temperature factors. It remains to be seen whether or not a sample with composition $R_6T_6M_5$ forms an identical structure but without T–T waist contacts.

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Structural Studies of Thortveitite-Like Dimanganese Diphosphate, $Mn_2P_2O_7$

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Abstract. $M_r = 283{\cdot}82$, monoclinic, $C2/m$, $a = 6{\cdot}633$ (1), $b = 8{\cdot}584$ (1), $c = 4{\cdot}546$ (1) Å, $\beta = 102{\cdot}67$ (1)°, $V = 252{\cdot}6$ (1) Å^3, $Z = 2$, $D_x = 3{\cdot}732$ (1) Mg m^{-3}, $F(000) = 272$, $T = 295$ K. X-ray powder diffraction data (Cr $K\alpha_1$, $\lambda = 2{\cdot}28975$ Å, $R = 0{\cdot}083$ for 35 reflections), X-ray single-crystal data (Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 5{\cdot}86$ mm^{-1}, $R = 0{\cdot}040$ for 672 reflections), and neutron powder diffraction ($\lambda = 1{\cdot}8820$ Å, $R_I = 0{\cdot}051$ for 50 reflections). Isomorphism with thortveitite, $Sc_2Si_2O_7$, is confirmed, but the refinements, using both a linear and a split-atom model, indicate a disordered bridging oxygen in the diphosphate anion with a non-linear P—O—P bond of 165·9 (1)°. The metal–oxygen distances conform with those of similar compounds. The JCPDS Diffraction File No. is 35-1497 for $Mn_2P_2O_7$.

Introduction. Among the condensed diphosphates there are often groups of isomorphous compounds, *e.g.* many divalent-metal $M_2P_2O_7$ diphosphates crystallize with the thortveitite-type structure. The crystal structure of thortveitite, $(Sc,Y)_2Si_2O_7$, was originally determined by Zachariasen (1930). The space-group symmetry was reported as $C2/m$, which implies a linear Si—O—Si bond in the disilicate anion. The metal ions are octahedrally coordinated. Since then many studies of thortveitite-type $M_2X_2O_7$ compounds (X = Si, P, V or As) have been published, which have in common the peculiarities that the bridging oxygen has a very large thermal motion, and the XO_4 tetrahedra are more regular than they should be, considering that they share corners with each other (*cf.* Cruickshank, 1961). The possibilities of a lower space-group symmetry or structural disorder have been considered by many authors, although with no definite results (*e.g.* Cruickshank, Lynton & Barclay, 1962; Dorm & Marinder, 1967; Robertson & Calvo, 1968).

We now report on some crystallographic studies of $Mn_2P_2O_7$. This compound is the only diphosphate known to possess the thortveitite structure at room temperature. Crystallographic investigations of this phase have been undertaken earlier, although with less accurate data, giving R factors of 0·18 (Lukaszewicz & Smajkiewicz, 1961) and 0·12 (Tondon & Calvo, 1981).

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Experimental. About 10 g of $Mn_2P_2O_7$ was synthetized by heating $NH_4MnPO_4.6H_2O$, precipitated from cold water solutions of manganous chloride and diammonium hydrogen phosphate. Single crystals were prepared at 1350 K in an evacuated platinum tube.

X-ray powder diffraction data: Guinier–Hägg type focusing camera, KCl internal standard, $\theta_{max} \simeq 44°$. Monoclinic unit-cell dimensions refined from 28 single-indexed reflections with conventional least-squares procedure. Transmission intensities measured with step lengths of 0·0127° in θ with a computer-controlled film scanner and associated programs (Johansson, Palm & Werner, 1980). These data used for preliminary refinement utilizing Rietveld (1969) technique, modified for X-ray data (Malmros & Thomas, 1977; Werner, Salomé, Malmros & Thomas, 1979). Space group $C2/m$ assumed. Some crucial data are given in Table 1, while the powder diffraction data and the atomic parameters have been deposited.*

