

The Crystal Structure of $\text{Na}_2[\text{B}_4\text{O}_6(\text{OH})_2]$

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The crystal structure of the synthetic compound $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}$, orthorhombic space group $Pbca$, $a = 8.540$ (4), $b = 10.263$, $c = 14.547$ (6) Å, was determined from single-crystal X-ray diffractometer data. The unit cell contains eight formula units. The crystal structure was solved by means of direct methods and refined by least-squares calculations to an R index of 0.050. Present in the structure are B–O chains, with repeat unit $[\text{B}_4\text{O}_6(\text{OH})_2]^{2-}$, which are the product of polymerization, by elimination of water, of the isolated polyanions $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ found in the structure of some sodium or potassium borates, e.g. borax and tincalconite. Na(1) and Na(2) are coordinated by six and seven O atoms respectively. The Na–O irregular polyhedra are connected to each other in various ways. Connexions between B–O chains are provided by Na polyhedra and by the hydrogen-bonding system to form a three-dimensional network. The crystal–chemical formula is $\text{Na}_2[\text{B}_4\text{O}_6(\text{OH})_2]$.

Introduction

The present work reports the structural study of a phase with $\text{Na}_2\text{O}:\text{B}_2\text{O}_3:\text{H}_2\text{O}$ oxide ratios 1:2:1 (hereafter named 1:2:1); it is part of a systematic investigation of hydrated sodium borates.

The only report in the literature about 1:2:1 is by Kemp (1956) and states that a phase with this composition exists in the ternary $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ system in the temperature range 115 to 200°C. However, this author does not give information about the form of the crystals nor about the powder pattern, but refers only to the British Patent 737925, 1955. A description of 1:2:1 is given by Corazza, Menchetti, Sabelli & Stoppioni (1977).

From a chemical point of view the title compound is the monohydrated phase of the series borax, tincalconite, kernite (1:2:10, 1:2:5 and 1:2:4 respectively). It therefore seemed interesting to study this crystal structure in relation to the other members of the series and also in relation to the several other anhydrous borate compounds with a ratio metal oxide to boron oxide of 1 to 2.

The present study, from which the crystal–chemical formula $\text{Na}_2[\text{B}_4\text{O}_6(\text{OH})_2]$ results, allows 1:2:1 to be classified among the *ino*-borates with two triangles and two tetrahedra in the repeat unit.

Experimental

Crystals of 1:2:1 were prepared in a pressure vessel under hydrothermal conditions at 150°C. The 1:2:1

Table 1. Crystal data

$\text{Na}_2[\text{B}_4\text{O}_6(\text{OH})_2]$	$V = 1275.0 \text{ \AA}^3$
FW 219.2	$Z = 8$
$a = 8.540$ (4) Å	$D_m = 2.226^* \text{ g cm}^{-3}$
$b = 10.263$ (4)	$D_x = 2.285$
$c = 14.547$ (6)	$\mu(\text{Mo K}\alpha) = 3.47 \text{ cm}^{-1}$
Space group $Pbca$	$F(000) = 864$

* This value is given by Kemp (1956).

phase was often associated with 3:5:4 and 2:5:5 (nasinite). Only in a few cases were well formed crystals obtained; they are almost equidimensional or slightly elongated, up to 0.5 mm. A clear prismatic crystal was chosen for the structural study.

The unit-cell dimensions were determined from the scattering angles of 25 high-angle reflexions measured on a Philips single-crystal diffractometer. The agreement between the specific gravity measured by Kemp (1956) and the calculated density is satisfactory. The space group, uniquely determined from the absences, is $Pbca$. Crystal data are given in Table 1.

Intensities were measured with a Philips PW 1100 four-circle computer-controlled diffractometer (Istituto di Mineralogia dell'Università di Perugia, Italy) with Mo $K\alpha$ radiation and the $\omega-2\theta$ scan technique. Of 1886 reflexions scanned within the range $3^\circ > \theta < 30^\circ$, only 901 were considered to be significant according to the following two criteria:

$$(I_{\text{peak}} - 2\sqrt{I_{\text{peak}}}) > I_{\text{back.}}; \quad I > 2\sigma(I).$$

Intensities were corrected for Lorentz–polarization effects; absorption was considered negligible.

