64 parameters
$w = 1/[\sigma^2(F_o) + (0.05F_o)^2]$
$(\Delta/\sigma)_{max} = 0.013$
$\Delta\rho_{max} = 2.42$ e Å^{-3}
$\Delta\rho_{min} = 1.63$ e Å^{-3}

Atomic scattering factors
from *International Tables
for X-ray Crystallography*
(1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent
isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	Occupancy	x	y	z	U_{eq}
Zn1	1.0	0.0941 (2)	0.0941 (2)	0.2305 (3)	0.015 (1)
Zn2	1.0	0.0590 (2)	0.0590 (2)	0.7321 (3)	0.016 (1)
Zn3	1.0	0.1617 (3)	0.1617 (3)	0.9783 (4)	0.040 (2)
Zn4	1.0	0.1437 (2)	0.1437 (2)	0.4698 (3)	0.012 (1)
Zn5	1.0	0.2010 (2)	0.2010 (2)	0.5936 (3)	0.016 (1)
Zn6	1.0	0.3916 (4)	0	0	0.010 (2)
Zn7	1.0	0.0722 (4)	1/4	1/4	0.021 (2)
Zn8	1.0	0.0850 (3)	0.0850 (3)	0.0850 (3)	0.027 (2)
Zn9	1.0	0.1978 (3)	0.1978 (3)	0.1978 (3)	0.017 (1)
Zn10	1.0	0.3352 (3)	0.3352 (3)	0.3352 (3)	0.016 (1)
Zn11	1.0	0.8339 (4)	0.8339 (4)	0.8339 (4)	0.023 (2)
Zn12	1.0	3/4	3/4	3/4	0.006 (3)
Fe,Ni1	1.0	0.1586 (7)	0	0	0.039 (3)
Fe,Ni2	1.0	0.5998 (3)	0.5998 (3)	0.5998 (3)	0.005 (1)
Fe,Ni31	0.25 (2)	0.926 (2)	0.926 (2)	0.926 (2)	0.04 (1)
Fe,Ni32	0.53 (2)	0.945 (1)	0.945 (1)	0.945 (1)	0.036 (5)
Fe,Ni4	0.68 (1)	0	0	0	0.016 (1)

Table 2. *Centre-to-vertex distances* (Å) *in the
polyhedra in Fig.* 1(c)

Rhombic dodecahedra (grey)	Zn8—3 Zn1	2.64
	—3 Zn3	2.75
	—3 Fe,Ni1	2.55
	—3 Fe,Ni3	2.89
	— Fe,Ni4	2.66
Icosahedra (green)	Zn10—3 Zn1	2.62
	—3 Zn4	2.49
	—3 Zn7	2.75
	—3 Zn9	2.62
Icosahedra (marine)	Fe,Ni2—3 Zn2	2.61
	—3 Zn4	2.61
	—3 Zn4	2.59
	—3 Zn6	2.56
Frihauf polyhedra (light blue)	Zn12—12 Zn5	3.09
	—4 Zn11	2.62

The composition was determined by means of energy dispersive X-ray analysis with a Jeol 840 scanning electron microscope. Since Fe and Ni are near neighbours in the Periodic Table, straddling Co, the mixed (Fe,Ni) positions were refined as pure Co. The final composition (1:6.5) differs from the microprobe analysis (1:9), but the deviation is within the uncertainty of the analysis and further details of the nature of the atomic species in the split position are uncertain, as is the nature of the atom at the origin that generates the split. The structure (Table 1) was refined from a starting model based on the structure of Fe$_{22}$Zn$_{78}$. All atoms except the (Fe,Ni) at the split position were refined anisotropically; the occupancy factors were refinable, but varied little from unity, with the exception of the occupancy at the origin and the split position. The nature of the atoms at the different positions was determined from the occupancy refinement and this determination was in agreement with the interatomic distances. The minimum Zn—Zn distance is 2.49 Å (2.64 Å in the element), minimum Zn—(Fe,Ni) 2.43 Å and min-

imum (Fe,Ni)—(Fe,Ni) 2.32 Å [Fe—Fe is 2.48 Å in the element and Ni—Ni is 2.40 Å (Donohue, 1974)]. All computer programs used are as described by Lundgren (1982).

