coordinat car toutes les molécules d'eau concourent à l'entourage du cation. De plus, dans les deux cas les molécules d'eau sont toutes liées par liaisons hydrogène aux atomes d'oxygène sulfonique ne participant pas à la coordination du métal. Mais à l'inverse de ce que l'on observe dans $[Cu(CH_3SO_3)_2(H_2O)_4]$ il n'y a pas dans le cristal de molécule individuelle $Cu[SO_3(CH_2)_2SO_3]$-$(H_2O)_4$.

Dans la série des acides α,ω-dicarboxyliques, l'acide succinique, $CO_2H(CH_2)_2CO_2H$, est l'homologue de l'acide éthanedisulfonique-1,2. Il forme avec le cuivre(II) un composé de formule $Cu[CO_2(CH_2)_2$-$CO_2].2H_2O$ (O'Connor & Maslen, 1966). Le taux d'hydratation est moitié de celui du présent composé et les structures sont totalement différentes. En effet dans le succinate l'atome de cuivre est entouré d'un octaèdre dont la base est formée par quatre atomes d'oxygène carboxylique appartenant à quatre groupements succinato différents $[Cu-O = 1,975 (3) Å]$, une molécule d'eau $[Cu-O = 2,102 (7) Å]$ et un autre atome de cuivre $[Cu-Cu = 2,610 (1) Å]$ se trouvant en position axiale. Des mesures magnétiques ont montré l'existence d'un couplage entre les deux atomes métalliques (Asai, Kishita & Kubo, 1959). Le seul point commun entre ces deux structures est l'existence de chaînes formées par les groupements acides reliant les atomes de cuivre.

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The Crystal Structure of Rb22W32O107

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The crystal structure of $Rb_{22}W_{32}O_{107}$ has been determined from three-dimensional X-ray diffractometer data and refined to an R value of 0·078 for 2259 observed reflexions. $Rb_{22}W_{32}O_{107}$ crystallizes in the tetragonal space group $I\bar{4}$, with $a = 15·966$ (2), $c = 10·099$ (1) Å, $Z = 1$, and $D_x = 6·11$ g cm^{-3}. The structure is built up of distorted WO_6 octahedra and RbO_n ($n = 12, 14, 15, 16$ and 18) coordination polyhedra. Four WO_6 octahedra are linked to form a W_4O_{18} group by sharing corners with each other. These groups are further linked by sharing corners to form a three-dimensional framework of the $[(W_{32}O_{107})^{22-}]_\infty$ anion. One eighth of the O(5) sites are assumed to be vacant to satisfy the stoichiometry. The W–O bond lengths range from 1·66 (5) to 2·25 (3) Å, with a mean value of 1·93 Å. Rb(1) and Rb(5) are located in the tunnels of the framework running along the c axis, and the remaining Rb atoms are at the open spaces in the walls of the tunnels, each being surrounded by two or six W_4O_{18} groups. The Rb–O bond lengths range from 2·94 (3) to 3·73 (3) Å. The mean values are 3·43 for Rb(1)–O, 3·55 for Rb(2)–O, 3·38 for Rb(3)–O, 3·31 for Rb(4)–O and 3·47 Å for Rb(5)–O.

Introduction

The study of the structures of alkali-metal isopolytungstates has seen considerable progress in the last few years. It was found in previous work that the isopolytungstate anions in these substances exist in the form of isolated WO_4 groups, infinite chains, layers or frameworks built up of WO_4 tetrahedra and/or WO_6 octahedra. The crystal structures of A_2WO_4 (A:alkali-metal atom) are always isostructural with those of A_2MoO_4. However, it was revealed that alkali-metal isopolytungstates showed a tendency to adopt structures different from those of the corresponding isopolymolybdates when the molar ratio of WO_3 became larger. For example, the $[(W_3O_{10})^{2-}]_\infty$ anion in $K_2W_3O_{10}$ (Okada, Morikawa, Marumo & Iwai, 1976) has a framework structure built up of WO_6 octahedra sharing edges and corners, whereas the $[(Mo_3O_{10})^{2-}]_\infty$

anion in $K_2Mo_3O_{10}$ (Seleborg, 1966; Gatehouse & Leverett, 1968) has a chain structure built up of MoO_6 octahedra and MoO_5 square pyramids sharing edges.

