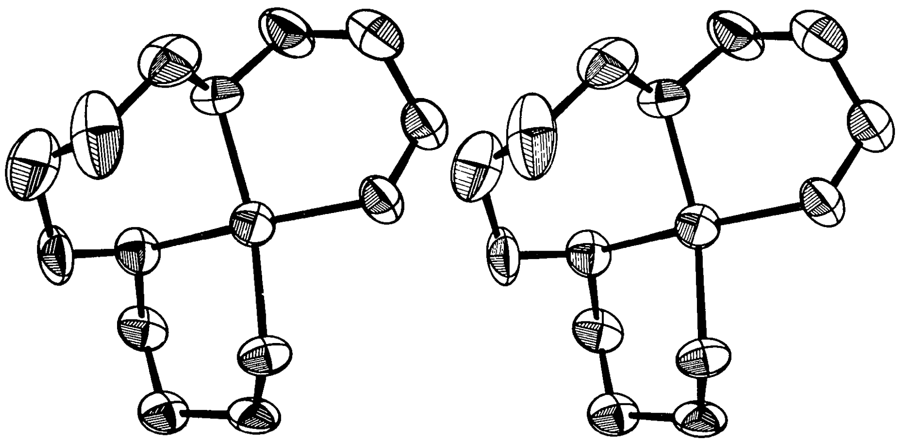

Fig. 3. Stereoscopic *ORTEP* drawing of spermine copper(II) perchlorate.

is markedly different from the average of $65 \pm 5°$ at the other six carbon–carbon single bonds. These distortions may result from the geometrical requirements of accommodating the seven-membered ring into the chelating system.

The bond lengths in the perchlorate ion of Cl(1) are 1·405 (7), 1·422 (7), 1·423 (8), and 1·436 (8), average $1·422 \pm 0·011$ Å. Those in the second perchlorate ion are 1·32, 1·38, 1·39, and 1·40, average, $1·37 \pm 0·03$ Å; the thermal parameters for these oxygen atoms are, however, all quite high, so that the positions of these atoms are much less certain.

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References

HUBBARD, C. R. & JACOBSON, R. A. (1971). *A Fortran* IV *Crystallographic System of Programs for Generalized Superpositions*. Ames Laboratory, Iowa State Univ.

TSOU, K. C., LO, K. W. & MILLER, E. (1973). Abstracts, Amer. Chem. Soc. Meeting, Chicago, M 166.

TSOU, K. C., LO, K. W., SELZER, M., WEINSTEIN, J. & BENDER, D. (1973). *Excerpta Med.* Int. Cong. Ser. No. 275, 300.

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Refinement of the Crystal Structure of Scorodite

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Abstract. $FeAsO_4$ $2H_2O$, orthorhombic, *Pbca*, $a=10·325$ (6), $b=8·953$ (3), $c=10·038$ (2) Å, $Z=8$, $D_m=3·27$, $D_x=3·276$ g cm^{-3}. Material from Kiura Mine, Oita, Japan. Each AsO_4 tetrahedron shares its vertices with four $FeO_4(OH_2)_2$ octahedra and *vice versa*. With Fe···O distances of 2·061 (5) and 2·125 (5) Å, the two water molecules coordinate to the metal ion in the *cis* position and donate two and one short hydrogen bonds, respectively, to arsenate oxygen atoms.

Introduction. Precession photographs exhibited orthorhombic symmetry. The systematic absences are *hk*0 for *h* odd, 0*kl* for *k* odd and *h*0*l* for *l* odd. Cell dimensions were determined from setting angles of a four-circle diffractometer. The intensity data of 1878 independent reflexions with $2\theta \leq 60°$ were collected from a crystal of dimensions $0·12 \times 0·11 \times 0·10$ mm on a Rigaku automatic four-circle diffractometer; a graphite monochromator, Mo $K\alpha$ radiation and a θ–2θ scan technique were used. Intensities of 183 reflexions smaller than $2\sigma(F)$ were considered to be zero, where