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Neutron and X-ray Diffraction Study of Magnesium Phosphite Hexahydrate, [Mg(H$_2$O)$_6$]$^{2+}$ [PHO$_3$]$^{2-}$

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Abstract

The original structure determination [Corbridge (1956). *Acta Cryst.* **9**, 991–994] indicated an ordered structure of [PHO$_3$]$^{2-}$ and [Mg(H$_2$O)$_6$]$^{2+}$ ions lying on threefold symmetry axes. Current refinement of H-atom positions allows full elucidation of the hydrogen-bonding network. This network connects each [PHO$_3$]$^{2-}$ anion to seven [Mg(H$_2$O)$_6$]$^{2+}$ cations by nine hydrogen bonds. Each [Mg(H$_2$O)$_6$]$^{2+}$ com-

plex makes three additional hydrogen bonds to neighboring cations producing a three-dimensional network. The Mg atom is surrounded by six H_2O molecules at the vertices of an octahedron.

Comment

The research reported in this paper is part of a continuing effort in our laboratory to gain a better understanding of how the molecular and electronic structure of phosphates and phosphites change as a function of pH and molecular environment. One part of this effort is directed toward the accurate measurement of bond distances, including the P—H bond distance, and the measurement of the P and H chemical-shift tensors, which are very sensitive to changes in the electronic structure. The phosphite dianion has been the subject of a number of recent publications concerning the application of NMR relaxation rate experiments to the question of structure and dynamics in solution (Farrar & Locker, 1987; Farrar & Decatur, 1990). The P—H internuclear distance, 1.46 (1) Å, obtained from these experiments agrees well with the value, 1.431 (8) Å (with riding correction for thermal vibration-induced bond shortening) obtained for the P—H bond distance from the neutron diffraction study reported here. *Ab initio* calculations on the dianion have also been performed (Farrar & Trudeau, 1990); they report a P—H bond distance of 1.47 Å in excellent agreement with the solution NMR measurements. The theoretical calculations also predict that the dianion exhibits a C_{3v} symmetry axis along the P—H internuclear vector. This high symmetry is desirable since it greatly simplifies the NMR relaxation equations. The title compound, magnesium phosphite hexahydrate, is an ideal candidate for careful comparison between solid-state and solution NMR studies because its high degree of hydration creates an almost complete first sphere of hydration around the dianion. In addition, the molecule was reported by Corbridge (1956) to have a symmetrical C_3 site environment along the P—H bond. Crystallographic studies of various normal phosphite salts have been reported previously, but in all cases except the title compound the ideal threefold symmetry of the phosphite is distorted to varying degrees in the solid state (Handlovič, 1969; McDonald & Eriks, 1980; Ortiz-Avila, Squattrito, Shieh & Clearfield, 1989; Rafiq, Durang & Cot, 1982; Shieh, Martin, Squattrito & Clearfield, 1990). The P—H bond distances reported in the X-ray studies vary widely. In the most precise work where refinements of the H-atom positions were carried out, the results obtained ranged from 1.34 (2) Å [(NH$_4$)$_2$PHO$_3$.H$_2$O; Rafiq, Durand & Cot, 1982] to 1.30 (3) Å [Zn$_2$(PHO$_3$)$_2$(H$_2$O)$_4$.H$_2$O; Ortiz-Avila, Squattrito, Shieh & Clearfield, 1989].

The original structure determination of $Mg(H_2O)_6PHO_3$ by Corbridge (1956) was based upon two-dimensional X-ray photographic data. Electron-density projections indicated a crystal-ordered arrangement consistent with presumed octahedral $[Mg(H_2O)]^{2+}$ cations and $[PHO_3]^{2-}$ anions each lying on a threefold axis. Although the H atoms were not located, Corbridge proposed a continuous three-dimensional hydrogen-bond network based upon close O···O contacts. A highly precise X-ray determination of the title compound was undertaken in order to compare solid- and liquid-state NMR data and theoretical calculations with other accurate independent studies of the structure. The study was performed at a reduced temperature (108 K) to reduce the thermal motion of the H atoms and thereby increase their contribution in the diffraction model.

After completing the X-ray work, a crystal of sufficient size (approximately 1 mm^3) for neutron diffraction was obtained. Therefore, a parallel study was initiated to determine more precisely the P—H bond length in the solution-like environment of $[Mg(OH_2)_6]^{2+} [HPO_3]^{2-}$.

