Conclusion

La conformation de la molécule du chlorhydrate de sotalol est comparable à celles des autres membres de cette série de médicaments. Néanmoins, la cohésion cristalline se fait d'une façon originale du fait de la présence d'un atome d'azote supplémentaire qui entraîne l'absence de liaisons fortes par l'intermédiaire de l'hydroxyle.

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The Crystal Structure of Ferrisicklerite, $Li_{<1}(Fe^{3+}, Mn^{2+})PO_4$

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Ferrisicklerite is a phosphate of the triphylite group isotypic with olivine. The sample in this study has the composition $Li_{1\cdot61}Na_{0\cdot07}Mg_{0\cdot15}Ca_{0\cdot07}Fe^{2+}_{0\cdot03}Mn^{2+}_{1\cdot35}Fe^{3+}_{2\cdot45}[(PO_4)_{3\cdot76}(O_4H_4)_{0\cdot25}]$, space group *Pmnb* with $a=5\cdot918$, $b=10\cdot037$, $c=4\cdot799$ Å. The refinement of the structure indicates a partial occupancy of the octahedral site M(1) by Li and Na, a complete occupancy of the octahedral site M(2) by the remaining cations with isomorphous substitution between Mn^{2+} and Fe^{3+} in this site and the partial substitution of the group PO_4 by the group $(OH)_4$. The distortion of the coordination polyhedra can be explained in terms of the strong imbalance of the bond strengths to the anions.

Introduction

Ferrisicklerite, $Li_{<1}(Fe^{3+},Mn^{2+})PO_4$, a phosphate of the triphylite group described for the first time by Quensel (1937), is generally a secondary mineral which forms in pegmatites by the alteration of triphylite and litiophilite either by weathering or by hydrothermal action in a late pegmatitic stage. Ferrisicklerite, like all the minerals of the triphylite group, is isotypic with olivine (Gossner & Strunz, 1932).

Structure refinements of minerals in this group are numerous: natrophilite, $NaMnPO_4$ (Byström, 1943; Moore, 1972), triphylite, $Li(Fe,Mn)PO_4$ (Destenay, 1950; Finger & Rapp, 1970), lithiophilite, $LiMnPO_4$ (Geller & Durand, 1960), heterosite, $(Fe^{3+},Mn^{3+})PO_4$ (Eventoff, Martin & Peacor, 1972). These refinements, however, do not concern the minerals sicklerite or ferrisicklerite, *i.e.* the members of the group in which at least one octahedral site is only partially filled. Therefore I thought it useful to refine one of the members containing trivalent, divalent and monovalent cations, such as ferrisicklerite (sicklerite being an alternative candidate), in order to determine the distribution of the cations and their occupancies in the two possible sites. From the structure of heterosite (Eventoff *et al.*, 1972) it was predicted that in ferrisicklerite the M(2) site would be fully occupied whereas the M(1) site would probably host monovalent cations. A study on ferrisicklerite would also verify if there is isomorphous substitution between Mn^{2+} and Fe^{3+} despite the large difference between their ionic radii.

The structure of a ferrisicklerite from Sidi-Bou-Othmane (Jebilet, Morocco) (Huvelin, Orliac & Permingeat, 1972), which occurs in large monocrystals and seems to be of primary origin, was refined; its

Table 1. *Chemical analysis of ferrisicklerite from Sidi-Bou-Othmane* (*Fontan et al.*, 1976)

Li_2O	3·95 %	Li	1·610	
Na_2O	0·40	Na	0·073	
FeO	0·34	Fe^{2+}	0·030	
Fe_2O_3	32·22	Fe^{3+}	2·452	
MnO	15·66	Mn^{2+}	1·348	
CaO	0·62	Ca	0·067	
MgO	0·96	Mg	0·146	
P_2O_5	43·73	P	3·757	4·007
H_2O^+	1·48	$(OH)_4$	0·250	
H_2O^-	0·63	O	15·000	
Insoluble	0·12			
Total	100·11			

chemical analysis (Fontan, Huvelin, Orliac & Permingeat, 1976) is given in Table 1. The analysis indicates a considerable lack of phosphorus and consequently substitution of the complex anion PO_4^{3-} by the tetrahedron $(OH)_4^{4-}$. This has only rarely been observed in phosphates, *e.g.* in viseite (McConnell, 1952) and in kehoeite (McConnell & Foreman, 1974). A refinement should therefore determine the occupancy of the tetrahedral site and consequently the correctness of the chemical formula proposed by Fontan *et al.* (1976).