In the $Rb_2WO_4-WO_3$ system, crystals of $Rb_2W_2O_7$, $Rb_2W_3O_{10}$ and $Rb_2W_6O_{19}$ have been obtained from the melt by Spitsyn & Kuleshov (1950) and also by Chang & Sachdev (1975). However, the crystal structures of these compounds have not been elucidated to date. The structure determination of $Rb_2W_3O_{10}$ was undertaken to add further information on the crystal chemistry of the alkali-metal isopolytungstates.

Experimental

Crystals of $Rb_2W_3O_{10}$ were synthesized by heating, at 960°C for 5 h, an intimate mixture of Rb_2CO_3 and $3WO_3$ in a platinum crucible, and then by cooling it at a rate of 20–30°C h^{-1}. Colourless and transparent crystals were obtained in the resulting massive aggregates.

From Weissenberg and precession photographs, the crystals were found to have tetragonal Laue symmetry $I4/m$. As the systematic absences were hkl for $h + k + l$ odd, the possible space groups were restricted to $I4$, $I\bar{4}$ and $I4/m$. Since a piezoelectric effect was observed along the c axis of the crystal, the space group was further restricted to $I4$ or $I\bar{4}$. The crystallographic data are given in Table 1.

A crystal with dimensions $0.13 \times 0.13 \times 0.06$ mm was used for intensity collection. Intensities were measured on an automated four-circle diffractometer (Philips PW 1100) with Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å) reflected from a graphite monochromator, up to $2\theta = 60°$ (partly up to 70°) by the ω–2θ scan technique. The scan speed was 8° min^{-1} in ω and the scan width was determined according to the formula $(1.2 + 0.2 \tan \theta)°$. The intensities were corrected for Lorentz–polarization factors. Absorption corrections were also applied by a local version of the program $ACACA$ (Wuensch & Prewitt, 1965), the maximum and minimum transmission factors being 0.1036 and

0.0435 respectively. Corrections for isotropic secondary extinction were carried out in the course of the structure refinement with a sphere of 0.11 mm diameter assumed for the crystal shape. In all, 2259 independent intensity data, satisfying the condition $|F| > 3\sigma(|F|)$, were collected and used for the structure determination, where $\sigma(|F|)$ is the standard deviation from counting statistics.

Structure determination

The structure was solved by the heavy-atom method. The true space group was revealed to be $I\bar{4}$ from a close examination of the Patterson maps. The space group $I4$ was rejected, since there exist no two peaks whose coordinates can be expressed as $(x + y, y - x, 0)$ and $(2x, 2y, 0)$ respectively. The arrangement of W atoms was then derived from the Patterson maps on the basis of the symmetry $I\bar{4}$. The positions of the Rb and O atoms were readily found on Fourier and difference Fourier maps synthesized with phases derived from the W atoms. The chemical composition was subsequently revealed not to be $Rb_2W_3O_{10}$, and the maps indicated instead the formula $Rb_{22}W_{32}O_{108}$. The R value dropped to 0.104 with the new formula, and site population analyses, carried out at this stage, indicated no cation deficiency. On the other hand, the temperature factor of O(5) became very large ($B = 7.8$ Å^2) compared to those of the remaining O atoms (the mean value = 0.9 Å^2), suggesting that the population of O(5) should be

Table 1. Crystallographic data for $Rb_{22}W_{32}O_{107}$ and $Cs_{22}W_{32}O_{107}$

	$Rb_{22}W_{32}O_{107}$	$Cs_{22}W_{32}O_{107}$
Crystal system	Tetragonal	Tetragonal
Space group	$I\bar{4}$	$I\bar{4}$
a	15.966 (2) Å	16.092 (1) Å
c	10.099 (1)	10.177 (1)
V	2574.4 (8) Å^3	2635.4 (4) Å^3
Z	1	1
M_r	9475.8	10519.1
D_x	6.11 g cm^{-3}	6.63 g cm^{-3}
D_m	6.13	6.56
μ (for Mo $K\alpha$)	487.5 cm^{-1}	

