2,13 Å. Ces valeurs sont tout à fait comparables à celles trouvées dans la bayldonite $(Cu,Zn)_3Pb(AsO_4)_2(OH)_2$ (Ghose & Wan, 1979) bien que les octaèdres y soient moins distordus car les angles varient entre 82 et 98°.

Liaisons hydrogène

Les atomes d'hydrogène n'ayant pu être localisés, l'interprétation des liaisons hydrogène a été faite sur une base géométrique. Les liaisons hydrogène proposées sont résumées dans le Tableau 3 et représentées sur la Fig. 1. L'angle entre les liaisons hydrogène venant de la molécule d'eau O(*W*) a une valeur égale à 96,9°.

Dans le Tableau 4 sont groupees les valeurs des liaisons électrostatiques arrivant aux différents atomes d'oxygène, calculées selon la formule de Brown & Wu (1976) pour les atomes lourds, tandis qu'il a été attribué à la valence électrostatique des atomes d'hydrogène donneurs O—H, une valeur égale à $\frac{5}{6}$, et à celle des atomes d'hydrogène accepteurs H···O, une valeur égale à $\frac{1}{6}$. La somme des valences électrostatiques afférentes à chaque atome d'oxygène reste voisine de deux à l'intérieur des limites généralement acceptées, la valeur moyenne étant égale à 1,99.

Tableau 3. *Liaisons hydrogène* (Å) *et angles* (°) *avec leurs écarts types*

O(H1)–O(5)	2,88 (2)		
O(H2)–O(6)	2,88 (2)		
O(H3)–O(7)	2,72 (2)		
O(*W*)–O(2)	3,23 (3)	O(2)–O(*W*)–O(5)	96,9
O(*W*)–O(5)	3,36 (3)*		

* Liaison devant plutôt être considérée comme une liaison de van der Waals.

Tableau 4. *Valeurs des liaisons électrostatiques et de leurs sommes autour des anions*

H(*d*) = liaison hydrogène donneur; H(*a*) = liaison hydrogène accepteur.

Anions	U^{6+}	Pb^{2+}	Se^{4+}	Cu^{2+}	H(*d*)	H(*a*)	$\sum$
O(1)	2,11						2,11
O(2)	1,96					$\frac{1}{6}$	2,13
O(3)	0,44	0,26	1,19				1,89
O(4)	0,59	0,14	1,22				1,95
O(5)	0,56		1,31			$2\times\frac{1}{6}$	2,20
O(6)	0,58		1,28			$\frac{1}{6}$	2,03
O(7)	0,53		1,16			$\frac{1}{6}$	1,86
O(8)			1,28	0,22+0,33			1,93
O(9)			1,31	0,22+0,36			2,02
O(10)			1,22	0,14+0,40			2,05
O(11)			1,28	0,43			1,90
O(H1)				0,50+0,47+0,14	$\frac{5}{6}$		1,94
O(H2)				0,47+0,12	$\frac{5}{6}$		1,85
O(H3)				0,43+0,44	$\frac{5}{6}$		2,05
O(*W*)				0,14	$2\times\frac{5}{6}$		1,91

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Redetermination of the Structure of Tetrasulphurtetranitrogen Dioxide,* $S_4N_4O_2$

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Abstract. $M_r = 216\cdot28$, monoclinic, $P2_1/c$, $a = 10\cdot359\ (4)$, $b = 8\cdot100\ (2)$, $c = 8\cdot687\ (3)$ Å, $\beta = 113\cdot81\ (2)°$, $U = 666\cdot9$ Å^3, $Z = 4$, $D_x = 2\cdot15$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot71069$ Å, $\mu = 13$ cm^{-1}, $F(000) = 432$, $T = 298$ K. Final $R = 0\cdot063$ for 2090 unique observed reflections. The molecular structure is qualitatively identical to that reported briefly by Roesky [*Z. Naturforsch. Teil B* (1976). **31**, 680–683], but the previously assigned space group *Abm*2 is probably incorrect due to twinning, resulting in an imprecise determination.