Experimental

The study was carried out on a cleavage fragment approximately 0·10 × 0·02 × 0·08 mm. The intensity data were collected on a Philips PW 1100 diffractometer (Mo $K\alpha$ radiation) of the Istituto di Mineralogia at the University of Perugia. 776 independent reflexions were measured, constituting approximately 23% of the total number of reflexions in the Mo $K\alpha$ limiting sphere. The systematic absences of the $hk0$ reflexions with $k=2n+1$ and of the $h0l$ reflexions with $h+l=2n+1$ indicate *Pmnb* and $P2_1nb$ as probable space groups for ferrisicklerite and reduce the number of reflexions to 677. Of these, 167 with $I<2\sigma(I)$ were assumed to be unobserved and set to 0.

The unit-cell data, obtained with the single-crystal diffractometer, are: $a=5·918$ (3), $b=10·037$ (6), $c=4·799$ (3) Å.

Refinement

The refinement was carried out on a CDC CYBER 76 computer. The atomic positions of Geller & Durand (1960) were used as initial coordinates and the structure was refined in the space group *Pmnb* with full-matrix least-squares refinement. No absorption correction was applied since Mo $K\alpha$ radiation was used with a very small crystal. The atomic scattering curves used for Li^+, Mn^{2+}, Fe^{3+}, Na^+, Ca^{2+}, Mg^{2+}, P^0 and O^- were from Cromer & Mann (1968). The curve of Li was applied to the M(1) position while to the M(2) position was applied an average curve obtained from the chemical analysis with 60·3% Fe, 32·8% Mn, 3·5% Mg, 1·6% Ca and 1·8% Na. The refinement was carried out with weights assigned according to counting statistics and variable occupancy factors of the cations. One cycle of refinement with isotropic temperature factors confirmed the correctness of the olivine-type structure of ferrisicklerite. At this point two independent refinements were carried out, one with isotropic temperature factors, the other with anisotropic temperature factors for all atoms except Li, starting from the coordinates provided by the cycle of isotropic refinement. Both refinements were carried out to compare the occupancies of the cation sites so that the vacancies of these sites could be confirmed. A correction for anomalous scattering was made, with the values of $\Delta f'$ and $\Delta f''$ taken from Cromer (1965). At the end of the refinements comparison of F_o and F_c for low values of 2θ indicated no appreciable extinction and therefore no correction was applied.

After several cycles of refinement the occupancy factors of the cation sites in the isotropic and anisotropic refinements agreed within the standard errors and were, for the anisotropic refinement, M(1) = 40·8 ± 2·2%, M(2) = 98·6 ± 0·4%, P = 95·8 ± 0·4%. These results seem to indicate that the M(1) site is occupied only by Li. Moreover the partial occupancy of the P site (95·8%) confirms the substitution of the PO_4 group by the $(OH)_4$ group as suggested by Fontan *et al.* (1976) and agrees satisfactorily with the calculated occupancy (93·9%). It is surprising, however, that there is a partial occupancy of the M(2) site. This could indicate that the cations not found occupy the two other empty octahedral sites [we can name them M(3) and M(4)] present in the olivine-type structures, which can be occupied only if the tetrahedral site is only partially occupied, as occurs in this case. However, neither the three-dimensional difference Fourier synthesis nor the least-squares refinement with cations having variable occupancy at the centres of the M(3) and M(4) octahedra indicates that these sites are occupied, even to a very low degree, by any cations. Therefore, even though the lack of occupancy of the M(2) site seems to be significant ($\sim 4\sigma$) I preferred to set the occupancy at 100% because either the chemical analysis indicates a number of cations greater than that found in the refinement or the value of σ is probably underestimated (Hamilton & Abrahams, 1970).

I left the occupancy factor of the P site variable because the lack of occupancy is more significant

Table 2. *Atomic coordinates, thermal parameters* ($\beta_{ij} \times 10^4$) *and occupancy factors with their standard deviations*

The anisotropic temperature factor is defined as $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$.

	x	y	z	β_{11} or B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy (%)	B^a
M(1)^b	0·00	0·00	0·00	2·2 (5)						31·5 (2·6)	2·0 (4)
M(2)^c	0·25	0·27815 (4)	−0·03639 (9)	47 (1)	16 (1)	85 (2)	0	0	−6 (1)	100	0·63 (1)
P	0·25	0·09593 (7)	0·41110 (14)	45 (2)	12 (1)	70 (3)	0	0	−1 (1)	96·5 (0·4)	0·54 (2)
O(1)	0·25	0·11485 (23)	−0·27659 (45)	90 (6)	36 (2)	88 (7)	0	0	−5 (3)	100	1·22 (4)
O(2)	0·25	0·44926 (20)	0·17125 (49)	81 (5)	18 (2)	183 (9)	0	0	10 (3)	100	1·19 (4)
O(3)	0·04701 (26)	0·16877 (14)	0·26785 (32)	76 (4)	30 (1)	122 (5)	11 (2)	−14 (4)	4 (2)	100	1·17 (3)

(*a*) Temperature factors at the end of the isotropic refinement. (*b*) M(1) hosts 95·7% Li and 4·3% Na. (*c*) M(2) hosts 60·7% Fe^{3+}, 33·3% Mn^{2+}, 3·6% Mg, 1·7% Ca and 0·7% Fe^{2+}.