The basic features of the structure (Fig. 1) are consistent with the original Corbridge (1956) work. The C_3 symmetry of the structure was confirmed, as both P and Mg atoms lie on the threefold axis (see Fig. 1). We found P—O and P—H distances similar to those of other X-ray studies in the literature (Rafiq, Durand & Cot, 1982; Ortiz-Avila, Squattrito, Sieh & Clearfield, 1989). The P—O bond length of 1.525 (2) Å is in good agreement with the distance of 1.519 Å obtained from theoretical calculations (Farrar & Trudeau, 1990) for an isolated phosphite anion. Refinement of the H-atom positions has clarified and confirmed the hydrogen-bonding network that was suggested in the Corbridge work. Water molecules are coordinated about the Mg^{2+} center to form a slightly distorted octahedron. Both water protons of O(1W) and one proton from O(2W) are involved in hydrogen bonding to the O atoms of the phosphite. The other proton of O(2W) is directed toward the O(1W) atom of an adjacent magnesium hydrate group, with an O···O distance of 2.839 (3) Å indicating a moderately strong interaction. This hydrogen bond provides tetrahedral coordination about O(1W) and leaves O(2W) with trigonal-planar geometry. The Mg—O(2W) bond is 0.046 Å shorter than the Mg—O(1W) bond indicating that the (2W) water molecules are more tightly complexed to the Mg than the (1W) water molecules. Tetrahedral coordination for each O atom on the phosphite is fulfilled through hydrogen bonds from three different $[Mg(H_2O)_6]^{2+}$ cations. The H atom directly bonded to P is over 2.3 Å away from the closest O atom; it gives no indication of forming a hydrogen bond. The

P—H bond points away from a pocket made up of seven interconnected $[Mg(H_2O)_6]^{2+}$ ions that holds the phosphite dianion in a highly organized three-dimensional network of hydrogen bonds.
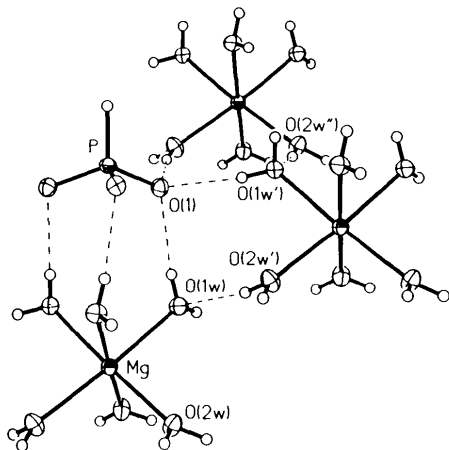

Fig. 1. Hydrogen-bonding network of $[Mg(H_2O)_6]^{2+}[PHO_3]^{2-}$. Non-H atoms are represented by 50% probability thermal ellipsoids.

A riding correction (Johnson, 1970) was made for the various bond distances in order to correct for the shortening of the bonds arising from thermal vibration. With this correction the P—H bond distance obtained is 1.431 (8) Å, in excellent agreement with the value obtained from our solid-state (Smith, 1991) and solution (Farrar & Locker, 1987) NMR experiments. Similarly, the neutron diffraction value of the P—H bond distance, 1.396 (4) Å, obtained in LiHPHO₃ (Johansson & Lindqvist, 1976) is in excellent agreement with our solid-state results (Smith, 1991) and ab initio calculations for $HPHO_3^-$ salts (Farrar & Trudeau, 1990). Thus, X-ray and neutron diffraction results confirm the infrared, NMR and ab initio results which show clearly that the P—H bond distance shortens by about 0.05 Å for each proton added to a phosphite O atom.

Experimental

The compound was prepared by reacting 0.24 g of Mg metal with 17 ml 0.6 M phosphorous acid (Aldrich). After the reaction subsided, the mixture was diluted to 250 ml, filtered and the filtrate diluted to 1000 ml. Small well formed trigonal crystallites suitable for X-ray diffraction were produced after four weeks.