Introduction. The structure of $S_4N_4O_2$ has been referred to briefly in the literature (Roesky, 1976; Roesky, Grosse Böwing, Rayment & Shearer, 1975); the space group was given as *Abm*2, and 'imperfections in the crystals' were mentioned. It therefore seemed worthwhile to redetermine the structure with a view to obtaining more accurate results.

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* Alternative name: $1\lambda^4,3,5\lambda^4$,7-tetrathia-2,4,6,8-tetraaza-1,4,5,8-cyclooctatetraene 3,3-dioxide.

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The crystallographic details of the earlier investigation (Roesky, 1983) included a description of split reflections and of disordered $S_4N_4O_2$ molecules such as might be consistent with systematic twinning. Our Weissenberg photographs of crystals obtained from liquid SO_2 indeed showed Laue symmetry no higher than $2/m$, although it was impossible to obtain crystals entirely free of satellites.

Experimental. Crystal 0·6 × 0·4 × 0·4 mm mounted in a glass capillary. Stoe–Siemens four-circle diffractometer, monochromated Mo $K\alpha$ radiation. A preliminary A-centred cell with axes 8·11, 18·95, 8·67 Å was found, which was, however, inconsistent with the previously reported orthorhombic cell because the α angle deviated significantly from 90° (89·0°). This preliminary cell could be converted by the matrix $[0\frac{1}{2}{-}\frac{1}{2}\ {-}100\ 001]$ to a primitive monoclinic cell, on the basis of which all further measurements and calculations were carried out.

2954 profile-fitted reflections (Clegg, 1981), $2\theta \leq 65°$. Cell constants refined using 2θ values of 32 strong reflections in range $20 < 2\theta < 24°$. Systematic absences indicated space group $P2_1/c$. After semi-empirical absorption corrections (transmission factors 0·61–0·66), averaging equivalents gave 2394 unique reflections, 2089 of which with $F > 4\sigma(F)$ used for all calculations: $R_{\text{int}} = 0{\cdot}022$. Three standard reflections, no intensity variation. Structure solved by routine direct methods and refined anisotropically on F (91 parameters) to $R = 0{\cdot}063$, $R_w = 0{\cdot}072$; weighting scheme $w^{-1} = \sigma^2(F) + 0{\cdot}00025\ F^2$. Ratio of max. LS shift to error 0·005. Max. and min. heights in final difference Fourier map 1 and −1 e Å^{-3}. All calculations performed with *SHELXTL* written by GMS.

Discussion. Final atomic coordinates and derived parameters are given in Tables 1 and 2 respectively.*

Table 1. *Atom coordinates* (×10^4) *and equivalent isotropic temperature factors* (Å^2 ×10^3) *with e.s.d.'s in parentheses*

	x	*y*	*z*	U_{eq}*
S(1)	2408 (1)	4506 (1)	1719 (1)	33 (1)
S(2)	4685 (1)	2721 (1)	4059 (1)	45 (1)
S(3)	2788 (1)	−3 (1)	2110 (1)	53 (1)
S(4)	397 (1)	2225 (1)	1851 (1)	50 (1)
N(1)	3709 (3)	4278 (3)	3512 (3)	38 (1)
N(2)	4148 (3)	1047 (4)	3193 (4)	46 (1)
N(3)	1269 (3)	708 (4)	1713 (4)	48 (1)
N(4)	1073 (3)	3984 (4)	2128 (4)	45 (1)
O(1)	2282 (3)	6230 (3)	1366 (4)	59 (1)
O(2)	2536 (3)	3425 (3)	494 (3)	45 (1)

* U_{eq} calculated from anisotropic U.

