spectra (Lutz, Kellersohn & Beckenkamp, 1989) are too broad to determine accurate mode energies, and therefore a clear comparison between the bromide and the chloride is not possible.

The observed hydrogen bond lengths of the hydroxides under investigation, however, are influenced additionally by constraints due to the symmetry of the structure and the dimensions of the unit cells. This means that the most favourable bond distance of the hydrogen bond donor–acceptor pair DOD⋯OD⁻ is modified, e.g. enlarged in the case of the bromide, due to packing effects (Lutz & Henning, 1987b; Henning, 1988). This might explain the discrepancies in hydrogen bond strength outlined above.

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Structure of Trisilylphosphine, P(SiH₃)₃, at 100 K

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Abstract. H$_9$PSi$_3$, $M_r = 124.30$, monoclinic, $P2_1/c$, $a = 6.0631$ (16), $b = 12.734$ (3), $c = 9.6784$ (20) Å, $\beta = 93.872$ (16)°, $V = 742.2$ Å^3, $Z = 4$, $D_x = 1.112$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 0.714$ mm^{-1}, $F(000) = 264$, $T = 100$ K, $R = 0.0287$ for 1778 unique observed reflections. Individual molecules have approximate, non-crystallographic C_{3v} symmetry: they are linked by P⋯Si intermolecular contacts to give a corrugated sheet structure with P—Si⋯P angles close to linear and [3 + 2] coordination at phosphorus.

Introduction. We have previously determined the crystal structures of several simple compounds con- taining Si—N bonds, such as trisilylamine (Barrow & Ebsworth, 1984) and dimethylsilylamine (Blake, Ebsworth & Welch, 1984a). These two compounds may be taken as representing two extremes: the former shows little if any difference between its gas-phase and solid-state structures, while the latter is monomeric in the vapour (Gundersen, Mayo, Rankin & Robertson, 1984) but forms a unique cyclic pentamer in the crystal. Although IR and Raman spectroscopic results (Davidson, Ebsworth, Sheldrick & Woodward, 1966) were consistent with trisilylphosphine being similar to trisilylamine in that the central atom was surrounded by a trigonal planar arrangement of Si atoms, electron diffraction studies (Beagley, Robiette & Sheldrick, 1968) established pyramidal geometry in the gas phase. The purpose of the present work was to discover the precise structure of trisilylphosphine in the solid state

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and to determine whether, unlike trisilylamine, it participates in significant intermolecular interactions.

Experimental. The title compound (m.p. 200 K) was prepared by reaction of SiH_3Br with KPH_2 in dimethyl ether at 177 K, purified by fractionation and sealed in a Pyrex capillary tube: this was mounted on a Stoe STADI-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device (Cosier & Glazer, 1986) and a colourless cylindrical crystal, $0.19 \times 0.50 \times 0.50$ mm, was grown by zone refinement. The crystal was then cooled to 100 ± 0.1 K and held at that temperature during the experiment. Cell parameters from 2θ values of 60 reflections measured at $\pm \omega$ ($30 \leq 2\theta \leq 32°$). For data collection, STADI-4 diffractometer, graphite-monochromated Mo $K\alpha$, ω–2θ scans with ω-scan width $(0.90 + 0.35\tan\theta)°$, $2\theta_{max} = 60°$, h $-8 \rightarrow 8$, k $0 \rightarrow 17$, l $0 \rightarrow 13$, linear isotropic crystal decay (ca 20%) corrected for during data processing, no absorption correction, 2869 reflections measured, 2078 unique (R_{int} 0.022), giving 1778 with $F \geq 6\sigma(F)$ for structure solution [by automatic direct methods (Sheldrick, 1986)] and refinement [using full-matrix least squares on F (Sheldrick, 1976)]. Anisotropic thermal parameters for P and Si, H atoms freely refined with individual isotropic thermal parameters, secondary-extinction parameter refined to $6.7 (12) \times 10^{-7}$. At final convergence, $R = 0.0287$, $wR = 0.0395$, $S = 1.069$ for 74 parameters, $(\Delta/\sigma)_{max}$ in final cycle 0.032, max. and min. $\Delta\rho$ in final ΔF synthesis 0.45 and -0.29 e Å^{-3}. The weighting scheme $w^{-1} = \sigma^2(F) + 0.000134F^2$ gave satisfactory agreement analyses. Scattering factors were inlaid (Sheldrick, 1976). The atom-numbering scheme for the molecule is shown in Fig. 1, which was generated using *ORTEP* (Mallinson & Muir, 1985): Fig. 2 was produced from *PLUTO* (Motherwell, 1976) and shows the molecular packing. Molecular geometry calculations were performed using *CALC* (Gould & Taylor, 1985).

