direkt an das N-Atom gebundenen C-Atome betroffen, während die terminalen C-Atom beiden Orientierungen gemeinsam sind (Fig. 1). Diese Art Fehlordnung wird bei Tetraethylammonium-Salzen häufig beobachtet (z.B. Krug, Koellner & Müller, 1988).

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Structure of Yttrium Nitrate Monohydrate

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Abstract. $Y(NO_3)_3.H_2O$, $M_r = 292·93$, triclinic, $P\bar{1}$, $a = 7·388\,(1)$, $b = 7·889\,(1)$, $c = 8·204\,(2)$ Å, $\alpha = 64·43\,(2)$, $\beta = 70·90\,(1)$, $\gamma = 62·74\,(1)°$, $V = 378·4\,(2)$ Å^3, $Z = 2$, $D_x = 2·570$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 78·02$ cm^{-1}, $F(000) = 284$, $T = 293\,(1)$ K, $R = 0·070$ for 1613 unique observed reflections. Eight nitrate O atoms and a water molecule produce a nine-coordinated Y atom. The coordination polyhedra are linked by four common nitrate oxygens, thus forming continuous chains parallel to the *b* axis. Water molecules form hydrogen bonds with two nitrate O atoms in adjacent chains.

Introduction. The title compound was prepared by thermal decomposition of crystals of $Y(NO_3)_3.6H_2O$ (Merck, Art. 12516) at 443 (1) K. The structure of $Y(NO_3)_3.6H_2O$ was solved by Ribár, Milinski, Budovalčev & Krstanović (1980) and the structure of $Y(NO_3)_3.5H_2O$ by Eriksson (1982). Differential thermal analysis of $Y(NO_3)_3.6H_2O$ within the temperature range from 293 to 630 K shows five endothermic peaks at 323, 355, 378, 443 and 533 K. The first peak corresponds to melting; the second peak corresponds to formation of a complex salt $Y_2(NO_3)_6.7H_2O$ (Radivojević, Milinski, Ribár & Lazar, 1984); the third to $Y(NO_3)_3.3H_2O$ (Ribár, Radivojević, Argay & Kálmán, 1988); the fourth to the title compound; the fifth to $Y(NO_3)_3$. Single crystals of the title compound have been grown by keeping $Y(NO_3)_3.6H_2O$ for two weeks at 443 K. The hygroscopic crystals obtained were sealed into Lindemann-glass capillary tubes.

Experimental. A crystal plate *ca* 0·70 × 0·20 × 0·10 mm was measured on an Enraf–Nonius CAD-4 diffractometer equipped with a graphite monochromator. Scan range $0 < \theta < 30°$, ω–2θ scan, h −9 to 10, k −9 to 10, l 0 to 11, no systematic absences. Cell parameters by least-squares fit for 25 reflections

Table 1. *Final fractional coordinates with e.s.d.'s in parentheses*

B_{eq} = 4/3 trace (**BG**) where **G** is the direct metric tensor.

	x	y	z	B_{eq}(Å^2)
Y	0·5296 (1)	0·2707 (1)	0·4260 (1)	0·86 (5)
O*W*	0·3087 (10)	0·3860 (11)	0·2241 (10)	1·5 (6)
N1	0·9010 (12)	0·2861 (11)	0·1949 (12)	1·4 (7)
O11	0·7359 (10)	0·3337 (11)	0·1352 (11)	1·6 (6)
O12	0·8831 (10)	0·2358 (10)	0·3617 (11)	1·6 (6)
O13	1·0579 (12)	0·2924 (12)	0·0882 (13)	2·4 (8)
N2	0·5931 (12)	0·2092 (12)	0·7808 (11)	1·4 (7)
O21	0·5568 (11)	0·3820 (9)	0·6464 (10)	1·4 (6)
O22	0·6140 (11)	0·0674 (9)	0·7309 (10)	1·6 (6)
O23	0·6034 (12)	0·1905 (12)	0·9282 (11)	2·0 (7)
N3	0·1681 (13)	0·1849 (12)	0·6596 (13)	1·6 (7)
O31	0·3202 (10)	0·0647 (9)	0·5752 (10)	1·3 (6)
O32	1·1926 (12)	0·3434 (10)	0·6282 (11)	1·7 (6)
O33	0·0262 (13)	0·1395 (13)	0·7573 (14)	2·7 (9)

Table 2. *Interatomic distances* (Å) *and selected angles* (°) *with e.s.d.'s in parentheses*