X-ray diffraction, 108 K

Crystal data

$[Mg(H_2O)_6][PHO_3]$
$M_r = 212.38$
Rhombohedral
$R3$
$a = 8.8281$ (11) Å
$c = 9.104$ (2) Å
$V = 614.47$ (16) Å³
$Z = 3$
$D_x = 1.722$ Mg m⁻³

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 12 reflections
$\theta = 32$–$39°$
$\mu = 4.039$ mm⁻¹
$T = 108$ K
Trigonal prism
$0.30 \times 0.30 \times 0.15$ mm
Colorless

Data collection

Siemens four-circle diffractometer
ω scans (width 0.5°)
Absorption correction: empirical
$T_{min} = 0.793$, $T_{max} = 0.941$
562 measured reflections
352 independent reflections
352 observed reflections
[$F \geq 4.0\sigma(F)$]

$R_{int} = 0.033$
$\theta_{max} = 55°$
$h = -9 \rightarrow 8$
$k = 0 \rightarrow 9$
$l = -9 \rightarrow 9$
3 standard reflections monitored every 50 reflections intensity variation: 2%

Refinement

Refinement on F
$R = 0.0209$
$wR = 0.0255$
$S = 1.23$
352 reflections
48 parameters
H-atom U's refined isotropically
$w = 1/[\sigma^2(F) + 0.0003F^2]$,
$\sigma(F)$ from counting statistics
$(\Delta/\sigma)_{max} = 0.002$

$\Delta\rho_{max} = 0.23$ e Å⁻³
$\Delta\rho_{min} = -0.43$ e Å⁻³
Extinction correction:
$F^* = F[1 + (0.002\chi \times F^2/\sin2\theta)]^{-1/4}$
(Larson, 1970)
Extinction coefficient:
$\chi = 0.0173$ (15)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Neutron diffraction, 293 K

Crystal data

$[Mg(H_2O)_6][PHO_3]$
$M_r = 212.38$
Rhombohedral
$R3$
$a = 8.868$ (2) Å
$c = 9.150$ (2) Å
$V = 623.2$ (4) Å³
$Z = 3$
$D_N = 1.698$ Mg m⁻³

Neutron (Cu[220]) radiation
$\lambda = 1.063$ (1) Å
Cell parameters from 29 reflections
$\theta = 17$–$30°$
$\mu = 2.77$ mm⁻¹
$T = 293$ K
Multi-faceted prism
1.0 mm (radius)
Colorless

Data collection

Four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction: spherical
$T_{min} = 0.804$, $T_{max} = 0.807$
3851 measured reflections
(1321 additional reflections tested for intensity but not scanned)
396 independent reflections

361 observed reflections
[$F \geq 2.0\sigma(F)$]
$R_{int} = 0.065$
$\theta_{max} = 47.5°$
$h = -10 \rightarrow 10$
$k = -10 \rightarrow 10$
$l = -12 \rightarrow 12$
3 standard reflections monitored every 100 reflections intensity variation: ±7%

Refinement

Refinement on F

$R = 0.041$

$wR = 0.023$

$S = 2.77$

361 reflections

78 parameters

H-atom parameters refined

$w = 4F^2/[\sigma^2(I) + P^2I^2]$

$(\Delta/\sigma)_{max} < 0.05$

$\Delta\rho_{max} = 0.04$ e Å^{-3} of the absolute value of the smallest H-atom peak

Extinction correction: Coppens & Hamilton (1970)

Atomic scattering factors from Koester & Yelon (1982)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *from X-ray and neutron diffraction data*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
X-ray, 108 K				
Mg	0	0	−0.0195 (2)	0.0131 (4)
P	0	0	1/2	0.0139 (3)
H	0	0	0.357 (6)	0.030 (4)
O	0.1845 (2)	0.1320 (2)	0.5508 (2)	0.0168 (7)
O(1W)	0.1916 (2)	0.1893 (2)	−0.1580 (2)	0.0169 (8)
O(2W)	0.0009 (3)	0.1951 (3)	0.1046 (2)	0.0203 (8)
H(1WA)	0.288 (5)	0.232 (4)	−0.138 (4)	0.030 (4)
H(1WB)	0.187 (4)	0.166 (5)	−0.236 (4)	0.030 (4)
H(2WA)	−0.088 (5)	0.184 (4)	0.136 (3)	0.030 (4)
H(2WB)	0.076 (5)	0.285 (6)	0.141 (4)	0.030 (4)
Neutron, 293 K				
Mg	0	0	−0.0205 (6)	0.021 (1)
P	0	0	1/2	0.022 (1)
H	0	0	0.3471 (9)	0.060 (1)
O	0.1837 (3)	0.1315 (3)	0.5507 (5)	0.027 (1)
O(1W)	0.1929 (3)	0.1883 (3)	−0.1592 (5)	0.026 (1)
O(2W)	0.0022 (4)	0.1962 (3)	0.1044 (5)	0.032 (1)
H(1WA)	0.3173 (6)	0.2507 (6)	−0.1355 (7)	0.038 (1)
H(1WB)	0.1888 (5)	0.1595 (5)	−0.2629 (6)	0.036 (1)
H(2WA)	−0.1012 (6)	0.1887 (5)	0.1409 (6)	0.045 (1)
H(2WB)	0.1001 (6)	0.2998 (6)	0.1458 (6)	0.041 (1)

