Table 2. *Interatomic distances* (Å) *in the environments of the potassium ions* K(1) *and* K(2), *with e.s.d.'s in parentheses* (*a complete table of distances and angles has been deposited*)

$K(1)—O(3^{v})$	2·737 (3)	$K(1)—O(2^{iv})$	2·912 (3)
$K(1)—O(1)$	2·791 (3)	$K(1)—O(1^{v})$	2·929 (2)
$K(1)—O(2^{vi})$	2·847 (4)	$K(1)—Cl^{iv}$	3·288 (2)
$K(1)—O(1^{iv})$	2·852 (3)	$K(1)—Cl$	3·301 (2)
$K(2)—O(2^{vi})$	2·704 (3)	$K(2)—Cl$	3·114 (2)
		$K(2)—Cl^{iii}$	3·147 (2)

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

The structural differences of the bromine compounds $K_3[Pd\{(SO_3)_2H\}Br_2]$ (3) and $K_3[Pt\{(SO_3)_2H\}Br_2].H_2O$ (4) may be due to the different conditions of preparation. This point will be studied further, since corresponding Pd and Pt compounds are usually found to be isotypic, with few exceptions.

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Structure of $Pb_{0.15}Nb_3S_4$

BY E. AMBERGER, K. POLBORN AND P. GRIMM

Institut für Anorganische Chemie der Universität München, Meiserstrasse 1, *D*-8000 *München* 2, *Federal Republic of Germany*

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Abstract. $M_r = 439·80$, hexagonal, $P6_3$, $a = 9·626$ (4), $c = 3·390$ (2) Å, $V = 272·0$ (4) Å^3, $Z = 2$, $D_x = 5·37$ (3) Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0·7107$ Å, $\mu = 11·9$ mm^{-1}, $F(000) = 398·34$, room temperature, final $R = 0·043$ for 635 independent reflections. Pb partially occupies the large channel parallel to **c** in the Nb_3S_4 host lattice, with no long-range order of the Pb atoms. The S atoms form flat trigonal antiprisms around Pb with the Pb atom moved away from the centre, which gives three long and three short Pb—S distances. [Pb—S(1) is 3·156 (18) and 3·227 (18) Å.]

Introduction. In the course of our investigations of metal clusters we have become interested in substances that have two properties: (1) short metal bonds, which cause metallic behaviour, and (2) channels that are empty or filled. Examples of compounds with empty channels are Nb_3X_4 (X = S, Se, Te) with the Nb_3Te_4 structure (Selte & Kjekshus, 1964) where partial exchange of S by Se is possible, which leads to vanishing of the superconducting properties (Amberger, Polborn, Grimm, Dietrich & Obst, 1978). $Tl_xV_6S_8$ (Vlasse & Fournès, 1976) is an example with a filled channel. Exchange of V by Nb or Ti is possible in the case of $Tl_xV_6Se_8$ (Boller & Klepp, 1983). Nb_3S_4 needles, pressed to an electrode and electrolysed in a metal-ion (Li^+, Na^+, K^+ or Ca^{2+}) containing electrolyte show an uptake of metal, corresponding to the formula $M_xNb_3S_4$. The index x increases with decreasing Nb_3S_4 needle cross section ($Na_xNb_3S_4$: $1·56 \times 10^{-2}$ to $1·6 \times 10^{-4}$ mm^2 corresponds to $0·15 \leq x \leq 0·25$). So Schöllhorn & Schramm (1979) assumed a partial uptake of sodium into the channels. On the other hand, a single crystal of Nb_3S_4 as electrode does not take up

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Table 1. *Atomic coordinates for* $Pb_{0.15}Nb_3S_4$

$$U_{eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a_ia_j\mathbf{a}_i^*.\mathbf{a}_j^*.$$

	x	y	z	Occupation probability	U_{eq}(Å^2)
Nb	0·4856 (1)	0·3724 (1)	$\frac{1}{4}$	1	0·0051 (2)
S(1)	0·3443 (2)	0·0579 (2)	0·2397 (25)	1	0·0070 (6)
S(2)	$\frac{1}{3}$	$\frac{2}{3}$	0·2421 (49)	1	0·0052 (6)
Pb	0	0	−0·0500 (177)	0·147 (6)	0·0496 (60)

For Pb: $U_{11} = U_{22} = 2U_{12} = 0\cdot0223$ (15), $U_{33} = 0\cdot1043$ (153), $U_{13} = U_{23} = 0$ Å^2.

copper (or zinc) into the channels. The depth profile shows a strong decay of the Cu concentration going from the surface to the bulk of the electrolysed crystal (Grimm, 1983). The aim of this work was to prepare single crystals of $Pb_xNb_3S_4$ and $Tl_xNb_3S_4$ suitable for single-crystal X-ray methods, to decide between (1) metal coating of the Nb_3S_4 crystal, (2) the pseudo-ternary compound $(Nb,M)_3S_4$ (M = Pb, Tl) with metal substitution and (3) the ternary compound $M_xNb_3S_4$ with filled channels in the Nb_3S_4 lattice.