Discussion. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1, while bond lengths, angles and torsion angles appear in Table 2.* As Fig. 1 shows, individual molecules of $P(SiH_3)_3$ possess approximate, non-crystallographic C_{3v} symmetry. The P—Si distances of 2.2401 (6), 2.2507 (6) and 2.2458 (6) Å do not differ significantly from the gas-phase value of 2.248 (3) Å (Beagley, Robiette & Sheldrick, 1968): analysis of P⋯Si inter-

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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 53513 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

molecular contacts (see below) suggests that the first of these values, 2.2401 (6) Å, provides the best available estimate of an unperturbed, solid-state P—Si bond length for this species. The Si—P—Si valence angles [97.495 (23), 95.619 (23), 95.225 (22)°] do not differ significantly from the gas-phase value of 96.5 (5)° and similarly the P—Si—H and H—Si—H angles are close to tetrahedral as in the vapour. There are few examples of structural characterizations of simple silylphosphines, although a recent electron diffraction study of $P(SiMe_3)_3$ (Forsyth, Rankin & Robertson, 1990) identified the steric effects of the bulky substituents, including a major increase in the Si—P—Si angles to 105.1 (2)° and a slight elongation of the P—Si bonds to 2.259 (1) Å.
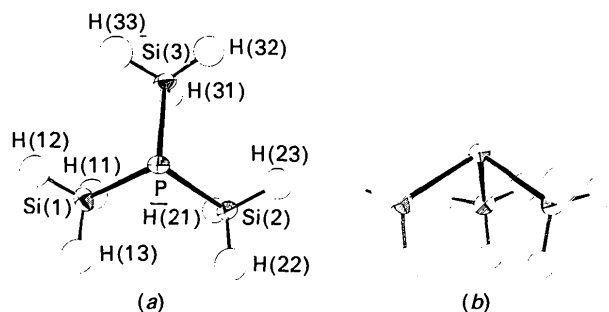

Fig. 1. (a) View of the molecule along the approximate threefold axis showing atom-numbering scheme. (b) Orthogonal view showing the pyramidal P atom. All thermal ellipsoids are drawn at the 30% probability level.
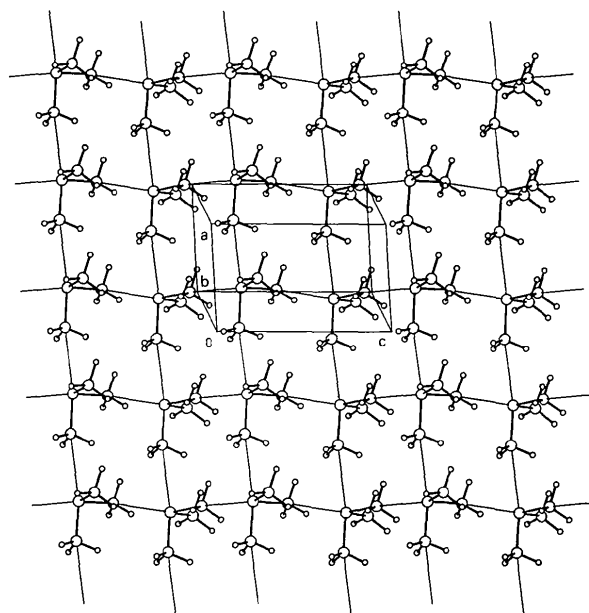

Fig. 2. Packing diagram showing one corrugated sheet of molecules linked by P⋯Si interactions.