X-ray single-crystal data: prismatic crystal 0·13 × 0·14 × 0·05 mm, PW1100 automatic four-circle diffractometer, graphite monochromator; θ–2θ scan, $\theta_{max} \simeq 40°$, $(\sin\theta/\lambda)_{max} \simeq 0{\cdot}90$ Å^{-1}, $|h| \leq 10$, $0 \leq k \leq 15$, $0 \leq l \leq 7$; 750 measured reflections, 672 unique observed with $\sigma(I)/I < 2$. Three strong reflections ($20\bar{1}$, 021, 060) measured every fifth hour, their intensity variations lay within ±1% during complete run. Correction for Lorentz, polarization and absorption effects (transmission factors 0·489–0·758). Systematic extinctions $h + k = 2n + 1$, suggesting $C2/m$, $C2$ or Cm. Statistical tests based on $|E|$ values (Main, Woolfson, Lessinger, Germain & Declercq, 1974) indicated non-centrosymmetric distribution of atoms, while the converse was observed from $N(z)$ test of Howells, Phillips & Rogers (1950). No positive signal obtained with Giebe–Scheibe piezoelectric tester. ^{57}Fe Mössbauer spectroscopy at 295 K of doped solid solution $(Mn_{0.95}Fe_{0.05})_2P_2O_7$, from powder diffraction data judged to be isostructural with $Mn_2P_2O_7$, revealed only one doublet, with an isomer shift of 1·26 mm s^{-1} and a quadrupole splitting of 1·91 mm s^{-1} relative to metallic iron. Accordingly, this experiment indicated that there is only one crystallographically unique MnO_n polyhedron in the crystal structure. $Mn_2P_2O_7$ was also analysed in a Siemens ELMISKOP 102 transmission electron microscope operated at 125 kV, but no evidence of a superstructure could be detected. Moreover, neither X-ray nor neutron diffraction data indicated a superstructure. Structural refinements, usually with unit weights, carried out in $C2/m$, $C2$ and Cm with *SHELX*76 (Sheldrick, 1976), minimizing $|F|^2$. Atomic scattering factors included real and imaginary anomalous-dispersion terms, taken from *International Tables for X-ray Crystallography* (1974). Refinements terminated when shifts <5% of e.s.d. To facilitate comparison among results, isotropic temperature factors were used throughout, except in final refinements (see below). Refinements in $C2/m$ with linear P—O—P bond ('linear model') clearly indicated strong thermal motion of bridging oxygen atom O(1), in agreement with earlier studies of $Mn_2P_2O_7$, thortveitite and thortveitite-like compounds (see *Introduction*). The atomic parameters have been deposited;* some data are given in Table 1 ($R = 0{\cdot}060$). Refinement in $C2$ yielded lower value for B[O(1)], but still somewhat larger than for other atoms ($R = 0{\cdot}054$). Trial refinement in Cm ($R = 0{\cdot}056$) arrived at unreasonably high e.s.d.'s and high correlations among many of the refined parameters, thus rendering this space group very unlikely. (Some data are given in Table 1.) At this stage, the possibility of a disordered bridging oxygen was considered. Refinements in $C2/m$ with O(1) split along the y axis to give a non-linear P—O(1)—P bond (the 'split-atom model') were significant improvements on earlier results in terms of e.s.d.'s and temperature factors ($R = 0{\cdot}056$, *cf.* Table 1). There was no high correlation between y[O(1)] and any other parameter. Moreover, B[O(1)] was now only slightly larger than the other temperature factors. A further trial refinement with an occupancy factor of 0·80 for O(1) was found to give almost identical temperature factors for the three distinct oxygen atoms, but it was not possible to locate the missing fifth of the bridging oxygen in the subsequent difference Fourier maps (max. and min. heights in final difference map 0·5, −0·6 e Å^{-3}). It is possible that the 1/5 bridging oxygen atom is still more strongly disordered than indicated by our simple 'split-atom model'. A further split of O(1) in the yz plane was tested, yielding anomalously large e.s.d.'s [$R = 0{\cdot}055$; O(1) parameters: $x = 0$, $y = 0{\cdot}0226$ (8), $z = 0{\cdot}0258$ (32), $B = 0{\cdot}10$ (18) Å^2]. Anisotropic refinements in $C2/m$ with linear and split-atom models were also carried out ($R = 0{\cdot}040$ and $R_w = 0{\cdot}042$ in both refinements). In these cases the weighting used was $w = 0{\cdot}0603/[\sigma(F)^2 + 0{\cdot}0052|F|]$. The thermal parameters of O(1) in the split-atom model are still rather high, although much lower than in the linear model [see Table 2 and Fig. 1, an *ORTEP* (Johnson, 1965) illustration of the diphosphate anion]. In particular a pronounced decrease in U_{22} with the split-atom model should be noted.