Table 2. Final atomic parameters for $Rb_{22}W_{32}O_{107}$

	x	y	z	B(Å^2)
W(1)	0.13072 (10)	0.18242 (10)	0.3530 (2)	1.01*
W(2)	0.27863 (11)	0.14773 (10)	0.0867 (2)	1.08*
W(3)	0.03788 (10)	0.39155 (9)	0.3833 (2)	0.74*
W(4)	0.01587 (10)	0.23759 (11)	0.6655 (2)	1.07*
Rb(1)	0.0	0.0	0.5	6.6*
Rb(2)	0.5	0.0	0.25	7.4*
Rb(3)	0.4106 (5)	0.2069 (7)	0.5067 (8)	4.5*
Rb(4)	0.2840 (3)	0.3844 (4)	0.2167 (6)	2.2*
Rb(5)	0.0	0.0	0.0	8.9*
O(1)	0.189 (2)	0.092 (2)	0.411 (3)	0.7 (4)
O(2)	0.296 (2)	0.056 (2)	0.226 (3)	0.5 (3)
O(3)	0.139 (2)	0.410 (2)	0.489 (3)	0.6 (4)
O(4)	0.198 (3)	0.102 (3)	0.012 (4)	2.0 (6)
O(5)	0.059 (3)	0.131 (3)	0.249 (6)	2.5 (8)
O(6)	0.067 (2)	0.183 (2)	0.508 (3)	0.7 (4)
O(7)	0.217 (2)	0.204 (2)	0.223 (3)	0.4 (3)
O(8)	0.390 (2)	0.200 (2)	0.190 (3)	1.0 (4)
O(9)	0.215 (2)	0.258 (2)	0.486 (3)	0.8 (4)
O(10)	0.088 (2)	0.301 (2)	0.313 (3)	0.9 (4)
O(11)	0.461 (2)	0.345 (2)	0.269 (3)	1.1 (4)
O(12)	0.0	0.5	0.441 (5)	1.5 (7)
O(13)	0.333 (2)	0.014 (2)	0.490 (3)	0.4 (3)
O(14)	0.109 (2)	0.459 (2)	0.244 (3)	1.0 (4)

* Calculated from the anisotropic thermal parameters according to the expression: $B = 4(B_{11}a^2 + B_{22}a^2 + B_{33}c^2)/3$.

decreased to $\frac{7}{8}$ to satisfy the stoichiometry. The structure, having the chemical composition Rb_{22}-$W_{32}O_{107}$, was further refined with the least-squares program *LINUS* (Coppens & Hamilton, 1970) by assigning anisotropic temperature factors to W and Rb atoms and isotropic ones to O atoms. After correction for secondary extinction, the calculations converged to give an R of 0·078 for the observed set of 2259 reflexions; the extinction parameter (G) was 0·94 (6) × 10^{-4}. The atomic scattering factors for neutral atoms and the dispersion correction factors were taken from *International Tables for X-ray Crystallography* (1974). Unit weights were given for all the terms. The final positional and thermal parameters are listed in Table 2.*

Discussion

The interatomic distances are shown in Table 3 with their estimated standard deviations in parentheses. The structure viewed along the c axis is shown in Fig. 1. There are four crystallographically independent W atoms in the unit cell, each being octahedrally surrounded by six O atoms. The WO_6 octahedra are largely distorted. The W—O bond lengths range from 1·66 (5) to 2·25 (3) Å. The mean lengths are 1·95 for W(1)—O, 1·93 for W(2)—O, 1·90 for W(3)—O and 1·94 Å for W(4)—O. The O—W—O angles between neighbouring W—O bonds range from 79·2 (12) to 100·6 (14)° and those between W—O bonds on the opposite sides of a W atom range from 162·6 (13) to 176·0 (18)°. W—O—W angles are in the range 138·1 (17) to 153·7 (19)°. There are five crystallographically independent Rb atoms per cell. The coordination number varies from 12 to 18. The mean Rb—O bond lengths are 3·43 in $Rb(1)O_{16}$, 3·55 in $Rb(2)O_{18}$, 3·38 in $Rb(3)O_{14}$, 3·31 in $Rb(4)O_{15}$ and 3·47 Å in $Rb(5)O_{12}$ coordination polyhedra.

