(Table 3) show less variation in the distances between the U and the neighboring Si atoms compared to the variation in the U—U distances. The longest as well as the shortest distances are between the U atoms. Furthermore, comparison with the room-temperature phase shows that there is no change in the relative positions between the U and the Si atoms during the transition, but the range of U—U distances is larger in the low-temperature phase. Thus, it may be assumed that the transition was caused by changes in the U—U bonding which becomes more anisotropic at lower temperatures.

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Thallium Dithiotricuprate(I)

BY K. KLEPP AND K. YVON

Laboratoire de Cristallographie aux Rayons X, Université de Genève, 24 *quai Ernest Ansermet,*
CH-1211 *Genève* 4, *Switzerland*

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Abstract. $TlCu_3S_2$, monoclinic, space group $C2/m$, $Z = 4$, $a = 14{\cdot}63$ (1), $b = 3{\cdot}863$ (3), $c = 8{\cdot}298$ (5) Å, $\beta = 111{\cdot}72$ (6)°, $D_x = 7{\cdot}00$ (1) Mg m^{-3}, $\mu(\text{Ag } K\alpha) = 27{\cdot}9$ mm^{-1}, crystallizes with the $CsAg_3S_2$ structure type. Final $R = 0{\cdot}065$ for 453 independent reflections. The compound is the first thallium thiocuprate containing Cu_4S_4 tubes as the basic structural unit.

Introduction. During an investigation of the Tl–Cu–chalcogen systems (Klepp & Boller, 1978; Klepp, Boller & Völlenkle, 1980) a new compound of composition $TlCu_3S_2$ was found. It was prepared from Tl_2S, Cu and S powders which were mixed in the stoichiometric ratio and sealed into a silica capsule at $1{\cdot}3 \times 10^{-2}$ Pa. The sample was slowly heated to 573 K and annealed at this temperature for six weeks. The sintered reaction product contained needle-shaped crystals with a metallic lustre whose powder diffraction diagram was identical to that of the bulk sample. Preliminary Weissenberg and precession photographs showed the crystals to be monoclinic. The systematic absences found (hkl: $h + k = 2n + 1$) led to $C2/m$, $C2$ or Cm as possible space groups. Cell dimensions were obtained by least squares from 32 2θ values measured with a four-circle diffractometer (Philips PW 1100, Ag $K\alpha$ radiation, graphite monochromator). Integrated intensities were collected in the θ–2θ scan mode ($4 < 2\theta < 44°$) yielding 903 unique reflexions of which 453 had $I > 3\sigma(I)$. In view of the small crystal ($30 \times 30 \times 40$ μm, $\mu R \sim 0{\cdot}6$) no absorption correction was made. Scattering factors were those of Cromer & Mann (1968) and the corrections for anomalous dispersion were those listed in *International Tables for X-ray Crystallography* (1974). The composition and cell dimensions suggested isotypy with the $CsAg_3S_2$ structure type (Burschka & Bronger, 1977*a*). Its positional parameters were taken as starting values for a refinement with *CRYLSQ* (XRAY system, 1976). After a few cycles with anisotropic temperature factors R converged to 0·065* [$w = 1/\sigma^2(F)$, $R_w = 0{\cdot}076$]. The final atomic parameters are given in Table 1, interatomic distances and angles in Table 2.

Discussion. $TlCu_3S_2$ crystallizes with the $CsAg_3S_2$ structure type, which has been reported (Burschka & Bronger, 1977*a*) and discussed in detail (Bronger, Eyck & Schils, 1978). Following the notation by Parthé

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35306 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Crystal data for* $\mathrm{TlCu_3S_2}$ (*this work*) *and* $\mathrm{KCu_3S_2}$ (*Burschka & Bronger*, 1977*b*)

The space group is $C2/m$, $Z = 4$. All atoms are in equipoint 4(*i*): $x,0,z$. The positional parameters are $\times 10^4$ and the equivalent isotropic temperature factors Å^2 × 10^3. E.s.d.'s are given in parentheses.