Experimental. A mixture of highly pure Nb, S, Pb powder, molar relation 3:4:1, was heated to 1023 K for 24 h in a sealed silica tube and later transported for one week between 1223 and 1323 K with chlorine as transporting agent. The Tl compound was prepared in the same way. The Pb mixture contained Pb-phase whiskers and some single crystals up to 1 mm (plates) of $Pb_xNb_3S_4$. The Tl mixture resulted in many extremely thin whiskers not suitable for single-crystal X-ray analysis. An ICP emission spectrometer analysis of a probe of some crystals of $Pb_xNb_3S_4$ resulted in (wt %): 60·7 Nb, 27·9 S and 11·2 Pb. This is consistent with the average formula $Pb_{0.25}Nb_3S_4$.

Metric of unit cell established with 18 reflections. Collection of data on Siemens automated four-circle diffractometer, Zr-filtered Mo $K\alpha$ radiation. Crystal plate (0·8 × 0·04 × 0·007 mm) mounted with **c** (longest axis of plate) parallel to φ axis of diffractometer. θ–2θ scans, scan speed 0·02° (2θ) s^{-1}, scan width 2° (2θ), background counted 1–10 s depending on intensity. $2 \leq \theta \leq 40°$, layers $\pm hk0$ to $\pm hk6$, Lp and absorption corrections ($0\cdot66 < T < 0\cdot92$); 635 unique reflections with $F_o \geq 2\sigma$ (28 unobserved). Heavy-atom method, full-matrix least-squares refinement on F (all atoms anisotropic, 1 scale factor, isotropic extinction correction – corresponding factor 0·01115 – 26 parameters refined), $R = 0\cdot043$, $wR = 0\cdot028$ [$w = \sigma(F)^{-2}$] for 635 reflections, $R = 0\cdot045$ for all 663 reflections, $(\Delta/\sigma)_{max}$ in final refinement cycle <0·06. All maxima in last $\Delta\rho$ map $< 1\cdot7$ e Å^{-3}, all minima $< 2\cdot2$ e Å^{-3}. Scattering factors for neutral atoms including f' and f'' from *International Tables for X-ray Crystallography* (1962), program *SHELX*76 (Sheldrick, 1976) used on the Cyber 175 of the Leibniz-Rechenzentrum in Munich.

Discussion. Atomic parameters are given in Table 1.* The atomic arrangement is given by Selte & Kjekshus (1964). The formula $Pb_{0.15}Nb_3S_4$ resulting from X-ray investigation differs from the average formula and shows the expected partial filling of the channels in the Nb_3S_4 host lattice. In $Pb_{0.15}Nb_3S_4$ the unit-cell volume is 1·4% greater than in Nb_3S_4 affecting both axes equally. Nb is used to define the origin in space group $P6_3$ by fixing the z parameter. The z parameters of S(1) and S(2) are shifted away from the centrosymmetric value in agreement with E statistics and therefore give a symmetry reduction from $P6_3/m$ (Nb_3Te_4) to $P6_3$ ($Pb_xNb_3S_4$). The z parameter of Pb was also allowed to refine but no significant improvement was correlated with a free z parameter for the Pb site. The difference Fourier synthesis without Pb shows distinct maxima at 0,0,0 and 0,0,0·5. Uniform electron density within the channel, which is observed for $Tl_xV_6S_8$ (Amberger, Polborn & Bensch, 1985) and for $Tl_xNb_6Se_8$ (Boller & Klepp, 1983), is not found for $Pb_{0.15}Nb_3S_4$. No diffuse scattering on long-exposure rotation photographs indicating long-range order for the Tl atoms as in $Tl_xTi_6Se_8$ can be observed for $Pb_{0.15}Nb_3S_4$. The anisotropic temperature factor components for Pb indicate disorder, the corresponding values for $Tl_xV_6S_8$ (Vlasse & Fournès, 1976; Amberger, Polborn & Bensch, 1985) and for $Tl_xNb_6Se_8$ (Boller & Klepp, 1983) are much higher. The atomic distances in $Pb_{0.15}Nb_3S_4$ are: Nb—S(1) 2·447 (2), 2·495 (2), 2·504 (2), 2·626 (2); Nb—S(2) 2·573 (11), 2·608 (11); Nb—Nb 2·882 (1), 3·392 (1); Pb—S(1) 3·156 (18), 3·227 (18) Å.

The polyhedra around the Pb atoms are flat trigonal antiprisms of S(1) with Pb shifted away from the centre. This leads to three shorter and three longer Pb—S(1) distances.

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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 39914 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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