As is observed in Table 4, each of the $W(1)O_6$, $W(2)O_6$, $W(3)O_6$ and $W(4)O_6$ octahedra shares corners with five or six neighbouring WO_6 octahedra. Four WO_6 octahedra form a W_4O_{18} group by sharing corners as shown in Fig. 2 in an idealized form. Such W_4O_{18} groups are further joined by sharing corners of the constituent octahedra to form a three-dimensional framework of $[(W_{32}O_{107})^{22-}]_\infty$. There are tunnels along the c axis in the framework and Rb(1) and Rb(5) atoms are located in them. Rb(2) and Rb(3) atoms are located in the spaces between two W_4O_{18} groups adjacent along the c axis. Rb(4) atoms are surrounded by six W_4O_{18} groups in the framework.

* Lists of observed and calculated structure amplitudes and anisotropic temperature factors for W and Rb atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32680 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Initially we supposed the chemical composition of this crystal to be $Rb_2W_3O_{10}$, but the actual composition was found to be $Rb_{22}W_{32}O_{107}$ (W/Rb = 1·455). Though the chemical composition of the present compound is slightly different from $Rb_2W_3O_{10}$, it is interesting to compare the structure with that of $K_2W_3O_{10}$ (Okada *et al.*, 1976) to examine the effect of alkaline-metal atoms on the structure of isopolytungstates. The structures of both isopolytungstates are based on frameworks of WO_6 octahedra.

Table 3. *Interatomic distances* (Å) *for* $Rb_{22}W_{32}O_{107}$

Symmetry code

(0)	x,y,z	(ix)	$x,y,-1+z$
(i)	$\frac{1}{2}-x,\frac{1}{2}-y,\frac{1}{2}+z$	(x)	$\frac{1}{2}-x,\frac{1}{2}-y,-\frac{1}{2}+z$
(ii)	$-y,x,1-z$	(xi)	$\frac{1}{2}-y,\frac{1}{2}+x,\frac{1}{2}-z$
(iii)	$-\frac{1}{2}+y,\frac{1}{2}-x,\frac{1}{2}-z$	(xii)	$\frac{1}{2}+x,\frac{1}{2}+y,\frac{1}{2}+z$
(iv)	$-\frac{1}{2}+y,\frac{1}{2}-x,\frac{3}{2}-z$	(xiii)	$\frac{1}{2}+x,\frac{1}{2}+y,-\frac{1}{2}+z$
(v)	$\frac{1}{2}-y,\frac{1}{2}+x,\frac{3}{2}-z$	(xiv)	$1-x,1-y,z$
(vi)	$y,1-x,1-z$	(xv)	$\frac{1}{2}+y,\frac{1}{2}-x,\frac{1}{2}-z$
(vii)	$-\frac{1}{2}+x,\frac{1}{2}+y,\frac{1}{2}+z$	(xvi)	$\frac{1}{2}+y,\frac{1}{2}-x,\frac{3}{2}-z$
(viii)	$-x,1-y,z$	(xvii)	$1-y,x,1-z$