Y—O*W*	2·312 (9)	N1—O11	1·297 (21)
Y—O11	2·357 (7)	N1—O12	1·228 (12)
Y—O12	2·396 (8)	N1—O13	1·210 (19)
Y—O21	2·418 (10)	N2—O21	1·307 (12)
Y—O21^i	2·347 (7)	N2—O22	1·279 (15)
Y—O22	2·420 (8)	N2—O23	1·177 (13)
Y—O31	2·424 (8)	N3—O31	1·312 (15)
Y—O31^{ii}	2·358 (7)	N3—O32	1·250 (17)
Y—O32	2·468 (7)	N3—O33	1·190 (21)

O11—N1—O12	115 (2)	O11—Y—O31^{ii}	83·2 (3)
O11—N1—O13	120 (2)	O12—Y—O21	75·5 (3)
O12—N1—O13	125 (2)	O12—Y—O21^i	86·9 (3)
O21—N2—O22	111 (2)	O12—Y—O22	81·6 (3)
O21—N2—O23	123 (2)	O12—Y—O31^{ii}	82·6 (3)
O22—N2—O23	125 (2)	O21—Y—O21^i	61·7 (3)
O31—N3—O32	113 (2)	O21—Y—O22	52·4 (3)
O31—N3—O33	121 (2)	O21—Y—O31	109·3 (3)
O32—N3—O33	126 (2)	O21—Y—O32	72·8 (3)
O*W*—Y—O11	75·8 (3)	O21^i—Y—O22	113·9 (3)
O*W*—Y—O21^i	82·9 (3)	O21^i—Y—O32	81·7 (2)
O*W*—Y—O31	75·4 (3)	O22—Y—O31	72·6 (3)
O*W*—Y—O31^{ii}	94·9 (3)	O22—Y—O31^{ii}	75·9 (2)
O*W*—Y—O32	79·1 (3)	O22—Y—O32	76·0 (3)
O11—Y—O12	53·3 (3)	O31—Y—O31^{ii}	62·0 (3)
O11—Y—O21	118·1 (3)	O31—Y—O32	51·8 (3)
O11—Y—O21^i	81·4 (3)	O31^{ii}—Y—O32	113·0 (3)

Symmetry code: (i) $1-x, 1-y, 1-z$; (ii) $1-x, -y, 1-z$.

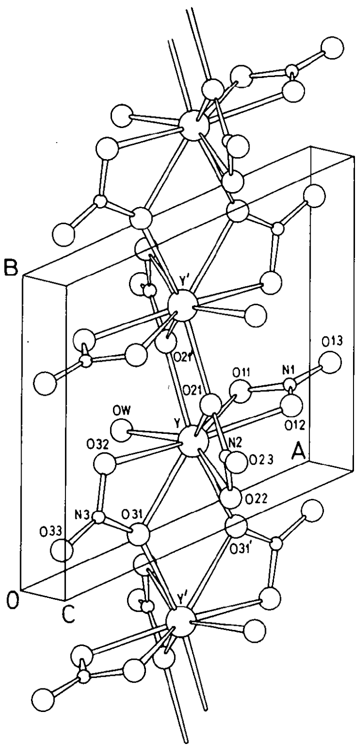

Fig. 1. Perspective view of the structure as viewed down the c axis.

with θ range from 8 to 10°. Intensities of 4390 reflections were measured; 2195 averaged unique, 1613 with $I > 3\sigma(I)$. Three standard reflections ($\bar{1}4\bar{2}$, $\bar{2}4\bar{3}$, $\bar{2}4\bar{2}$) were measured every 2 h. Intensity decrease 0·5%. Structure was solved by *MULTAN*82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). No H-atom positions could be located. Full-matrix least-squares refinement minimized $\sum w(\Delta F)^2$ for 127 parameters with unit weight. Final R = 0·070, wR = 0·091, R_{tot} = 0·096. Maximum residual electron density in final difference map is 3·93 e Å^{-3}, 0·87 Å from yttrium, probably caused by irregular shape of the crystal and missing absorption correction. Max. Δ/σ = 0·21. S = 2·19. Scattering factors were taken from Enraf–Nonius (1983) *SDP-Plus*. Program applied: Enraf–Nonius *SDP-Plus* with local modification adapted to PDP11/34 minicomputer.