Table 1. *Final fractional atomic coordinates* ($\times 10^5$) *with e.s.d.'s in parentheses*

	x	*y*	*z*
As	34799 (6)	3556 (7)	−13618 (7)
Fe	37359 (9)	14651 (11)	18278 (10)
O(1)	19917 (42)	327 (51)	−19453 (46)
O(2)	35791 (45)	678 (50)	2939 (42)
O(3)	39294 (43)	21230 (50)	−16644 (47)
O(4)	44796 (45)	−8264 (51)	−21656 (46)
O(*W*1)	19851 (43)	23012 (54)	11835 (52)
O(*W*2)	44653 (47)	32843 (56)	6932 (47)

Table 2. *Thermal parameters with e.s.d.'s in parentheses*

The anisotropic thermal factors are of the form $\exp\left[-\frac{1}{4}(h^2a^{*2}B_{11}+\ldots 2klb^*c^*B_{23})\right]$.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
As	0·43 (2)	0·42 (2)	0·42 (2)	−0·02 (2)	−0·01 (2)	−0·03 (2)
Fe	0·36 (3)	0·48 (3)	0·41 (3)	0·01 (3)	−0·02 (3)	0·00 (3)
O(1)	0·61 (16)	0·84 (19)	0·84 (18)	0·03 (15)	−0·20 (15)	−0·67 (16)
O(2)	1·07 (18)	0·58 (17)	0·45 (17)	−0·05 (16)	−0·03 (16)	0·02 (14)
O(3)	1·11 (18)	0·53 (18)	1·05 (21)	−0·35 (16)	0·17 (16)	0·26 (16)
O(4)	0·88 (18)	0·79 (18)	0·71 (19)	0·21 (16)	−0·03 (16)	−0·28 (15)
O(*W*1)	0·74 (16)	0·97 (20)	1·42 (21)	0·31 (16)	−0·25 (17)	0·14 (18)
O(*W*2)	1·25 (19)	1·18 (21)	0·75 (19)	−0·37 (18)	0·14 (17)	0·12 (17)

$\sigma(F)$ was determined from counting statistics. No correction for absorption ($\mu=109$ cm^{-1}) was applied.

A block-diagonal least-squares refinement on F was started from non-hydrogen atom parameters reported by Kiriyama & Sakurai (1949). The form factors for As^{5+}, Fe^{3+} and O were taken from *International Tables for X-ray Crystallography* (1962). The weighting scheme employed was: $w=1/\sigma^2$, $\sigma=5\cdot0$ if $\sigma(F)/F>0\cdot2$, $\sigma=(I-I_m)/I_m+\sigma(F)$ if $I_m<I$, where I_m was one sixth of the maximum intensity observed, and $\sigma=\sigma(F)$ for the rest of the reflexions. The refinement with anisotropic thermal parameters was continued until the maximum shift of any parameter was less than one tenth of its e.s.d. The final conventional R value was 0·074, while $R_2[=\{\sum w(|F_o|-|F_c|)^2/\sum wF_o^2\}^{1/2}]$ was 0·048. Three-dimensional difference Fourier maps were checked at this stage, but it was not possible to detect any of the hydrogen positions. All ripples observed were lower than 2 e Å^{-3}.

As the refinement with the anomalous dispersion corrections, $\Delta f'$ and $\Delta f''$ for As and Fe, did not converge below $R_2=0\cdot078$, it was terminated without these corrections.

The computations were carried out on an NEAC 2200/700 at the Computer Center, Osaka University. The programs *RSSFR*-5, *HBLS*-IV and *RSDA*-4 in the UNICS program system (1967) were used with some modifications. The final positional and thermal parameters are given in Tables 1 and 2.*

* The observed and calculated structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30698 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

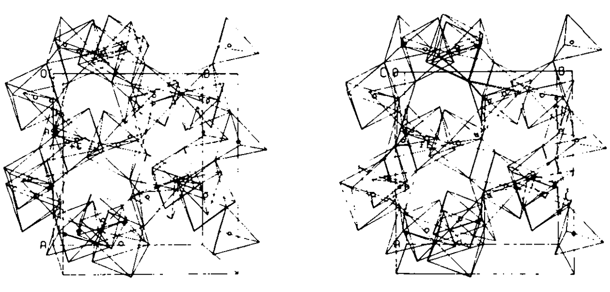

Fig. 1. Stereoscopic drawing of the crystal structure of scorodite by the program *ORTEP* (Johnson, 1965).