(~10σ) and because this result agrees with the chemical analysis. Na was placed in the M(1) site for the reasons discussed below.

The occupancies finally obtained are:

	X-ray refinement	Chemical analysis
M(1)	31·5 ± 2·6 %	42·1 %
P	96·5 ± 0·4	93·9 .

Table 3. *Root-mean-square thermal vibrations* (Å) *along the ellipsoid axes and angles* (°) *between the crystallographic axes and the principal axes* (U_l) *of the vibration ellipsoids, with their standard deviations*

	R.m.s.	U_la	U_lb	U_lc
M(2)	0·086 (1)	90°	30 (2)°	60 (2)°
	0·092 (1)	0	90	90
	0·104 (1)	90	60 (2)	150 (2)
P	0·079 (2)	90	8 (6)	82 (6)
	0·090 (2)	0	90	90
	0·091 (2)	90	98 (6)	8 (6)
O(1)	0·101 (4)	90	81 (5)	9 (5)
	0·126 (4)	0	90	90
	0·137 (3)	90	9 (5)	99 (5)
O(2)	0·094 (4)	90	11 (3)	101 (3)
	0·120 (4)	0	90	90
	0·148 (3)	90	79 (3)	11 (3)
O(3)	0·099 (3)	136 (4)	59 (4)	118 (5)
	0·124 (3)	73 (8)	112 (10)	151 (6)
	0·134 (3)	51 (5)	40 (7)	97 (10)

Table 4. *Bond lengths* (Å) *and angles* (°) *with their standard deviations*

P tetrahedron

P–O(1)	1·511 (2)	O(1)–P–O(2)	112·25 (13)
P–O(2)	1·524 (2)	O(1)–P–O(3)	112·15 (8) (×2)
P–O(3)	1·565 (2) (×2)	O(2)–P–O(3)	109·71 (8) (×2)
Average	1·541	O(3)–P–O(3)	100·25 (12)
O(1)–O(2)	2·520 (3)		
O(1)–O(3)	2·553 (2) (×2)		
O(2)–O(3)	2·526 (2) (×2)		
O(3)–O(3)	2·403 (3)		
Average	2·513		

M(1) octahedron

M(1)–O(1)	2·298 (2) (×2)	O(1)–M(1)–O(2)	95·53 (5) (×2)
M(1)–O(2)	2·222 (2) (×2)	O(1)–M(1)–O(2)	84·47 (5) (×2)
M(1)–O(3)	2·145 (2) (×2)	O(1)–M(1)–O(3)	82·32 (7) (×2)
Average	2·222	O(1)–M(1)–O(3)	97·68 (7) (×2)
O(1)–O(2)	3·347 (3) (×2)	O(2)–M(1)–O(3)	109·32 (7) (×2)
O(1)–O(2)	3·039 (1) (×2)	O(2)–M(1)–O(3)	70·68 (7) (×2)
O(1)–O(3)	2·926 (2) (×2)		
O(1)–O(3)	3·346 (2) (×2)		
O(2)–O(3)	2·526 (2) (×2)		
O(2)–O(3)	3·562 (2) (×2)		
Average	3·124		

M(2) octahedron

M(2)–O(1)	2·004 (2)	O(1)–M(2)–O(2)	175·01 (9)
M(2)–O(2)	1·986 (2)	O(1)–M(2)–O(3)	88·48 (7) (×2)
M(2)–O(3)	2·186 (2) (×2)	O(1)–M(2)–O(3)	87·09 (6) (×2)
M(2)–O(3)	2·063 (2) (×2)	O(2)–M(2)–O(3)	90·30 (5) (×2)
Average	2·081	O(2)–M(2)–O(3)	95·69 (7) (×2)
O(1)–O(3)	2·926 (2) (×2)	O(3)–M(2)–O(3)	66·66 (8)
O(1)–O(3)	2·802 (2) (×2)	O(3)–M(2)–O(3)	88·03 (3) (×2)
O(2)–O(3)	2·871 (2) (×2)	O(3)–M(2)–O(3)	154·41 (7) (×2)
O(2)–O(3)	3·096 (3) (×2)	O(3)–M(2)–O(3)	116·86 (9)
O(3)–O(3)	2·954 (2) (×2)		
O(3)–O(3)	3·515 (3)		
O(3)–O(3)	2·403 (3)		
Average	2·935		

At the end of the refinement the residual indices reached the values $R = 0·034$ and $wR = 0·047$ for the isotropic refinement, $R = 0·027$ and $wR = 0·033$ for the anisotropic refinement. The residual index for observed and non-observed reflexions, where the measured structure factors for the non-observed reflexions were set to zero, was $R = 0·075$.