Neutron powder diffraction data: JEEP-2 nuclear reactor (Kjeller, Norway), germanium monochromator crystal, five ^{3}He detectors, $3 \leq \theta \leq 40°$, $\Delta\theta = 0{\cdot}025°$, 4 d. Neutron diffraction is advantageous for evaluating

* Primary neutron diffraction data, observed and calculated structure factors and integrated intensities and the atomic parameters from all isotropic refinements have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39691 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* See deposition footnote.

anomalies in the bridging oxygen, since it here represents 13% of the total neutron scattering power. Refinements were carried out as summarized in Table 1, again indicating that the split-atom $C2/m$ model is the more realistic one. The observed and calculated intensity profiles from this refinement are shown in Fig. 2. The structure factor and intensity tables from the final X-ray and neutron data refinements have been deposited.*

* See deposition footnote.

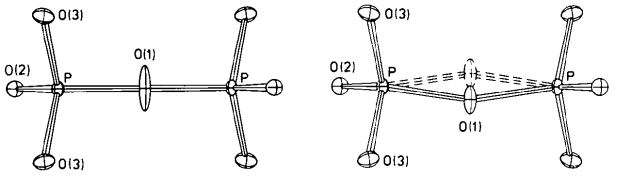

Fig. 1. *ORTEP* plots of the two anisotropic models of the diphosphate anion in $Mn_2P_2O_7$, both in space group $C2/m$: the 'linear' model (left) and the 'split-atom' model (right).

Discussion. Interatomic distances and angles for the two anisotropic $C2/m$ split-atom model refinements are given in Table 3. These values can be compared with the reduced data given in Table 1, showing that the

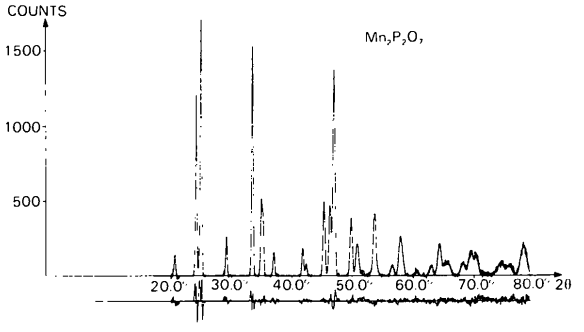

Fig. 2. The least-squares fit obtained in the Rietveld neutron-data refinement of $Mn_2P_2O_7$ ($R_I = 0{\cdot}051$) between observed intensities (continuous curve) and calculated intensities (points). The discrepancy in the fit, $I_{obs} - I_{calc}$, is plotted below on the same scale.

Table 1. *Some crucial data from the isotropic structural refinements of* $Mn_2P_2O_7$

XSC = X-ray single-crystal data, XPD and NPD stand for Rietveld refinements based on X-ray and neutron powder diffraction data, respectively. The R factor cited is R_F for X-ray and R_I for neutron diffraction data. E.s.d.'s are 0·1 Å or better, and 0·5° or better.