Table 1. *Atomic coordinates and thermal parameters* (Å²) *with e.s.d.'s*

	x	y	z	U_{iso} or U_{eq}
P	0·26477 (6)	0·38598 (3)	0·19007 (4)	0·02114 (21)
Si(1)	0·29330 (9)	0·54069 (5)	0·29999 (5)	0·0300 (3)
Si(2)	0·28691 (7)	0·28252 (4)	0·37904 (4)	0·02422 (23)
Si(3)	−0·10782 (7)	0·38558 (4)	0·16485 (5)	0·02528 (24)
H(11)	0·156 (4)	0·5518 (20)	0·406 (3)	0·057 (7)
H(12)	0·250 (4)	0·6211 (18)	0·2091 (24)	0·055 (7)
H(13)	0·508 (5)	0·5509 (18)	0·351 (3)	0·066 (8)
H(21)	0·175 (3)	0·3206 (17)	0·4832 (21)	0·039 (6)
H(22)	0·492 (5)	0·2752 (18)	0·426 (3)	0·060 (7)
H(23)	0·213 (4)	0·1861 (19)	0·3382 (23)	0·051 (7)
H(31)	−0·194 (4)	0·3945 (16)	0·2841 (21)	0·040 (6)
H(32)	−0·178 (4)	0·2982 (20)	0·105 (3)	0·053 (7)
H(33)	−0·171 (4)	0·4692 (21)	0·088 (3)	0·065 (8)

Table 2. *Bond lengths* (Å), *angles and torsion angles* (°) *with e.s.d.'s*

P—Si(1)	2·2401 (6)	Si(2)—H(21)	1·342 (21)
P—Si(2)	2·2507 (6)	Si(2)—H(22)	1·292 (25)
p—Si(3)	2·2458 (6)	Si(2)—H(23)	1·356 (24)
Si(1)—H(11)	1·37 (3)	Si(3)—H(31)	1·303 (21)
Si(1)—H(12)	1·364 (24)	Si(3)—H(32)	1·310 (25)
Si(1)—H(13)	1·36 (3)	Si(3)—H(33)	1·35 (3)
Si(1)—P—Si(2)	97·5 (2)	P—Si(2)—H(23)	107·0 (10)
Si(1)—P—Si(3)	95·6 (2)	H(21)—Si(2)—H(22)	106·2 (14)
Si(2)—P—Si(3)	95·2 (2)	H(21)—Si(2)—H(23)	112·0 (13)
P—Si(1)—H(11)	114·6 (11)	H(22)—Si(2)—H(23)	108·9 (15)
P—Si(1)—H(12)	110·4 (10)	P—Si(3)—H(31)	111·2 (9)
P—Si(1)—H(13)	107·3 (11)	P—Si(3)—H(32)	109·8 (11)
H(11)—Si(1)—H(12)	107·9 (15)	P—Si(3)—H(33)	107·5 (11)
H(11)—Si(1)—H(13)	109·0 (15)	H(31)—Si(3)—H(32)	109·2 (14)
H(12)—Si(1)—H(13)	107·4 (15)	H(31)—Si(3)—H(33)	108·5 (15)
P—Si(2)—H(21)	113·2 (9)	H(32)—Si(3)—H(33)	110·6 (15)
P—Si(2)—H(22)	109·4 (11)		
Si(2)—P—Si(1)—H(11)	−48·4 (12)	Si(3)—P—Si(2)—H(21)	−56·5 (10)
Si(2)—P—Si(1)—H(12)	−170·5 (11)	Si(3)—P—Si(2)—H(22)	−174·7 (12)
Si(2)—P—Si(1)—H(13)	72·8 (11)	Si(3)—P—Si(2)—H(23)	67·4 (10)
Si(3)—P—Si(1)—H(11)	47·6 (12)	Si(1)—P—Si(3)—H(31)	−56·6 (10)
Si(3)—P—Si(1)—H(12)	−74·4 (11)	Si(1)—P—Si(3)—H(32)	−177·6 (11)
Si(3)—P—Si(1)—H(13)	168·8 (11)	Si(1)—P—Si(3)—H(33)	62·0 (12)
Si(1)—P—Si(2)—H(21)	39·9 (10)	Si(2)—P—Si(3)—H(31)	41·4 (10)
Si(1)—P—Si(2)—H(22)	−78·4 (12)	Si(2)—P—Si(3)—H(32)	−79·5 (11)
Si(1)—P—Si(2)—H(23)	163·8 (10)	Si(2)—P—Si(3)—H(33)	160·1 (12)