Table 2. *Bond lengths* (Å), *bond angles and torsion angles* (°)

N(1)–S(1)	1·607 (3)	N(1)–S(2)	1·566 (4)
N(2)–S(2)	1·541 (4)	N(2)–S(3)	1·589 (4)
N(3)–S(3)	1·578 (5)	N(3)–S(4)	1·558 (5)
N(4)–S(1)	1·617 (5)	N(4)–S(4)	1·563 (4)
O(1)–S(1)	1·424 (4)	O(2)–S(1)	1·425 (4)
N(1)–S(1)–N(4)	102·4 (3)	N(1)–S(1)–O(1)	106·8 (2)
N(4)–S(1)–O(1)	106·9 (3)	N(1)–S(1)–O(2)	111·0 (2)
N(4)–S(1)–O(2)	110·5 (3)	O(1)–S(1)–O(2)	118·0 (3)
N(1)–S(2)–N(2)	119·9 (2)	N(2)–S(3)–N(3)	120·1 (3)
N(3)–S(4)–N(4)	119·6 (3)	S(1)–N(1)–S(2)	124·9 (3)
S(2)–N(2)–S(3)	145·0 (3)	S(3)–N(3)–S(4)	146·0 (3)
S(1)–N(4)–S(4)	125·0 (3)		
N(4)–S(1)–N(1)–S(2)	97·6 (4)	O(1)–S(1)–N(1)–S(2)	−150·3 (4)
O(2)–S(1)–N(1)–S(2)	−20·3 (4)	N(1)–S(1)–N(4)–S(4)	−95·0 (3)
O(1)–S(1)–N(4)–S(4)	152·9 (3)	O(2)–S(1)–N(4)–S(4)	23·2 (4)
N(2)–S(2)–N(1)–S(1)	−22·9 (5)	N(1)–S(2)–N(2)–S(3)	−20·2 (7)
N(3)–S(3)–N(2)–S(2)	−5·3 (7)	N(2)–S(3)–N(3)–S(4)	5·9 (7)
N(4)–S(4)–N(3)–S(3)	20·5 (6)	N(3)–S(4)–N(4)–S(1)	20·3 (4)

Sign convention as defined by Klyne & Prelog (1960).

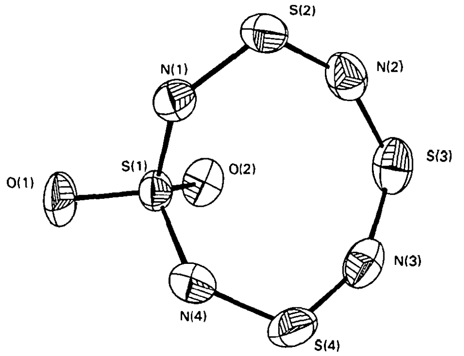

Fig. 1. Thermal-ellipsoid plot (50% probability) of the $S_4N_4O_2$ molecule, showing the atom-numbering scheme.

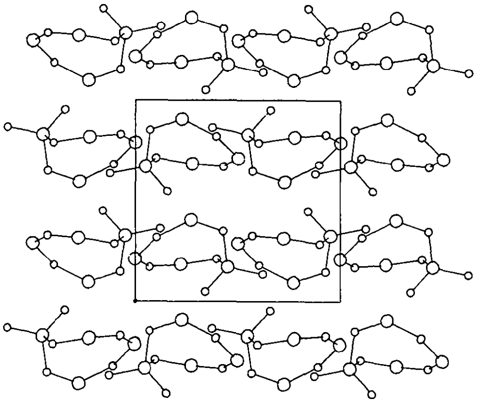

Fig. 2. Packing plot projected down **a**. The larger circles represent S atoms.

Fig. 1 shows the $S_4N_4O_2$ molecule; the connectivity reported previously (Roesky, 1976; Roesky *et al.*, 1975) is confirmed. A non-crystallographic mirror plane passes through S(1), S(3) and the O atoms. The five ring atoms S(2)–N(2)–S(3)–N(3)–S(4) form a planar fragment (r.m.s. deviation 0·014 Å), with N(1),

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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 38482 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

N(4) and S(1) lying 0·55, 0·58 and 1·57 (1) Å respectively out of this plane. The four S—N bonds involving S(2) and S(4) are appreciably shorter than those at S(1) and S(3), indicating some localization of multiple-bond character [see Table 2; *cf.* S—N bond lengths 1·548–1·566 Å in $S_4N_3^+$ (Kruss & Ziegler, 1972)].

Fig. 2 shows a packing plot of the structure; the shortest intermolecular contacts are O(2)···N(3), 3·08, O(2)···S(4), 3·09, and O(2)···S(2), 3·10 (1) Å (second atoms at $x, \frac{1}{2}-y, -\frac{1}{2}+z$).

