot k \cdot (1 + 0.001 \cdot x \cdot F_c^2 \cdot \lambda^3/\sin 2\Theta)^{-1/4}$; k = OSF. – [b] Weighting scheme: $w^{-1} = \sigma^2(F_o^2) + (y \cdot P)^2$; $P = [\max.\ (0 \text{ or } F_o^2) + 2 \cdot F_c^2]/3$.

Table 2. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement coefficients [$Å^2 \cdot 10^3$] for $KCuEu_2S_6$

	x	y	z	U(eq)
Eu(1)	1250	1250	328(1)	9(1)
Eu(2)	6250	1250	348(1)	9(1)
Cu	8750	3750	409(1)	20(1)
S(1)	-1262(9)	2193(1)	804(1)	18(1)
S(2)	-1203(8)	260(1)	728(1)	14(1)
S(3)	1200(2)	3747(2)	127(1)	9(1)
K	6250	3759(2)	1250	25(1)

Table 3. Interatomic distances [Å] and angles [°] in $KCuEu_2S_6$

$KCuEu_2S_6$			
Eu(1)-S(2) 2x	2.817(5)	Eu(1)-S(3) 2x	2.818(2)
Eu(1)-S(3) 2x	2.823(1)	Eu(1)-S(1) 2x	3.032(5)
Eu(2)-S(3) 2x	2.822(1)	Eu(2)-S(2) 2x	2.824(5)
Eu(2)-S(3) 2x	2.850(2)	Eu(2)-S(1) 2x	2.965(5)
Eu(1)-Cu	3.3851(2)	Eu(1)-Cu	3.3852(2)
Eu(2)-Cu	3.1920(9)	Eu(2)-Cu	3.3780(2)
Cu-S(3) 2x	2.314(2)	Cu-S(1) 2x	2.362(2)
DP_d[a]	0.0411		
S(1)-S(2)	2.104(2)		
K-S(1) 2x	3.234(5)	K-S(1) 2x	3.236(5)
K-S(2) 2x	3.378(4)	K-S(2) 2x	3.432(4)
S(3)-Cu-S(1)2x	111.4(2)	S(3)-Cu-S(1)2x	111.0(2)
S(1)-Cu-S(1)	90.35(7)	S(3)-Cu-S(3)	118.27(7)
DP_a[b]	0.0568		
S(2)-Eu(1)-S(2)	106.4(2)	S(2)-Eu(1)-S(3)2x	80.21(4)
S(2)-Eu(1)-S(3)2x	122.06(7)	S(3)-Eu(1)-S(3)	144.94(4)
S(2)-Eu(1)-S(3)2x	83.7(1)	S(2)-Eu(1)-S(3)2x	157.71(5)
S(3)-Eu(1)-S(3)2x	78.71(5)	S(3)-Eu(1)-S(3)2x	77.62(3)
S(3)-Eu(1)-S(3)	94.13(6)	S(2)-Eu(1)-S(1)2x	41.97(4)
S(2)-Eu(1)-S(1)2x	87.25(5)	S(3)-Eu(1)-S(1)2x	121.85(6)
S(3)-Eu(1)-S(1)2x	82.56(4)	S(3)-Eu(1)-S(1)2x	87.6(1)
S(3)-Eu(1)-S(1)2x	160.32(5)	S(1)-Eu(1)-S(1)	97.3(2)
S(3)-Eu(2)-S(3)	89.49(6)	S(3)-Eu(2)-S(2)2x	83.60(9)
S(3)-Eu(2)-S(2)2x	156.77(4)	S(2)-Eu(2)-S(2)	110.7(1)
S(3)-Eu(2)-S(3)2x	76.08(5)	S(3)-Eu(2)-S(3)2x	77.11(3)
S(2)-Eu(2)-S(3)2x	122.12(8)	S(2)-Eu(2)-S(3)2x	80.76(4)
S(3)-Eu(2)-S(3)	141.90(4)	S(3)-Eu(2)-S(1)2x	89.0(1)
S(3)-Eu(2)-S(1)2x	159.86(5)	S(2)-Eu(2)-S(1)2x	42.54(4)
S(2)-Eu(2)-S(1)2x	89.98(5)	S(3)-Eu(2)-S(1)2x	83.03(4)
S(3)-Eu(2)-S(1)2x	123.00(7)	S(1)-Eu(2)-S(1)	99.2(2)
S(1)-K-S(1)	117.2(1)	S(1)-K-S(1)2x	62.39(5)
S(1)-K-S(1)2x	179.5(2)	S(1)-K-S(1)	118.0(1)
S(1)-K-S(2)2x	103.7(1)	S(1)-K-S(2)2x	105.2(2)
S(1)-K-S(2)2x	75.23(6)	S(1)-K-S(2)2x	76.26(5)
S(2)-K-S(2)	122.9(1)	S(1)-K-S(2)	75.73(5)
S(1)-K-S(2)2x	75.53(4)	S(1)-K-S(2)2x	104.5(1)
S(1)-K-S(2)2x	103.9(2)	S(2)-K-S(2)2x	57.02(4)
S(2)-K-S(2)2x	179.0(2)	S(1)-K-S(2)	75.73(5)
S(2)-K-S(2)	123.1(1)		