Table 3. *Intermolecular* Si—P···Si—P *contacts*

				Distance P···Si(Å)	Angle (°) Si—P···Si	Angle (°) P···Si—P
Si(1)	P	Si(2')	P'	3·706	152·75	174·52
Si(2)	P	Si(2')	P'		108·52	
Si(3)	P	Si(2')	P'		90·07	
Si(1)	P	Si(3'')	P''	3·811	89·24	170·11
Si(2)	P	Si(3'')	P''		92·67	
Si(3)	P	Si(3'')	P''		170·11	
Si(2')	P	Si(3'')	P''		81·76	

Singly and doubly primed atoms are related to their unprimed equivalents by the symmetry operations $(x, \frac{1}{2} - y, -\frac{1}{2} + z)$ and $(1 + x, y, z)$ respectively.

The crystal structure of trisilylphosphine may be contrasted with those of trisilylamine and trimethylamine. As $N(SiH_3)_3$ has a planar heavy-atom skeleton and concomitantly lacks a stereochemically active lone pair (Barrow & Ebsworth, 1984), the absence of discrete intermolecular Si···N contacts – seen in solid dimethylsilylamine (Blake, Ebsworth & Welch, 1984a) and chlorosilyl-*N,N*-dimethylamine (Anderson, Blake, Cradock, Ebsworth, Rankin & Welch, 1986) – is unsurprising. Like $P(SiH_3)_3$, trimethylamine is clearly pyramidal [$\angle CNC = 110·40$ (7)°] but the absence of vacant *d* orbitals on the C atoms removes the possibility of these acting as acceptors and the crystal comprises isolated molecules (Blake, Ebsworth & Welch, 1984b). Table 3 describes the geometry of the P···Si(2,3) intermolecular contacts, there being no P···Si(1) contact below 4 Å, the sum

of the van der Waals radii for P and Si. There is a positive correlation between the shortness of the P···Si contact and the lengthening of the associated primary P—Si bond. The [4 + 1] coordination at Si(2) and Si(3) is characterized by approximately linear P—Si···P angles, but the [3 + 2] coordination at P defies an equally straightforward description. However, given that with the exception of two *transoid* values of 152·75 (2) and 170·11 (2)° all angles lie in the range 81·76 (2)–108·52 (2)°, the best description is of a distorted octahedron with the site *trans* to Si(2) vacant. The intermolecular contacts link molecules into infinite, corrugated sheets running in the *ac* plane: these sheets stack along **b** but are not linked by specific interactions. The relatively long contacts between molecules in this structure are consistent with our observation of a melting point for $P(SiH_3)_3$, 200 K, which is only 12 K above that of PMe_3.

Finally, although comparison with the solid-state structure of $S(SiH_3)_2$ shows parallels, such as the [4 + 1] coordination at Si and the S···Si contacts of 3·55 Å which lie 0·35 Å within the van der Waals sum for S and Si (Barrow & Ebsworth, 1982), the structures are clearly not analogous. In $S(SiH_3)_2$ the two lone pairs on S each participate in one intermolecular interaction with one Si to give [2 + 2] distorted tetrahedral coordination at S, as might have been predicted. An analogous structure for $P(SiH_3)_3$ would have shown [3 + 1] distorted tetrahedral coordination at P, whereas we have shown that the molecule adopts the unexpected [3 + 2] coordination described above.