Table 2. *Geometric parameters* $(\text{Å}, \degree)$ *from X-ray and neutron diffraction data*

X-ray, 108 K			
P—H	1.30 (5)	O(1W)—H(1WA)	0.76 (4)
P—O	1.525 (2)	O(1W)—H(1WB)	0.74 (4)
Mg—O(1W)	2.102 (2)	O(2W)—H(2WA)	0.77 (5)
Mg—O(2W)	2.056 (3)	O(2W)—H(2WB)	0.81 (3)
O—P—O	111.2 (1)	Mg—O(1W)—H(1WA)	121 (3)
O—P—H	107.6 (1)	Mg—O(1W)—H(1WB)	117 (2)
O(1W)—Mg—O(2W)	89.9 (1)	Mg—O(2W)—H(2WA)	120 (2)
O(1W)—Mg—O(1WA)	87.7 (1)	Mg—O(2W)—H(2WB)	134 (4)
O(1W)—Mg—O(2WA)	176.4 (1)	H(1WA)—O(1W)—H(1WB)	105 (4)
O(2W)—Mg—O(1WA)	89.5 (1)	H(2WA)—O(2W)—H(2WB)	105 (4)
O(2W)—Mg—O(2WA)	92.7 (1)		
Neutron, 293 K			
P—H	1.399 (8)	O(1W)—H(1WA)	0.979 (6)
P—O	1.526 (2)	O(1W)—H(1WB)	0.979 (5)
Mg—O(1W)	2.114 (3)	O(2W)—H(2WA)	0.947 (6)
Mg—O(2W)	2.073 (3)	O(2W)—H(2WB)	0.971 (6)
O—P—O	111.2 (1)	Mg—O(1W)—H(1WA)	123.5 (3)
O—P—H	107.7 (2)	Mg—O(1W)—H(1WB)	117.8 (3)
O(1W)—Mg—O(2W)	90.2 (1)	Mg—O(2W)—H(2WA)	122.2 (3)
O(1W)—Mg—O(1WA)	87.7 (1)	Mg—O(2W)—H(2WB)	129.6 (3)
O(1W)—Mg—O(2WA)	176.5 (2)	H(1WA)—O(1W)—H(1WB)	104.3 (4)
O(2W)—Mg—O(1WA)	89.4 (1)	H(2WA)—O(2W)—H(2WB)	107.8 (4)
O(2W)—Mg—O(2WA)	92.6 (2)		

X-ray study: The structure was solved by Patterson methods. H-atom positions were determined from a difference map. All non-H atoms were refined anistropically and the H atoms isotropically. Refinement was by full-matrix least squares. Absolute structure was confirmed by the refinement of a multiplier to the complex anomalous scattering factors to 1.26 (7) (Rogers, 1981). All computations were performed with Siemens *SHELXTL-Plus* software (Sheldrick, 1991).

