Crystal structure of hexapraseodymium(III) trinitride tetrasulfide chloride, $Pr_6N_3S_4Cl$

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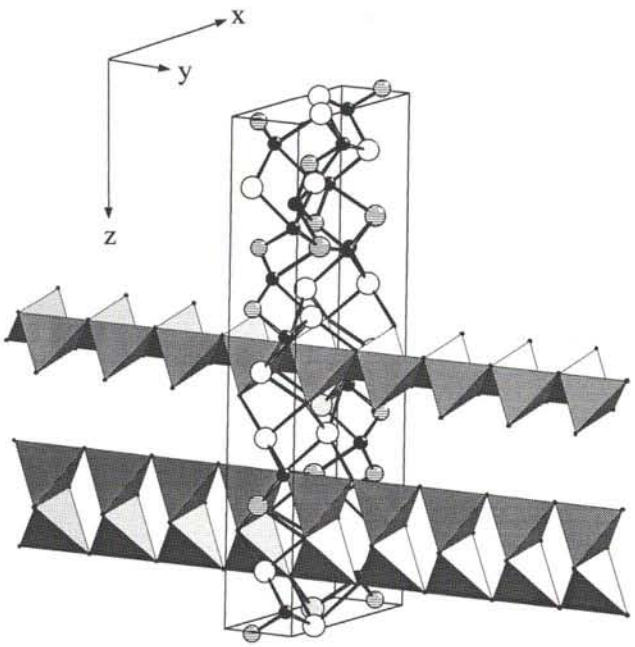

Abstract

$ClN_3Pr_6S_4$, orthorhombic, *Pnma* (No. 62), $a = 11.3987(8)$ Å, $b = 4.0235(3)$ Å, $c = 26.999(1)$ Å, $V = 1238.3$ Å^3, $Z = 4$, $R_{gt}(F) = 0.037$, $R_w(F^2) = 0.079$, $T = 293$ K.

Source of material

$Pr_6N_3S_4Cl$ was prepared from $PrCl_3$, praseodymium powder, sulfur, and sodium azide (NaN_3) as nitrogen source (molar ratio 2:16:12:3) with small amounts of NaCl or a slight excess of $PrCl_3$ as fluxing agents [1, 2]. The mixture was heated in a sealed evacuated silica vessel at 1123 K (7 d) and subsequently cooled down (25 K/d) at ambient temperature.

Discussion

$Pr_6N_3S_4Cl$ belongs to the $Nd_6N_3S_4Cl$-type of structure [1]. The orthorhombic unit cell contains two different types of chains built up by edge- and vertex-sharing N^{3-}-centred $(Pr^{3+})_4$ tetrahedra

$$^1_\infty[(N1)(Pr1)_{3/3}(Pr2)_{1/1}]^{3+}$$

and

$$^1_\infty[(Pr5)_{2/2}(N2)(Pr3)_{(1+1)/(1+1)}(Pr4)_{(1+1)/(1+1)}(N3)(Pr6)_{2/2}]^{6+},$$

both commensurate in translation along [010], which are depicted in the figure (Pr: black, N: small, S and Cl: large circles) by closed polyhedra [3–7].

Table 1. Data collection and handling.

Crystal:	reddish brown, transparent, lath-shaped needles, size 0.03 x 0.08 x 0.15 mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ:	239.9 cm^{-1}
Diffractometer, scan mode:	Siemens-Stoe, profile fitted ω-2θ-scan [11]
$2\theta_{max}$:	64.4°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4648, 2350
Criterion for F_{obs}, $N(hkl)_{gt}$:	$F_{obs} > 3\,\sigma(F_{obs})$, 1665
$N(param)_{refined}$:	86
Programs:	SHELXS-86 [8], SHELXL-93 [9], DIAMOND [10]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pr(1)	4c	0.40104(5)	1/4	0.46236(2)	0.0116(2)	0.0132(3)	0.0138(2)	0	–0.0012(2)	0
Pr(2)	4c	0.24374(6)	1/4	0.06443(2)	0.0138(3)	0.0140(3)	0.0158(2)	0	–0.0023(2)	0
Pr(3)	4c	0.43801(5)	1/4	0.19285(2)	0.0124(3)	0.0146(3)	0.0151(2)	0	–0.0008(2)	0
Pr(4)	4c	0.24533(6)	1/4	0.32661(2)	0.0130(3)	0.0134(3)	0.0138(2)	0	–0.0004(2)	0
Pr(5)	4c	0.44107(6)	1/4	0.92262(2)	0.0126(3)	0.0181(4)	0.0158(2)	0	–0.0010(2)	0
Pr(6)	4c	0.38142(6)	1/4	0.71331(2)	0.0135(3)	0.0142(3)	0.0149(2)	0	–0.0012(2)	0
N(1)	4c	0.0980(8)	1/4	0.0133(3)	0.009(4)	0.017(5)	0.012(3)	0	0.000(3)	0
N(2)	4c	0.0621(9)	1/4	0.3747(3)	0.020(5)	0.004(4)	0.017(4)	0	–0.004(3)	0
N(3)	4c	0.1111(9)	1/4	0.2606(3)	0.018(5)	0.016(5)	0.016(4)	0	–0.004(3)	0
S(1)	4c	0.2041(3)	1/4	0.89640(9)	0.014(1)	0.013(1)	0.016(1)	0	0.0017(9)	0

Table 2. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(2)	4*c*	0.0431(3)	1/4	0.13630(9)	0.015(1)	0.022(2)	0.016(1)	0	–0.0018(9)	0
S(3)	4*c*	0.1449(3)	1/4	0.50411(9)	0.013(1)	0.018(2)	0.019(1)	0	0.0001(9)	0
S(4)	4*c*	0.1900(3)	1/4	0.63676(9)	0.016(1)	0.017(2)	0.014(1)	0	0.0035(9)	0
Cl	4*c*	0.1374(3)	1/4	0.76448(9)	0.017(1)	0.018(1)	0.017(1)	0	–0.0007(9)	0

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