Model (P–O–P)	Linear	Linear	Split-atom	Bent	Bent	Linear	Split-atom	Bent
Space group	$C2/m$	$C2/m$	$C2/m$	$C2$	Cm	$C2/m$	$C2/m$	$C2$
Data	XPD	XSC	XSC	XSC	XSC	NPD	NPD	NPD
R factor	0·083	0·060	0·056	0·054	0·056	0·055	0·051	0·047
y[O(1)]	0	0	0·0226 (9)	0·0226 (11)	0	0	0·029 (2)	0·027 (5)
B[O(1)] (Å^2)	2·8 (5)	2·34 (14)	1·21 (10)	1·49 (13)	2·58 (16)	0·86 (3)	−0·3 (3)	−0·1 (3)
Mn–O range (Å)	2·15–2·31	2·13–2·32	2·13–2·32	2·11–2·27 2·11–2·39	2·10–2·39	2·14–2·32	2·14–2·32	2·17–2·28 2·08–2·36
Mn–O mean (Å)	2·22 (2)	2·203 (2)	2·204 (2)	2·187 (4) 2·234 (5)	2·20 (1)	2·20 (1)	2·20 (1)	2·21 (3) 2·19 (3)
P–O range (Å)	1·50–1·55	1·52–1·57	1·51–1·58	1·52–1·58	1·50–1·59 1·50–1·55	1·52–1·57	1·52–1·60	1·43–1·61
P–O mean (Å)	1·52 (2)	1·532 (2)	1·535 (2)	1·535 (4)	1·544 (9) 1·525 (9)	1·53 (1)	1·54 (1)	1·54 (3)
O–P–O range (°)	108–111	104–113	101–113	98–116	104–115	104–113	99–115	103–114
O–P–O mean (°)	109·5	109·4	109·4	109·3	109·2	109·4	109·3	109·3
P–O–P (°)	180	180	165·9	164·5	179·0	180	161·9	165·4

Table 2. *Final atomic coordinates* ($\times 10^4$) *and thermal parameters* (Å$^2 \times 10^4$) *from the anisotropic refinements of* $Mn_2P_2O_7$ ($C2/m$)

Values for the 'split-atom' model are given first; corresponding values for the linear model are given in italics. The temperature factor has the form $T = \exp[-2\pi^2(U_{11}h_2a^{*2} + \cdots + 2U_{12}hk\,a^*b^* + \cdots)]$. E.s.d.'s are given within parentheses.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn	0	3087 (1)	5000	86 (2)	67 (2)	89 (2)	—	−3 (1)	—
	0	*3088 (1)*	*5000*	*83 (2)*	*63 (2)*	*89 (2)*	—	*−2 (2)*	—
P	2151 (1)	0	−904 (2)	43 (3)	86 (3)	49 (3)	—	6 (2)	—
	2150 (1)	*0*	*−904 (3)*	*44 (3)*	*81 (3)*	*50 (3)*	—	*6 (3)*	—
O(1)	0	226†	0	70 (12)	266 (40)	247 (20)	—	71 (14)	—
	0	*0*	*0*	*60 (18)*	*699 (53)*	*261 (29)*	—	*75 (18)*	—
O(2)	3713 (3)	0	2090 (4)	81 (7)	100 (8)	47 (7)	—	−6 (6)	—
	3715 (4)	*0*	*2084 (6)*	*80 (9)*	*86 (9)*	*52 (9)*	—	*−11 (8)*	—
O(3)	2247 (2)	1472 (2)	7266 (3)	147 (6)	80 (5)	100 (6)	32 (5)	10 (5)	25 (5)
	2249 (3)	*1469 (2)*	*7266 (4)*	*148 (8)*	*77 (7)*	*98 (7)*	*32 (7)*	*12 (6)*	*22 (6)*

† Parameter fixed from the isotropic refinement (Table 1).

Table 3. *Interatomic distances* (Å) *and angles* (°) *in* $Mn_2P_2O_7$

The data refer to the anisotropic refinements in space group $C2/m$ (*cf.* Table 2). Values for the 'split-atom' model are given first; values for the linear model are given in italics. The e.s.d.'s are $< \pm 0{\cdot}003$ Å and $\pm 0{\cdot}1°$.