Discussion. Atomic coordinates of non-H atoms are in Table 1.* The atomic arrangements around the Y atom and packing of coordination polyhedra are shown in Fig. 1. Bond distances and angles are listed in Table 2. The Y atom has ninefold coordination involving eight nitrate O atoms and one water molecule. The coordination polyhedron is irregular. The Y—O distances range from 2·312 (9) to 2·468 (7) Å, the Y—O*W* distance being the shortest. All nitrate groups are bidentately bound to Y. O21 and O31 belong to two coordination polyhedra. The coordination polyhedra form infinite chains by means of edge sharing. The chains run parallel to the b axis. Direct linkage of coordination polyhedra increases the crystal-packing efficiency, resulting in a substantially higher density of the compound (2·570 g cm^{-3}) with respect to the trihydrate (2·246 g cm^{-3}). All nitrate groups are strictly planar; the non-

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52429 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

coordinated O atom is closer to N than the other two and the metal-bound O—N—O angles are significantly smaller than the other O—N—O angles, as usual in bidentate nitrate groups. The Y atom is displaced from the plane of the three nitrate groups by 0·048 (1), 0·233 (1) and 0·052 (1) Å respectively. Dihedral angles between the planes of the nitrate groups are 83·3 (5), 80·7 (4) and 67·2 (5)°. Chains of coordination polyhedra are linked together by hydrogen bonds, the water O atom forming two hydrogen bonds with two neighbouring chains [O*W*—O11($1-x$, $1-y$, $\bar{z}$): 2·834 (10) Å and O*W*—O13($x-1$, y, z): 2·922 (16) Å].

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Refinement of the Structure of Robinsonite, $Pb_4Sb_6S_{13}$

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Abstract. The structure of robinsonite, $Pb_4Sb_6S_{13}$, M_r = 1976·1, previously determined by Petrova, Kaplunnik, Bortnikov, Pobedimskaya & Belov [*Dokl. Akad. Nauk SSSR* (1978), **241**, 88–90] in the triclinic space group $P1$, has been refined in monoclinic $I2/m$, a = 23·698 (8), b = 3·980 (8), c = 24·466 (8) Å, β = 93·9 (3)°, V = 2302 Å^3, Z = 4, D_x = 5·7 g cm^{-3}, Mo $K\alpha$ radiation, λ = 0·71069 Å, μ = 356·4 cm^{-1}, $F(000)$ = 3368, room temperature, R = 0·071, wR = 0·064 for 2361 independent reflections. The crystal was prepared by annealing at 723 K in the presence of I_2 in vacuum-sealed ampoules. The basic arrangement of atoms proposed by Petrova *et al.* (1978) is confirmed but both the space group and the cation distribution, determined by site-occupancy refinement and by bond-valence analysis, are shown to be different. A bond-valence analysis of the homeotypic $Sn_4Sb_6S_{13}$ [Jumas, Olivier-Fourcade, Philippot & Maurin (1980). *Acta Cryst.* B**36**, 2940–2945], shows that it has a distribution of Sb atoms similar to that in the Pb analogue.

Introduction. Several crystallographic studies (Berry, Fahey & Bailey, 1952; Jambor & Lachance, 1968; Wang, 1977; Petrova, Kaplunnik, Bortnikov, Pobedimskaya & Belov, 1978; Ayora & Gali, 1981; Jambor & Owens, 1982) have been devoted to both natural and synthetic robinsonite. As a result the composition of the phase has been firmly established as $Pb_4Sb_6S_{13}$ but the symmetry and the details of the structure remain controversial. Our unit cell agrees with most previous results but only Petrova *et al.* (1978) report the structure. The space group they use ($P1$) differs from that ($B2/m$) assigned by Wang (1977) and they also appear to have permuted the lattice angles. Jumas, Olivier-Fourcade, Philippot & Maurin (1980) have reported a similar structure for $Sn_4Sb_6S_{13}$ in the space group $I2/m$ (equivalent to Wang's $B2/m$). We have undertaken an independent structure determination to resolve these uncertainties.

Experimental. Single crystals of $Pb_4Sb_6S_{13}$ were synthesized from elemental lead, antimony, and sulfur of 'Specpure' grade, supplied by Johnson Matthey plc. The elements were combined in the proportions of 60 mol % of PbS and 40 mol % of Sb_2S_3, sealed in evacuated silica tubes, melted at 1073 K and quenched. The ingot was then ground and pelletized. Three 1 g pellets were each placed in separate silica tubes with approximately 1 mg of I_2. The tubes were then evacuated, sealed and annealed in a two-zone

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