		$\mathrm{TlCu_3S_2}$	$\mathrm{KCu_3S_2}$
Tl, K	x	1390 (1)	1346 (3)
	z	451 (2)	433 (6)
	U_{eq}	35 (6)	–*
Cu(1)	x	5933 (4)	5964 (2)†
	z	6474 (7)	6436 (3)
	U_{eq}	26 (2)	–*
Cu(2)	x	6878 (5)	6884 (2)†
	z	4290 (10)	4265 (4)
	U_{eq}	58 (3)	–*
Cu(3)	x	571 (4)	606 (2)
	z	3947 (6)	4021 (3)
	U_{eq}	31 (2)	–*
S(1)	x	1889 (6)	1953 (3)
	z	6673 (10)	6847 (6)
	U_{eq}	17 (2)	–*
S(2)	x	5231 (6)	5204 (3)
	z	2302 (11)	2395 (6)
	U_{eq}	19 (2)	–*

* U_{eq} values cannot be calculated from the U_{ij} values published.
† These values are obtained by adding 0·5 to those published.

Table 2. *Interatomic distances* (Å) *and selected bond angles* (°) *for* $\mathrm{TlCu_3S_2}$ (*this work*) *and* $\mathrm{KCu_3S_2}$ (*Burschka & Bronger*, 1977*b*)

E.s.d.'s are given in parentheses.

	$\mathrm{TlCu_3S_2}$	$\mathrm{KCu_3S_2}$
Tl(K)–2S(2)	3·251 (6)	3·20
2S(2)	3·300 (9)	3·39
2S(1)	2·364 (6)	3·27
S(1)	3·47 (1)	3·39
Cu(1)–S(2)	2·28 (1)	2·28
–2S(1)	2·355 (6)	2·40
–Cu(2)	2·66 (1)	2·63
–2Cu(3)	2·755 (6)	2·69
–2Cu(3)	2·851 (6)	2·95
Cu(1)	2·915 (7)	2·88
Cu(2)–S(1)	2·23 (1)	2·24
S(2)	2·36 (1)	2·34
2S(1)	2·76 (1)	2·86
2Cu(2)	2·617 (6)	2·63
Cu(1)	2·66 (1)	2·63
2Cu(3)	2·657 (7)	2·68

	$\mathrm{TlCu_3S_2}$	$\mathrm{KCu_3S_2}$
Cu(3)–2S(2)	2·311 (5)	2·32
S(1)	2·368 (9)	2·37
2Cu(2)	2·657 (7)	2·68
2Cu(1)	2·755 (6)	2·69
Cu(3)	2·83 (1)	2·85
2Cu(1)	2·851 (6)	2·95
S(1)–Cu(2)	2·23 (1)	2·24
Cu(3)	2·368 (9)	2·37
2Cu(1)	2·355 (6)	2·40
2Cu(2)	2·76 (1)	2·86
S(2)–Cu(1)	2·28 (1)	2·28
2Cu(3)	2·311 (5)	2·32
Cu(2)	2·36 (1)	2·34

	$\mathrm{TlCu_3S_2}$	$\mathrm{KCu_3S_2}$
Cu(1)–S(1)–Cu(3)	71·4 (2)	68·7
Cu(2)–S(2)–Cu(3)	69·3 (2)	70·3
Cu(1)–S(2)–Cu(3)	76·7 (3)	79·8
Cu(3)–S(1)–Cu(2)	98·0 (4)	94·9
S(1)–Cu(1)–S(2)	119·4 (3)	117·5
S(1)–Cu(2)–S(2)	120·1 (5)	121·3
S(2)–Cu(3)–S(1)	119·1 (2)	118·8

(1980) the crystal chemical formula may be written as $\mathrm{Tl_2}\,{}^{2}_{\infty}[\mathrm{Cu_2^{[2]}}\,{}^{1}_{\infty}(\mathrm{Cu_4^{[3]}S_4})]$. As shown in Fig. 1 infinite ${}^{1}_{\infty}\mathrm{Cu_4S_4}$ tubes running along **b** are connected by bridging Cu atoms in such a way as to form ${}^{2}_{\infty}\mathrm{Cu_3S_2}$ double sheets parallel to the *ab* plane. The sheets are separated from each other by intercalation of Tl atoms which are coordinated by seven S atoms in a distorted monocapped prismatic configuration.