P—O(1)		1·582	*1·568*	O(1)—P—O(2)	104·1	*104·4*
P—O(2)		1·519	*1·518*	O(1)—P—O(3^{i})	100·9	*107·1*
P—O(3^{i})	(×2)	1·522	*1·520*	O(1^{ii})—P—O(3^{i})	113·1	*107·1*
Average		1·536	*1·531*	O(2)—P—O(3^{i}) (×2)	112·8	*112·7*
				O(3^{i})—P—O(3^{iii})	112·2	*112·1*
				Average	109·3	*109·4*
O(1)—O(2)		2·446	*2·439*	P—O(1)—P	165·9	*180*
O(1)—O(3^{i})		2·393	*2·486*			
O(1)—O(3^{iii})		2·590	*2·486*			
O(2)—O(3^{i})	(×2)	2·533	*2·529*			
O(3^{i})—O(3^{iii})		2·527	*2·522*			
Average		2·504	*2·498*			
Mn—O(2^{iv})	(×2)	2·163	*2·164*	O(2^{iv})—Mn—O(2^{v})	81·2	*81·3*
Mn—O(3)	(×2)	2·129	*2·132*	O(2^{v})—Mn—O(3^{vi}) (×2)	81·3	*81·1*
Mn—O(3^{iv})	(×2)	2·317	*2·316*	O(2^{iv})—Mn—O(3^{iv}) (×2)	84·5	*84·6*
Average		2·203	*2·204*	O(2^{v})—Mn—O(3^{vii}) (×2)	93·3	*93·4*
				O(2^{v})—Mn—O(3) (×2)	158·6	*158·5*
				O(3)—Mn—O(3^{iv}) (×2)	77·6	*77·6*
				O(3)—Mn—O(3^{vii})	98·7	*98·6*
				O(3)—Mn—O(3^{v}) (×2)	115·3	*115·4*
				O(3^{iv})—Mn—O(3^{v})	161·2	*161·1*

Symmetry code: (i) $x,y,z-1$; (ii) $x,-y,z$; (iii) $x,-y,z-1$; (iv) $\frac{1}{2}-x,\frac{1}{2}-y,1-z$; (v) $x-\frac{1}{2},\frac{1}{2}-y,z$; (vi) $x,\frac{1}{2}-y,1-z$; (vii) $-x,y,1-z$

metal–oxygen distances are reasonable for all refinements. The average Mn—O distances are around 2·20 Å, while Lukaszewicz & Smajkiewicz (1961) reported an average of 2·12 (3) Å, and Tondon & Calvo (1981) 2·195 (7) Å. Two other average Mn—O values for six-coordinated Mn^{2+} in phosphate structures may be cited for comparison: 2·22 (2) Å in β'-$Mn_3(PO_4)_2$ (Stephens & Calvo, 1969) and 2·195 (5) Å in $Mn_2P_2O_7.2H_2O$ (Schneider & Collin, 1973).

The dimensions of the phosphate tetrahedra, on the other hand, might give a clue towards the space-group symmetry and the configuration of the diphosphate ion in $Mn_2P_2O_7$. The average P—O distances presented in Table 1 agree well with the P—O grand mean, 1·537 (1) Å, observed in divalent-metal phosphate structures (Nord & Kierkegaard, 1980). In all refinements the bridging P—O distance is longer than the terminal distances, in agreement with theory (Cruickshank, 1961). In $M_2P_2O_7$ diphosphates with non-linear P—O—P links, though, the bridging P—O distances are around 1·60 Å, with O—P—O angles in the range 102–117° (*cf.* Nord & Kierkegaard, 1980). The $Mn_2P_2O_7$ model with a linear P—O—P link gives too regular PO_4 tetrahedra, in disagreement with theories on corner-sharing XO_4 tetrahedra (Cruickshank, 1961). A displacement of the bridging oxygen away from the P—P line by means of split atoms implies a longer P—O bridging distance and a slightly 'better' P—O average distance (Table 1). It is interesting that the P—O—P angle obtained with the $(0,y,0)$ split-atom model in $C2/m$, 165·9 (4)°, agrees within a few e.s.d.'s with the value, 164·5 (5)°, obtained assuming the non-centrosymmetric space group $C2$. We attribute this coincidence to the presence of a real non-linear P—O—P link.