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Structure of Photoluminescent Polyoxomolybdoeuropate (NH₄)₁₂H₂[Eu₄(MoO₄)(H₂O)₁₆(Mo₇O₂₄)₄].13H₂O

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Abstract. Dodecaammonium dihydrogen hexadecaaqua-29-molybdotetraeuropate(14−) tridecahydrate, $(NH_4)_{12}H_2[Eu_4Mo_{29}O_{100}(H_2O)_{16}].13H_2O$, $M_r = 5731 \cdot 0$, monoclinic, $C2/c$, $a = 19 \cdot 539\,(6)$, $b = 43 \cdot 31\,(1)$, $c = 20 \cdot 358\,(6)$ Å, $\beta = 117 \cdot 88\,(2)°$, $V = 15229\,(8)$ Å³, $Z = 4$, $D_x = 2 \cdot 47$ Mg m⁻³, $\lambda(Mo\,K\alpha) = 0 \cdot 71069$ Å, $\mu = 3 \cdot 97$ mm⁻¹, $F(000) = 10424$, $T = 298$ K, $R = 0 \cdot 065$ and $wR = 0 \cdot 080$ for 6705 independent reflections. The title compound is obtained from aqueous methanolic solutions containing $[Mo_7O_{24}]^{6-}$ and Eu^{3+}. The central $[Eu_4(MoO_4)(H_2O)_{16}]^{10+}$ core of the anion is coordinated by four heptamolybdate groups in the location of D_{2d} symmetry. Each Eu^{3+} atom in the core exhibits ninefold coordination by O atoms belonging to H_2O, MoO_4 and Mo_7O_{24} units.

Introduction. There have been three structural studies of lanthanide polyoxotungstate complexes, Na_6H_2-$[Ce(W_5O_{18})_2].30H_2O$ (Iball, Low & Weakley, 1974), $K_{16}[Ce(P_2W_{17}O_{61})_2].50H_2O$ (Molchanov, Kazanskii, Torchenkova & Simonov, 1979), and $K_{15}H_3$-$[Eu_3(H_2O)_3(W_5O_{18})_3(SbW_9O_{33})].25 \cdot 5H_2O$ (Yamase, Naruke & Sasaki, 1990). The former two complexes contain lacunary units of W_5O_{18} and $P_2W_{17}O_{61}$ which are prepared by removing a WO_6 octahedron from the Lindqvist and Dawson structures, respectively. The latter is a potassium salt of the luminescent mixed-polyoxotungstates anion $[Eu_3(H_2O)_3$-

$(W_5O_{18})_3(SbW_9O_{33})]^{18-}$ in which the central $Eu_3(H_2O)_3$ core is coordinated by a B-type α-SbW_9O_{33} and three W_5O_{18} units with tetrahedral conformation. The polyoxometalloeuropates are interesting from the point of view of the intramolecular energy transfer from the oxygen-to-metal charge transfer state of polyoxometallate lattices to the emitting $^5D_0$ level of the Eu^{3+} atoms. Our recent interest has been focused on the crystal structure of luminescent polyoxometalloeuropates. There have been few studies of their crystal structures, although luminescence properties for $[Eu(W_5O_{18})_2]^{9-}$, $[Eu(P_2W_{17}O_{61})_2]^{17-}$ and $[Eu(XW_{11}O_{39})_2]^{n-}$ ($n = 13$ and $n = 15$ for $X = $ Si and B, respectively) (Stillman & Thomson, 1976; Blasse, Dirksen & Zonnevijlle, 1981; Ballardini, Chiorboli & Balzani, 1984) have been reported and discussed in relation to their structures. This paper describes the crystal structure of the luminescent $(NH_4)_{12}H_2[Eu_4(MoO_4)(H_2O)_{16}(Mo_7$-$O_{24})_4].13H_2O$ in the course of our extension of the structural study of polyoxotungstoeuropates to that of the polyoxomolybdoeuropates. Very recently, a similar structure of non-luminescent dimeric $[Pr_4(MoO_4)(Mo_7O_{24})_4]_2^{28-}$ was reported (Kazansky, 1988). However, no further information on its detailed structure has been published.

Experimental. $0 \cdot 93$ g of $(NH_4)_6Mo_7O_{24}.4H_2O$ was dissolved in 9 ml of water, to which 1 ml of CH_3OH was added. An aqueous solution (1 ml) containing

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