The interatomic distances indicate that the bonding has partial ionic and partial covalent character. The Tl—S distances for instance are near to the sum of the ionic radii of $\mathrm{S^{2-}}$ and monovalent $\mathrm{Tl^+}$ [$\bar{d}$(Tl—S) = 3·33, $r_{\mathrm{Tl^+}} + r_{\mathrm{S^{2-}}}$ = 3·24 Å] whereas the Cu—S distances within the ${}^{2}_{\infty}\mathrm{Cu_3S_2}$ double sheets approach the sum of the covalent radii [$\bar{d}$(Cu—S) = 2·32, $r_{\mathrm{Cu}} + r_{\mathrm{S}}$ = 2·19 Å]. As in many other copper-rich thiocuprates the Cu—Cu distances are relatively short [d(Cu—Cu) ~ 2·6–2·7 Å] but they are all longer than twice the atomic or covalent radii of Cu.

All the compounds known to crystallize with the $\mathrm{CsAg_3S_2}$ structure type are listed in Table 3. Besides $\mathrm{TlCu_3S_2}$ the only other thiocuprate is $\mathrm{KCu_3S_2}$ (Burschka & Bronger, 1977*b*). Surprisingly the cell volume and in particular the *a* and *b* cell parameters of this compound are larger than those of $\mathrm{TlCu_3S_2}$ although the size of the $\mathrm{K^+}$ ion is smaller than that of $\mathrm{Tl^+}$ [$r(\mathrm{K^+})$ = 1·33, $r(\mathrm{Tl^+})$ = 1·40 Å]. This anomaly is probably related to the flexibility of the ${}^{1}_{\infty}\mathrm{Cu_4S_4}$ tubes which can easily change their shape as the spherical $\mathrm{K^+}$ ions are replaced by the non-spherical $\mathrm{Tl^+}$. As expected

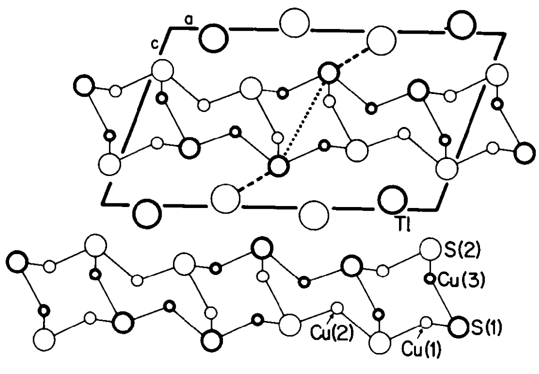

Fig. 1. $\mathrm{TlCu_3S_2}$, viewed along **b**. Heavy circles: $y = 0$, light circles: $y = \frac{1}{2}$.

Table 3. *Lattice dimensions of compounds with the* $\mathrm{CsAg_3S_2}$ *structure type*

	a (Å)	b (Å)	c (Å)	Angle (°)
$\mathrm{RbAg_3S_2}$$^{\mathrm{i}}$	16·13 (2)	4·306 (5)	8·77 (1)	114·6 (1)
$\mathrm{CsAg_3S_2}$$^{\mathrm{i}}$	16·175 (9)	4·325 (2)	8·980 (4)	113·0 (1)
$\mathrm{RbAg_3Se_2}$$^{\mathrm{ii}}$	16·641 (10)	4·406 (3)	8·857 (5)	113·92 (7)
$\mathrm{CsAg_3Se_2}$$^{\mathrm{ii}}$	16·757 (10)	4·444 (3)	9·113 (3)	112·60 (7)
$\mathrm{KCu_3S_2}$$^{\mathrm{iii}}$	14·773*	3·946*	8·182*	113·5*
$\mathrm{TlCu_3S_2}$$^{\mathrm{iv}}$	14·63 (1)	3·863 (3)	8·298 (5)	111·72 (6)

References: (i) Burschka & Bronger (1977*a*); (ii) Bronger, Eyck & Schils (1978); (iii) Burschka & Bronger (1977*b*); (iv) this work.