The split-atom hypothesis gives a more realistic model (in $C2/m$) than the linear model, or models in $C2$ or Cm, as judged from lower e.s.d.'s and correlation factors among the refined parameters. It also yields a more realistic temperature factor for O(1), and $P_2O_7^{4-}$ dimensions which agree better with theory and with observations on most other diphosphate structures. Moreover, the values for y[O(1)] are fairly similar for X-ray and neutron data, and agree well with corresponding values observed in refinements of two other thortveitite-type structures assuming the split-atom model: 0·0256 (23) in β-$Cu_2P_2O_7$ (Robertson & Calvo, 1968), and 0·026 (2) in $Mn_2V_2O_7$ (Nord, 1984). We therefore conclude that the thortveitite-type $Mn_2P_2O_7$ structure should preferably be described in the centrosymmetric space group $C2/m$ with a disordered bridging oxygen. The disorder is very closely related to a split of the atom along the y axis, but this is likely to be a slightly oversimplified model.

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Structure of the Adduct of Orthotelluric Acid and Potassium Iodate, $Te(OH)_6.KIO_3$

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Abstract. $M_r = 443{\cdot}65$, $Pn2_1a$, $a = 8{\cdot}702$ (2), $b = 6{\cdot}719$ (1), $c = 14{\cdot}279$ (3) Å, $V = 834{\cdot}9$ (3) Å^3, $Z = 4$, $D_m = 3{\cdot}50$ (1), $D_x = 3{\cdot}528$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 7{\cdot}94$ mm^{-1}, $F(000) = 808$, $T = 296$ K, $R = 0{\cdot}031$, 1315 unique reflections. The orthotelluric acid molecules and the iodate anions are connected by hydrogen bonds, so that they form a three-dimensional network. The orthotelluric acid is in a slightly distorted octahedral arrangement and the iodate ion is a trigonal pyramid. The K atom is surrounded by six O atoms.

Introduction. The title compound was studied as part of an investigation of the adducts of orthotelluric acid with various organic or inorganic compounds, see, for example, Loub, Haase & Mergehenn (1979), Boudjada, Boudjada & Guitel (1983).

Experimental. Crystals prepared by mixing 0·02 *M* aqueous solutions of orthotelluric acid and iodic acid in 1:1 molar ratio, adding potassium hydroxide solution to pH 5·3 and crystallization at 296 K (Weinland & Prause, 1901). D_m by the pycnometric method at 296 K in xylene; colourless prismatic crystals stable in air and to X-rays, spherical crystal, max. dimensions 5 mm, $2R = 0{\cdot}36$ mm; Hilger & Watts four-circle diffractometer controlled by computer M 7000; ω–2θ scan; lattice parameters refined using 19 reflections with $\theta = 5{\cdot}3$ to $28{\cdot}7°$; absorption correction applied ($5{\cdot}94 < A^* < 7{\cdot}04$); max. $\sin\theta/\lambda = 0{\cdot}703$ Å^{-1}, $h_{max} = 12$, $k_{max} = 9$, $l_{max} = 19$; 2 standard reflections after every 30 measured reflections with no significant variation; 1315 measured unique reflections, 49 unobserved with $I < 1{\cdot}96\ \sigma(I)$; heavy-atom method, F magnitudes in full-matrix least-squares refinement; all positional and anisotropic thermal parameters of non-H atoms refined; $wR = 0{\cdot}053$, $w = 1/\sigma^2(F_o)$; max. $\Delta/\sigma = 0{\cdot}20$, max. and min. heights in final difference map 1·45 and $-1{\cdot}83$ e Å^{-3} at 0·81 and 0·13 Å from I atom, corrected for secondary extinction, $I_o^{cor} = I_o(1 + 2{\cdot}06 \times 10^{-5} I_c)$; atomic scattering factors and corrections for anomalous dispersion of Te, I and K from *International Tables for X-ray Crystallography* (1974); programs *TLS* (Sklenář, 1973) and *ORTEP* (Johnson, 1965).‡

Discussion. The final atomic parameters are given in Table 1. The intramolecular and selected intermolecular bond distances and angles are given in Table 2. The molecule is depicted in Fig. 1. The projection of the structure along **a** is depicted in Fig. 2. The systematic absences point either to centrosymmetric space group *Pnma* or to noncentrosymmetric space group $Pn2_1a$. Refinement in the centrosymmetric group led to the R value of 0·16, non-positive-definite temperature factors of almost all atoms and unreliable bond angles in tellurate octahedra and iodate tetrahedra. Hence, the

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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 39695 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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