W(1)—O(1⁰)	1·81 (3)	W(3)—O(3⁰)	1·96 (3)
W(1)—O(5⁰)	1·76 (5)	W(3)—O(10⁰)	1·80 (3)
W(1)—O(6⁰)	1·87 (3)	W(3)—O(12⁰)	1·92 (2)
W(1)—O(7⁰)	1·93 (3)	W(3)—O(13ⁱⁱ)	1·79 (3)
W(1)—O(9⁰)	2·25 (3)	W(3)—O(14⁰)	2·10 (3)
W(1)—O(10⁰)	2·05 (3)	W(3)—O(14ⁱⁱⁱ)	1·80 (3)
W(2)—O(2⁰)	2·05 (3)	W(4)—O(1ⁱⁱ)	2·04 (3)
W(2)—O(3⁰)	1·88 (3)	W(4)—O(2ⁱᵛ)	1·84 (3)
W(2)—O(4⁰)	1·66 (5)	W(4)—O(6⁰)	1·99 (3)
W(2)—O(7ⁱ)	1·92 (3)	W(4)—O(8⁰)	1·82 (3)
W(2)—O(8⁰)	2·22 (3)	W(4)—O(11⁰)	1·72 (3)
W(2)—O(9⁰)	1·82 (3)	W(4)—O(13ⁱⁱ)	2·24 (3)

Rb(1)—O(1ˣ,ˣⁱ,ˣⁱⁱⁱ,ˣᵛ)	3·47 (3) (×4)
Rb(1)—O(5ˣ,ˣⁱ,ˣⁱⁱⁱ,ˣᵛ)	3·42 (6) (×4)
Rb(1)—O(6ˣ,ˣⁱ,ˣⁱⁱⁱ,ˣᵛ)	3·11 (3) (×4)
Rb(1)—O(11ˣ,ˣⁱ,ˣⁱⁱⁱ,ˣᵛ)	3·73 (3) (×4)
Rb(2)—O(2⁰,ⁱᵛ,ᵛ,ᵛⁱⁱⁱ)	3·39 (3) (×4)
Rb(2)—O(3⁰,ⁱᵛ,ᵛ,ᵛⁱⁱⁱ)	3·73 (3) (×4)
Rb(2)—O(8⁰,ⁱᵛ,ᵛ,ᵛⁱⁱⁱ)	3·69 (3) (×4)
Rb(2)—O(12⁰,ᵛ)	3·12 (5) (×2)
Rb(2)—O(13ⁱ,ⁱⁱ,ᵛⁱ,ᵛⁱⁱ)	3·61 (3) (×4)

Rb(3)—O(2ⁱⁱⁱ)	3·30 (3)	Rb(4)—O(1ˣ)	3·14 (3)
Rb(3)—O(3ⁱⁱⁱ)	3·06 (3)	Rb(4)—O(3⁰)	3·62 (3)
Rb(3)—O(4ⁱⁱⁱ)	3·42 (5)	Rb(4)—O(4⁰)	3·00 (4)
Rb(3)—O(4ˣ)	3·51 (5)	Rb(4)—O(5ˣⁱ)	3·12 (5)
Rb(3)—O(5⁰)	3·59 (6)	Rb(4)—O(6ˣ)	3·36 (3)
Rb(3)—O(7⁰)	3·31 (3)	Rb(4)—O(6ˣⁱ)	3·73 (3)
Rb(3)—O(8ⁱˣ)	3·22 (3)	Rb(4)—O(7⁰)	3·07 (3)
Rb(3)—O(9ˣ)	3·23 (3)	Rb(4)—O(8ˣ)	3·41 (3)
Rb(3)—O(10⁰)	3·10 (3)	Rb(4)—O(9⁰)	3·56 (3)
Rb(3)—O(11ⁱˣ)	3·36 (3)	Rb(4)—O(9ˣ)	3·26 (3)
Rb(3)—O(12ˣⁱ)	3·64 (1)	Rb(4)—O(10⁰,ˣⁱ)	3·54 (3) (×2)
Rb(3)—O(13ˣ)	3·32 (3)	Rb(4)—O(11ˣ)	2·94 (3)
Rb(3)—O(14⁰)	3·59 (3)	Rb(4)—O(13ˣ)	3·37 (3)
Rb(3)—O(14ⁱⁱⁱ)	3·62 (3)	Rb(4)—O(14⁰)	3·05 (3)