Discussion. The structure of scorodite is of considerable interest as regards the chemical nature of the water of crystallization. In the early 'precomputer' analysis, only 160 reflexions were measured by a photographic method. The refinement was undertaken with a sample from the same locality.

The crystal structure consists of AsO_4 tetrahedra and $FeO_4(OH_2)_2$ octahedra connected alternately at vertices. None of the water oxygens participates in this linkage. The packing and the connexion of these polyhedra are illustrated in Fig. 1. Interatomic distances and angles are listed in Table 3. Arsenate groups and ferric ions form a three-dimensional framework, $\{FeAsO_4\}_\infty$, which has wide channels parallel to **c**. Water oxygens, O(*W*1), stack one above the other at intervals of **c**/2 to fill these channels, while water oxygens O(*W*2) fill other open spaces among these channels. The water oxygen O(*W*1) acts as the hydrogen-bond donor to two arsenate oxygens belonging to other octahedra at distances of 2·603 and 2·697 Å. O(*W*2) bonds in a similar way to only one oxygen at a distance of 2·643 Å, and the remaining hydrogen atom does not participate in any hydrogen bonding. The infrared spectra of a hydrothermally synthesized sample are consistent with the present result.

In the case of $InPO_4.2H_2O$, isomorphous with scorodite, the water oxygen in the channel, O(*W*1), is close to three phosphate oxygens other than those in the same octahedron and the dissociation of water

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

(*a*) Coordination around As

As—O(1)	1·670 (5)	O(1)–As–O(3)	110·8 (2)
As—O(2)	1·685 (4)	O(1)–As–O(4)	106·7 (2)
As—O(3)	1·677 (5)	O(2)–As–O(3)	107·8 (2)
As—O(4)	1·684 (5)	O(2)–As–O(4)	109·8 (2)
O(1)–As–O(2)	112·1 (2)	O(3)–As–O(4)	109·7 (2)

(*b*) Coordination around Fe

Fe—O(1^{ii})	1·970 (5)	O(2)—Fe–O(3^{i})	178·6 (2)
Fe—O(2)	1·990 (4)	O(2)—Fe–O(4^{iii})	91·5 (2)
Fe—O(3^{i})	1·982 (5)	O(2)—Fe–O(*W*1)	85·1 (2)
Fe—O(4^{iii})	1·959 (5)	O(2)—Fe–O(*W*2)	95·5 (2)
Fe—O(*W*1)	2·061 (5)	O(3^{i})—Fe–O(4^{iii})	87·7 (2)
Fe—O(*W*2)	2·125 (5)	O(3^{i})—Fe–O(*W*1)	95·5 (2)
O(1^{ii})–Fe–O(2)	91·4 (2)	O(3^{i})—Fe–O(*W*2)	83·4 (2)
O(1^{ii})–Fe–O(3^{i})	89·7 (2)	O(4^{iii})–Fe–O(*W*1)	170·3 (2)
O(1^{ii})–Fe–O(4^{iii})	93·0 (2)	O(4^{iii})–Fe–O(*W*2)	89·0 (2)
O(1^{ii})–Fe–O(*W*1)	96·3 (2)	O(*W*1)–Fe–O(*W*2)	82·2 (2)
O(1^{ii})–Fe–O(*W*2)	172·7 (2)		

Table 3 (*cont.*)

(*c*) Environment of water (1)

O(*W*1)···O(4^{ii})	2·603 (7)	O(*W*1)···O(*W*2^{v})	3·255 (7)
O(*W*1)···O(2^{iv})	2·697 (7)	O(4^{ii})····O(*W*1)···Fe	97·2 (2)
O(*W*1)···O(1^{i})	3·037 (7)	O(2^{iv})····O(*W*1)···Fe	128·8 (2)
O(*W*1)···O(3^{v})	3·233 (7)	O(4^{ii})····O(*W*1)···O(2^{iv})	123·5 (2)