[a] Distortion parameter DP_d for the CuS_4 tetrahedra: d_i = 4 M–S [Å]; $d_m = \langle M-S \rangle$ [Å]; $DP_d = (\Sigma_{i=1,4}|d_i - d_m|)/4\, d_m$. – [b] Distortion parameter DP_a for the CuS_4 tetrahedra: a_i = 6 S–M–S [°]; $a_m = \langle S-M-S \rangle$ [°]; $DP_a = (\Sigma_{i=1,6}|a_i - a_m|)/6\, a_m$.

X-ray Crystallographic Study[19]: Single-crystal X-ray work was performed at room temp. with a STOE AED II diffractometer (λ = 0.7107 Å, graphite monochromator). The intensities were reduced to F_o. Lorentz, polarization as well as a numerical absorption correction (face-indexed) were applied. A full-matrix refinement against F-squared with anisotropic displacement parameters for all atoms was used. All calculations were done with the software package SHELXL-93. Technical details of data acquisition as well as some refinement results are summarized in Table 1. Atomic coordinates are given in Table 2 and interatomic distances as well as selected angles are summarized in Table 3. – X-ray powder diffractometry investigations were performed with a Siemens D 5000 diffractometer (Cu-K_α, λ = 1.54056 Å) equipped with a high temperature furnace (Fa. Bühler). – The crystal structure determination was first carried out at room temp. All 62 reflections found in reciprocal space to determine the orientation as well as the lattice parameters could be indexed on the basis of an orthorhombic *I*-centered unit-cell with axes a = 4.049, b = 5.380, and c = 21.093 Å. The crystal was then cooled to 120 K and a new search revealed two reflections which demanded a doubling of all three axes leading to an orthorhombic *F*-centered unit-cell. With this *F*-centered cell the final data collection was carried out. It must be stressed that all reflections with uneven indices exhibited extremely weak intensities and therefore can be regarded as superstructure reflections, with the highest intensity being only 3% of the most intense substructure reflection. – In order to make sure that the superstructure is not due to a phase transition from orthorhombic *I* to orthorhombic *F* upon cooling, several experiments at various temperatures were conducted. – After data collection at 120 K the crystal was heated to room temp. in steps of 20 K while recording the four most intense superstructure reflections. Up to 290 K these reflections did not show any variation in shape or intensity. In addition, about 6 crystals taken from different batches were investigated on the diffractometer. In all cases the *F*-centered unit cell was confirmed. – Homogeneous powder samples were treated under Argon at different temperatures (373 K, 473 K, 573 K) for 2 d with subsequent quenching to room temp. The powder patterns of the products of these experiments still showed the superstructure reflections. The sample treated at 573 K was already decomposed. – These results were confirmed by in-situ high-temperature X-ray powder diffractometry. The samples were heated (under N_2) to 473 K and then in steps of 100 K to 673 K. At each temperature X-ray powder data were collected. At 473 K and 573 K the very weak (111) and (113) superstructure reflections located at $2\Theta = 13.87$ and 15.10° were still present, while at 673 K the sample decomposed.

[☆] Dedicated to Professor *W. Jeitschko* on the occasion of his 60th birthday.

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[19] Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-405838 the names of the authors and the journal citation.

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