* No e.s.d.'s were given.

this replacement leads to an increase of the average metal—sulphur distances [$\bar{d}$(K—S) = 3·30 Å] and hence to a greater separation of the ${}^{2}_{\infty}\mathrm{Cu}_3\mathrm{S}_2$ sheets along **c**, but there exists a particular metal—sulphur distance (marked by a broken line in Fig. 1) which is 0·09 Å shorter in the Tl than in the K compound. As a consequence the ${}^{1}_{\infty}\mathrm{Cu}_4\mathrm{S}_4$ tubes are deformed in the **c** direction such that the S(2)—S(2) distances (marked by a dotted line in Fig. 1) are 0·2 Å longer in $\mathrm{TlCu_3S_2}$ than in $\mathrm{KCu_3S_2}$. Since the anionic ${}^{2}_{\infty}\mathrm{Cu}_3\mathrm{S}_2$ network has a tendency to maintain the length of its Cu—S bonds [$\bar{d}$(Cu—S) = 2·32 ($\mathrm{TlCu_3S_2}$), 2·33 Å ($\mathrm{KCu_3S_2}$)] it will tend to compensate the expansion along **c** by a contraction along **a** and **b** mainly through a change of the S—Cu—S bond angles of the ${}^{1}_{\infty}\mathrm{Cu}_4\mathrm{S}_4$ units (Table 2).

There exist several other thiocuprates which contain ${}^{1}_{\infty}\mathrm{Cu}_4\mathrm{S}_4$ units as structural elements. These units may be isolated as in $\mathrm{Na_3Cu_4S_4}$ (Burschka, 1979*a*) or connected with each other by additional atoms (Cu,S) and thus take part in the formation of a more complex thioanion as in the title compound, in $\mathrm{NH_4Cu_7S_4}$, which may be written as $\mathrm{NH_4}[{}^{3}_{\infty}\mathrm{Cu}_3\,{}^{1}_{\infty}(\mathrm{Cu_4S_4})]$ (Gattow, 1957), and in $\mathrm{K_3Cu_8S_6}$—$\mathrm{K_3}\ {}^{2}_{\infty}[\mathrm{C}^{[3]}_{2}\mathrm{Cu}^{[4]}_{2}\mathrm{S}_2\ {}^{1}_{\infty}(\mathrm{Cu_4S_4})]$ (Burschka, 1979*b*). On the other hand the complex anion $[{}^{2}_{\infty}(\mathrm{Cu_4S_3})]^{2-}$ in β-$\mathrm{BaCu_4S_3}$ (Iglesias, Pachali & Steinfink, 1972) is built up by ${}^{1}_{\infty}\mathrm{Cu}_4\mathrm{S}_4$ units which share S atoms. A comparison of all these compounds shows that the ${}^{1}_{\infty}\mathrm{Cu}_4\mathrm{S}_4$ units cannot be considered as rigid structural elements since their shape varies strongly as a function of the packing and connexion type. Thus it may for certain purposes be useful to describe the thiocuprates differently, for instance in terms of layer structure compounds (Bronger, Eyck & Schils, 1978).

Finally it is worth pointing out that the powder diffraction diagram of the mineral chalcothallite, $\mathrm{TlCu_3S_2}$ (Semenov, Sorenson, Bessmertnaja & Novorossova, 1967), shows no similarity to that of the present compound.

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Structure of Potassium Phosphoramidate

BY T. STANLEY CAMERON, CHRISTINE CHAN AND WALTER J. CHUTE

Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3

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Abstract. $\mathrm{K[H_3NO_3P]}$, monoclinic, $P2_1/n$, a = 6·143 (2), b = 6·872 (1), c = 10·288 (1) Å, β = 89·25 (2)°, Z = 4, D_c = 2·066 Mg m^{-3}, μ(Mo $K\alpha_1$) = 1·346 mm^{-1}, λ = 0·70926 Å (graphite monochromator). The structure was solved by an application of the tangent formula, and refined by full-matrix least squares to R = 0·027. The anion contains an 'ideal' P—N single bond with a length of 1·800 (4) Å.

Introduction. There are many factors that influence the length of a nominal P—N single bond (Bullen & Dann, 1973). It has been shown, for example, that the P—N distance is significantly shortened when the N atom is sp^2 rather than sp^3 hybridized (Cameron, Cordes & Jackman, 1979) and particularly for the sp^2-hybridized N atom the P—N bond lengths further vary according to the extent of the overlap of the P atomic orbitals and

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