(*d*) Environment of water (2)

O(*W*2)···O(3)	2·643 (7)	O(*W*2)···O(1^{vi})	3·264 (7)
O(*W*2)···O(4^{i})	3·130 (7)	O(3)·····O(*W*2)···Fe	96·0 (2)
O(*W*2)···O(*W*1^{vi})	3·255 (7)		

Symmetry operations

(i)	$x, \frac{1}{2}-y, \frac{1}{2}+z$	(iv)	$\frac{1}{2}-x, \frac{1}{2}+y, z$
(ii)	$\frac{1}{2}-x, -y, \frac{1}{2}+z$	(v)	$-\frac{1}{2}+x, \frac{1}{2}-y, -z$
(iii)	$1-x, -y, -z$	(vi)	$\frac{1}{2}+x, \frac{1}{2}-y, -z$

molecules to OH_3^+ and OH^- has been suggested (Mooney-Slater, 1961). Such pseudo-water species, however, have not been found in metavariscite, $AlPO_4.2H_2O$; two types of water molecules are bound to the nearest phosphate oxygens with two normal and two bifurcated hydrogen bonds, respectively (Kniep & Mootz, 1973). Furthermore, in contrast to $InPO_4.2H_2O$, the distances of Me–O(*W*1) are shorter than those of Me–O(*W*2) for both scorodite and metavariscite. Thus, the bond nature of water in scorodite is more similar to that in metavariscite, in spite of the different space group, than to that in the isomorphous $InPO_4$ $2H_2O$.

The variation of hydrogen-bonding schemes in these homologous compounds seems to reflect the difference in size ratios of the cations to the anionic clusters and also in amphotericity of the trivalent cations.

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References

International Tables for X-ray Crystallography (1962). Vol. III, pp. 202–207. Birmingham: Kynoch Press.

Johnson, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.

Kiriyama, R. & Sakurai, K. (1949). *X-rays*, **5**, 85–88. *Struct. Rep.* (1949). **12**, 251–252.

Kniep, R. & Mootz, D. (1973). *Acta Cryst.* B**29**, 2292–2294.

Mooney-Slater, R. C. L. (1961). *Acta Cryst.* **14**, 1140–1146.

UNICS program system (1967). Edited by T. Sakurai, Crystallographic Society of Japan.

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Tetrabromobis-[σ-phenylenebis(dimethylarsino)]tantalum(V) Hexabromotantalate(V)

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Abstract. $C_{20}H_{20}As_4Br_{10}Ta_2$, $M=1721{\cdot}06$, tetragonal, $a=12{\cdot}525$ (9), $c=25{\cdot}474$ (23) Å, $U=3996{\cdot}25$ Å^3, $Z=4$, $d_c=2{\cdot}81$, $d_m=2{\cdot}85$ (4), Cu $K\alpha$ radiation $\lambda=1{\cdot}54178$ Å, μ(Cu $K\alpha$)$=272{\cdot}97$ cm^{-1}. Space group $I4_1/amd$ from systematic absences hkl, $h+k+l=2n+1$; $hk0$, $h=2n+1$; hhl, $2h+l\neq4n$. This compound was prepared by Clark, Kepert & Nyholm [*J. Chem. Soc.* (1965), pp. 2877–2883] and formulated as $TaBr_5$(diars), diars = σ-phenylenebis(dimethylarsine). In fact the crystal structure determination shows it to be $[TaBr_4(diars)_2]^+$ $TaBr_6^-$. The cation is a crystallographically imposed dodecahedron [Ta–Br(1) 2·583 (10), Ta–As(1) 2·765 (1) Å] and the anion an octahedron [Ta–Br(1) 2·487 (12), Ta–Br(3) 2·490 (15) Å]. The 316 independent reflexions, measured by counter methods, have been refined to R 0·108.

Introduction. Crystals of $TaBr_5$(diars) were prepared following the method of Clark, Kepert & Nyholm (1965) and recrystallized from dichloromethane by slow evaporation of the solvent. A crystal with dimensions 0·2 × 0·15 × 0·35 mm was mounted with the a axis