Neutron study: A crystal of total mass 1.69 mg was mounted on the 2XE diffractometer at the University of Missouri Research Reactor (MURR). Monochromatic neutrons were obtained by reflection from a Cu monochromator in [220] orientation [$\lambda = 1.063$ (1) Å]. Almost all of the fluctuation observed in the standard reflections resulted from the relatively low intensities obtained from the small sample [$\sigma(I)$ for the standards was 2% of I]. No systematic effects were observed. A total of 5172 reflection positions were tested for intensity. Of these, 1321 were judged too weak for peak scans and the resulting 3851 scans were symmetry averaged to 396 independent reflections ($R_{int} = 0.065$). Each reflection was measured two or more times; the internal agreement was the same for multiple measurements as it was for symmetry averaging, confirming that the relatively high value resulted from the weak data rather than from a change of symmetry. The model for least-squares refinement started with the X-ray model and included anisotropic displacement parameters for H atoms and anisotropic type I extinction (Coppens & Hamilton, 1970). The extinction model was tested on the full data set, but the corrections proved to be small and consistent with the space-group symmetry. The final extinction model was refined on the symmetry-averaged data and indicated that only about 6% of the reflections were affected by as much as 5%. The largest correction (20% for the 223 reflection) was twice the next-largest value; correction for extinction produced only minor adjustments in the displacement parameters of the model.

The standard weighting scheme, $w = 4F^2/[\sigma^2(I) + P^2I^2]$, was applied with varying choices of P. The best model fit was obtained with $P = 0$, indicating the preference for the stronger data over the weaker observations. The weights only varied by about a factor of 10 from the lowest to the highest values and a plot of $w(\Delta F^2)$ *versus* F indicated that the weaker data still made larger contributions to the overall error.

Computer programs used for reducing and refining the neutron data were local modifications of the Oak Ridge National Laboratory programs *DATALIB, DATASORT, ORFLS3* (Busing, Martin & Levy, 1962) and *ORFFE3* (Busing, Martin & Levy, 1964) adapted for MicroVAX and NeXT computers.

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sides of the Zr atom; the coordination polyhedron may be described as a distorted quadratic antiprism. The distances between the Si atoms [2.614 (1) Å] are longer than that of a Si—Si single bond (2.35 Å), but comparable with the Si—Si separations in transition-metal disilicides. The Te—Te separations within the Te$_4$ plane give no indication of significant interactions. The distances between Zr and Te atoms of neighbouring layers [3.957 (1) Å] are too long for Zr—Te bonds. Hence, contrary to the isotypic compounds ZrSiX (X = S, Se) and ZrGeX (X = S, Se, Te), ZrSiTe is best described as a layer compound.

Comment

During a systematic study of the Zr–S, Zr–Se and Zr–Te systems, binary compounds with the composition Zr$_4$X$_3$ were obtained (Hahn, Harder, Mutschke & Ness, 1957; Hahn & Ness, 1959). These compounds were later identified as silicide chalcogenides of Zr with the composition ZrSiX (X = S, Se, Te) (Jellinek & Hahn, 1962). The first crystal structure determination of tetragonal ZrSiTe used X-ray powder data (Klein-Haneveld & Jellinek, 1964). It was demonstrated that compounds with the formal compositions ZrGeX, HfSiX and HfGeX (X = O, S, Se, Te) are isotypic with ZrSiX and crystallize in the PbFCl-type structure (Onken, Vierheilig & Hahn, 1964). The single-crystal data presented here are in good agreement with the results of Jellinek & Hahn (1962). The Zr—Te interatomic separation is of the order observed in zirconium tellurides

Structure of the Layer Compound ZrSiTe

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Abstract

Zirconium silicon telluride, ZrSiTe, crystallizes in a layer-type structure which is related to the PbFCl type. The Zr atom is coordinated by four Si and four Te atoms. The Si and Te atoms are arranged in square planes. These planes are situated at opposite
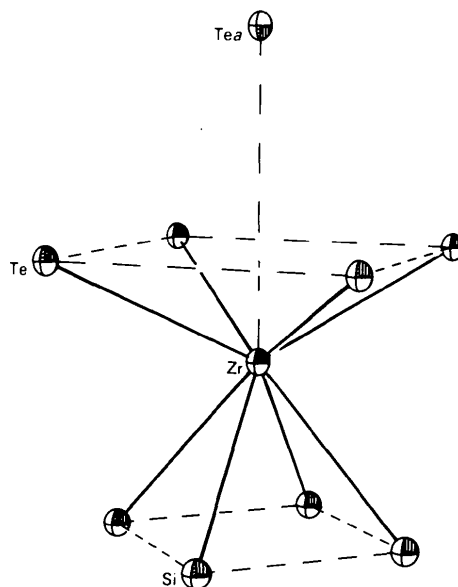
Fig. 1. The coordination polyhedron about the Zr atom. The atom Tea is in the neighbouring layer. Probability ellipsoids are drawn at the 70% level.