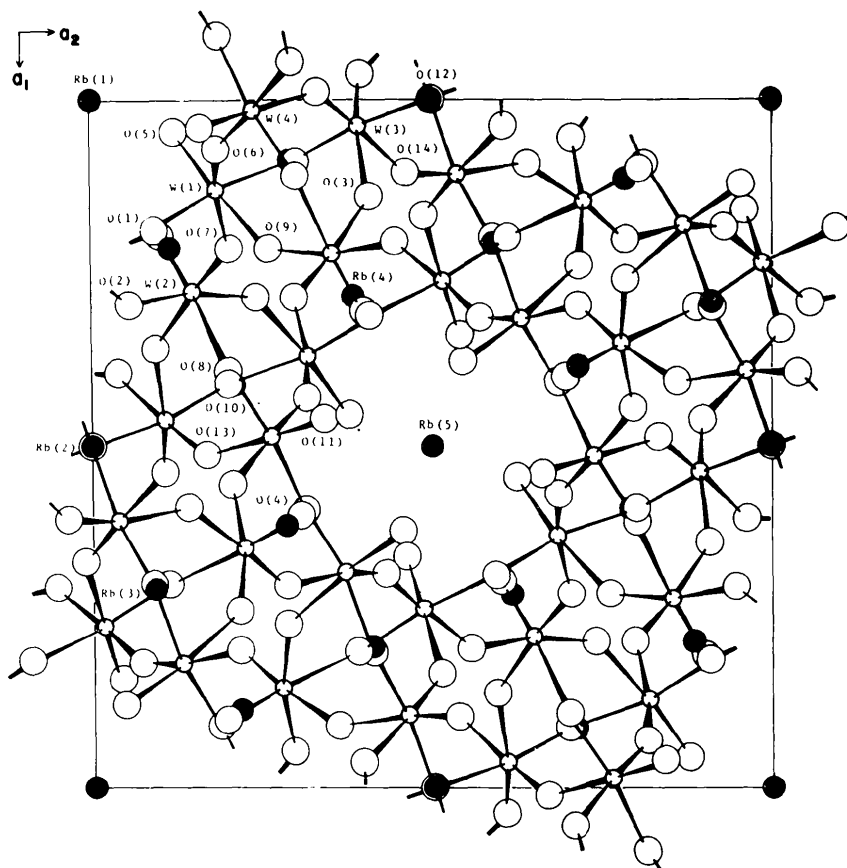|	
Rb(5)—O(4⁰,ᵛⁱ,ˣⁱᵛ,ˣᵛⁱⁱ)	3·56 (5) (×4)
Rb(5)—O(5ⁱ,ˣⁱ,ˣⁱⁱ,ˣᵛ)	3·40 (6) (×4)
Rb(5)—O(11ᵛ,ˣ,ˣⁱⁱⁱ,ˣᵛⁱ)	3·46 (3) (×4)

Fig. 1. The crystal structure of $Rb_{22}W_{32}O_{107}$ viewed along the c axis. Small open and shaded circles represent W and Rb atoms respectively. Large open circles represent O atoms.

Table 4. *Corner-sharing scheme between the* WO_6 *octahedra*

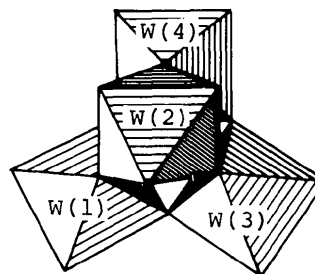| Neighbouring WO_6 octahedra	$W(1)O_6$	$W(2)O_6$	$W(3)O_6$	$W(4)O_6$	Total
$W(1)O_6$	–	two	one	two	five
$W(2)O_6$	two	–	one	two	five
$W(3)O_6$	one	one	three	one	six
$W(4)O_6$	two	two	one	–	five

Fig. 2. The W_4O_{18} group shown in an idealized form.