The positional and thermal parameters are given in Tables 2 and 3, interatomic distances and bond angles in Table 4. Observed and calculated structure factors are available from the Istituto di Mineralogia dell'Università di Modena upon request and have also been deposited.*

The density calculated from the chemical analysis (3·52 g cm^{-3}) is higher than the density of 3·41 ± 0·02 g cm^{-3} measured by Fontan *et al.* (1976), who explain this discrepancy by assuming that in the transformation triphylite → ferrisicklerite the contraction of the unit cell is not accompanied by a contraction of the volume of the crystal. In this event, porosities can remain in the crystal, thus lowering the measured density. It is noteworthy that the difference between the calculated and measured densities agrees well with the difference in volume between the unit cells of triphylite and ferrisicklerite.

Discussion

Since the structure of the olivine type is well known, it will not be described here [see, for example, Geller & Durand (1960)].

The occupancy factor found for the M(1) position seems to indicate that this site is only occupied by Li. I believe, however, that Na atoms also occupy this site for two reasons: (1) The number of cations found by the chemical analysis is too high for them to occupy only the M(2) sites. The refinement indicates that the other two octahedral sites possible in a structure of the olivine type are empty. Therefore some other cations, besides Li, must occupy the M(1) site. (2) In the phosphates with an olivine-type structure the cations tend to occupy only the M(2) site and if this is not possible, owing to an excess of cations, the M(1) site is occupied by the cations with lower charge.

The interatomic distances of the M(1) polyhedron confirm this distribution. In fact the mean M(1)–O distance in lithiophilite and in triphylite is 2·16 Å whereas in ferrisicklerite it is 2·22 Å, thus indicating the presence in the M(1) site of a cation of larger radius

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31808 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

than Li. The lowering of charge at the centre of the octahedron as a consequence of the incomplete occupancy of this site seems in fact to be insufficient to explain this lengthening, the mean M(1)–O distance being 2·20 Å in heterosite where the M(1) site is empty.

The results of the refinement indicate isomorphous substitution between Mn^{2+} and Fe^{3+} in the M(2) site in spite of the strong difference in ionic radii (25%) and the simplicity of the structure. The very low value of the final residual index (R = 2·7%) and the normal values of the temperature factors leave no doubt on the subject.

The distortion of the coordination polyhedra in the structure can be explained in terms of the strong imbalance of the bond strengths to the anions. According to the Ferguson (1974) method the bond strengths to O(1) and O(2) are 1·85 and to O(3) 2·15, whereas for natrophilite they are 1·93, 1·94 and 2·06; for lithiophilite 1·90, 1·95 and 2·08; for triphylite 1·91, 1·94 and 2·07; for heterosite 1·80, 1·80 and 2·20. Ferrisicklerite is therefore an intermediate member of the group natrophilite, lithiophilite, triphylite and heterosite. In fact the variations in the O–cation distances tend to decrease the imbalance of the bond strengths but not by such a drastic amount as in heterosite, thus confirming the statement of Eventoff, Martin & Peacor (1972): 'during the oxidation and leaching of triphylite there is a gradual and continuous change in the average geometry of the (Fe, Mn)O_6 octahedron in response to charge redistribution'.

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Structures of Nitrogen-Containing Aromatic Compounds.
II. 2,5-Diphenylpyrazine

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2,5-Diphenylpyrazine is monoclinic, $P2_1/c$, $a = 13{\cdot}42$ (2), $b = 5{\cdot}73$ (1), $c = 7{\cdot}66$ (1) Å, $\beta = 93{\cdot}4$ (2)°, $Z = 2$. $R = 0{\cdot}052$ for 761 observed data (diffractometer, monochromated Mo $K\alpha$); all C and N anisotropic, 6 H included. Mean C–C in the phenyl ring is 1·386 Å (not corrected for thermal motion which is relatively large). In the pyrazine ring, C–C = 1·389, C–N = 1·336, 1·331 Å. The structure is closely isostructural with those of terphenyl and the dimer of phenyl isocyanate. A discussion is given of the solution of the structure by direct methods.

Introduction

A crystallographic study of 2,5-diphenylpyrazine was begun at the University, Glasgow, in 1948 with the aim of obtaining the bonding parameters in the pyrazine ring. The cell dimensions and space group were established but no further work was done because of the limitations of facilities and time. The availability of automatic data collection on a diffractometer and vastly improved computing facilities have now made