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Barium Strontium Niobate and Barium Strontium Tantalate, $Ba_3SrNb_2O_9$ and $Ba_3SrTa_2O_9$, a Rietveld Refinement of Neutron Powder Diffraction Data

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Abstract. $Ba_3SrNb_2O_9$: $M_r = 829{\cdot}45$, hexagonal, $P6_3/m$, $a = 6{\cdot}0704\ (1)$, $c = 15{\cdot}3758\ (5)$ Å, $V = 490{\cdot}68\ (3)$ Å^3, $Z = 2$, $D_x = 5{\cdot}61$ Mg m^{-3}. $Ba_3SrTa_2O_9$: $M_r = 1005{\cdot}53$, hexagonal, $P6_3/m$, $a = 6{\cdot}0776\ (1)$, $c = 15{\cdot}3360\ (5)$ Å, $V = 490{\cdot}58\ (3)$ Å^3, $Z = 2$, $D_x = 6{\cdot}81$ Mg m^{-3}. The structures have been refined by Rietveld analysis of powder neutron diffraction data at room temperature, $\lambda = 2{\cdot}5907\ (3)$ Å. $R_I = 2{\cdot}28$, 2·68%; $R_p = 4{\cdot}93$, 5·46%; $R_{wp} = 6{\cdot}12$, 6·49% respectively for 86 reflections. The structure of both compounds is of a modified hexagonal $BaTiO_3$ type.

Introduction. In a programme to investigate compounds with perovskite or related structures on their properties as a host lattice for nuclear waste we prepared $Ba_3SrNb_2O_9$ and $Ba_3SrTa_2O_9$. The latter compound is reported as an ordered 3*L* perovskite structure (Galasso, Barrante & Katz, 1961). Kemmler-Sack, Thumm & Hermann (1981), however, reported the hexagonal 6*L* $BaTiO_3$ structure (Burbank & Evans, 1948) for both compounds.

Experimental. The compounds were prepared by solid-state reaction of $BaCO_3$, $SrCO_3$ and Nb_2O_5 or Ta_2O_5. These AR materials were thoroughly mixed in an agate mortar in the appropriate ratios. The mixtures were heated in alumina crucibles at 1273 K for one day and 1573 K for a week, with repeated grindings. The compounds were annealed at 923 K for a week. X-ray powder-diffraction patterns were obtained with a Philips PW 1050 diffractometer and could be indexed with hexagonal cells. The symmetry and systematic absences indicated space group $P6_3/m$ or $P6_322$. Since no single crystals were available the Rietveld (1969) method for refinement of neutron powder diffraction data was used. Neutrons of wavelength 2·5907 (3) Å were obtained from the (111) planes of a copper crystal. Pyrolytic graphite with a total thickness of 12 cm was employed as a second-order filter. Soller slits with a horizontal divergence of 30′ were placed between the reactor and the monochromator and in front of each of the four ^{3}He counters. The sample holder (⌀ = 20 mm) consisted of a vanadium tube, closed with copper plugs fitted with O-rings. No precautions were taken against preferred orientations. The maximum absorption correction was 1·0%, $\mu R = 0{\cdot}191$ (Weber, 1967) for $Ba_3SrNb_2O_9$ and 2·5%, $\mu R = 0{\cdot}322$ for $Ba_3SrTa_2O_9$. The background was determined from parts of the diagrams, which did not contain any contribution from reflections, and linear extrapolation between these points. The statistically expected values of R_{wp} are 3·60 and 3·54% respectively.

The hexagonal $BaTiO_3$ structure (Burbank & Evans, 1948) was used as the trial model, modified for space group $P6_3/m$: Ba(1) in 2(*a*) $(0,0,\frac{1}{4})$; Ba(2) in 4(*f*) $(\frac{1}{3}, \frac{2}{3}, z)$; Sr in 2(*b*) (0,0,0); Nb in 4(*f*); O(1) in 6(*h*) $(x,y,\frac{1}{4})$ and O(2) in 12(*i*) (*x*,*y*,*z*). The parameters in the refinement were: a scale factor, three half-width

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