However, there exists a large difference between these two framework structures. The framework in $Rb_{22}W_{32}O_{107}$ is built up of corner-shared W_4O_{18} groups. On the other hand, that in $K_2W_3O_{10}$ (Okada *et al.*, 1976) is built up of parallel strings of WO_6 octahedra, which are combined laterally by sharing corners of the octahedra. All the K atoms are located in the flat tunnels existing in the framework. The tunnels are too narrow to accommodate Rb atoms.

A compound was synthesized in the system $Cs_2WO_4-WO_3$ which had a composition close to $Cs_2W_3O_{10}$. It gives similar crystallographic data to those of $Rb_{22}W_{32}O_{107}$ as listed in Table 1, and is considered to be isomorphous with $Rb_{22}W_{32}O_{107}$. The relationship between this compound and $Cs_2W_3O_{10}$ reported by Chang & Sachdev (1975) is not clear.

Computations were carried out on a HITAC 8700 computer at the Computer Centre of Tokyo Institute of Technology.

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Thiamine Pyrophosphate Tetrahydrate: A Structure with the Pyrophosphate Ester in an Extended Conformation

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Thiamine pyrophosphate, cocarboxylase, is a coenzyme in a number of enzyme systems for which its pyrophosphate group is believed to provide the principal mode of binding to the enzyme. A previous structure determination of thiamine pyrophosphate (TPP) as the hydrochloride, in which the pyrophosphate ester is mono-ionized, indicated that the pyrophosphate was folded back over the thiazolium ring of the thiamine. In the current structure, TPP is a neutral zwitterion with its pyrophosphate doubly ionized and its pyrimidine ring still protonated. In contrast to the hydrochloride structure, the pyrophosphate ester in the neutral zwitterion is extended away from the thiamine moiety. This structure also presents a model which differs substantially from that previously proposed [Carlisle & Cook, *Acta Cryst.* (1969), B25, 1359–1367] for the TPP neutral zwitterion, which is shown here to have some unacceptably close intermolecular contacts. For the current structure there is good agreement between the structural features in the two independent molecules, not only with respect to the pyrophosphate ester conformation but also in terms of the bond distances and angles. In addition, both thiamine molecules exhibit the characteristic F conformation with respect to the C(3,5′) methylene bridge atom. The crystal structure was determined using diffractometer data obtained by the $\theta:2\theta$ scan technique with Cu radiation from a crystal having space-group symmetry $P\bar{1}$ ($P1$) and unit-cell parameters $a = 13{\cdot}418$ (35), $b = 12{\cdot}296$ (9), $c = 15{\cdot}572$ (13) Å, $\alpha = 56{\cdot}62$ (4), β 96·27 (8), $\gamma = 92{\cdot}67$ (1)°. The structure was solved by direct methods and refined by full-matrix least squares to R 0·045 for 6416 observed reflections and $R = 0{\cdot}048$ for all 6864 reflections.

Introduction

Thiamine pyrophosphate, which is also known as cocarboxylase, is a coenzyme in enzyme systems which catalyze the decarboxylation of α-keto acids and the transfer of aldehyde or acyl groups. The conformation of the coenzyme is important for several aspects of the catalytic mechanism (Sax, Pulsinelli & Pletcher, 1974; Gallo, Mieyal & Sable, 1977; Pletcher, Sax, Blank & Wood, 1977). The pyrophosphate ester of the C(5) dimethylene side chain is generally considered to provide the primary site for attachment to the various enzymes and thus an understanding of its conforma-

tional properties will be helpful in later studies of the enzyme–coenzyme complexes. An examination of the currently known thiamine structures reveals that there is a marked variability in the $\varphi_{5\alpha}$ torsion angle but that the $\varphi_{5\beta}$ angle is normally found at $\sim\pm60°$ (Shin, Pletcher, Blank & Sax, 1977). In the thiamine pyrophosphate hydrochloride (TPP.HCl) structure, the mono-ionized pyrophosphate group was observed to be folded back over the positively charged thiazolium ring (Pletcher & Sax, 1966, 1972). It was suggested that the minimization of separation of unlike charges was largely responsible for the stabilization of the folded conformation of the pyrophosphate side chain. This