Table 2. Fractional atomic coordinates ($\times 10^4$, of the hydrogen atoms $\times 10^3$) and isotropic thermal parameters

B's of the non-hydrogen atoms are the equivalent ones after Hamilton (1959).

	x	y	z	B (\AA^2)
Na(1)	9187 (2)	5444 (1)	3200 (1)	2.08
Na(2)	7931 (1)	4834 (1)	607 (1)	1.76
O(1)	4836 (2)	3315 (2)	2373 (1)	1.07
O(2)	7488 (2)	3179 (2)	1819 (1)	1.00
O(3)	5657 (2)	1405 (2)	1526 (1)	1.00
O(4)	5458 (2)	3523 (2)	774 (1)	1.13
O(5)	2974 (2)	1686 (2)	1964 (1)	1.55
O(6)	3721 (2)	1794 (2)	365 (1)	1.25
O(7)	3682 (2)	-217 (2)	1089 (2)	1.59
O(8)	4164 (3)	3520 (2)	-665 (1)	1.40
B(1)	5862 (4)	2802 (3)	1623 (2)	0.92
B(2)	4055 (4)	1156 (3)	1242 (2)	1.11
B(3)	3411 (4)	2720 (3)	2491 (3)	0.93
B(4)	4462 (4)	2938 (3)	180 (2)	1.10
H(1)	413 (3)	-77 (3)	160 (2)	6.56
H(2)	354 (3)	296 (3)	-97 (2)	4.28

Structure determination and refinement

The structure was solved with *MULTAN*. All 140 reflexions with $|E| > 1.42$ were included in the phase-determining process with eight sets of starting phases. On the first F_o Fourier map, all atoms but H were recognized. Scattering factor curves for non-hydrogen atoms were taken from *International Tables for X-ray Crystallography* (1974) and for H from Stewart, Davidson & Simpson (1965). Refinement was carried out by full-matrix least-squares techniques. A weight $1/\sqrt{\sigma}$ was given to each observed reflexion. Two cycles, with isotropic thermal parameters, led to $R = 0.072$. A further cycle of refinement with anisotropic thermal parameters reduced R to 0.056. At this stage a difference Fourier synthesis clearly revealed two maxima attributable to the H atoms. In the next and last cycle all positional and thermal parameters (isotropic for H atoms and anisotropic for B, O, and Na atoms) were allowed to vary. The final R value is 0.050 for 901 'observed' reflexions and 0.149 for all 1886 reflexions.

Positional parameters, with their standard deviations, and equivalent isotropic thermal parameters are given in Table 2.*

Discussion

The basic unit of the present structure is represented by B—O chains with repeat unit $[\text{B}_4\text{O}_6(\text{OH})_2]^{2-}$, in which

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33205 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

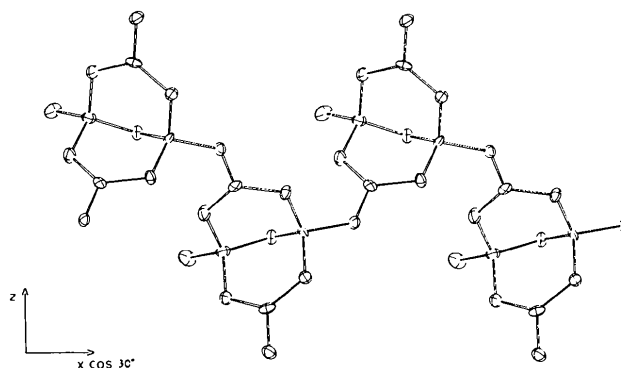


Fig. 1. B—O chain running along [100].

Table 3. Na—O, B—O bond distances, B—B distances and O—O edges of boron coordination polyhedra

Na(1)—O(5 ^v)	2.258 (2) \AA	B(1) tetrahedron	
O(1 ^{viii})	2.406 (2)	O(1)—O(2)	2.411 (3) \AA
O(8 ^{vii})	2.422 (3)	O(1)—O(3)	2.422 (3)
O(3 ^{iv})	2.635 (2)	O(1)—O(4)	2.401 (3)
O(4 ^{viii})	2.704 (2)	O(2)—O(3)	2.440 (3)
O(7 ^v)	2.749 (3)	O(2)—O(4)	2.336 (3)
Mean	2.529	O(3)—O(4)	2.442 (3)
		Mean	2.409
Na(2)—O(6 ⁱⁱ)	2.294 (2)	B(2) tetrahedron	
O(3 ^{iv})	2.420 (2)	O(3)—O(5)	2.399 (3)
O(8 ⁱ)	2.464 (3)	O(3)—O(6)	2.402 (3)
O(2)	2.482 (2)	O(3)—O(7)	2.456 (3)
O(4)	2.519 (2)	O(5)—O(6)	2.420 (3)
O(7 ⁱⁱ)	2.585 (3)	O(5)—O(7)	2.411 (3)
O(7 ^{iv})	2.981 (3)	O(6)—O(7)	2.320 (3)
Mean	2.535	Mean	2.401
B(1)—O(1)	1.498 (4)	B(3) triangle	
O(2)	1.472 (4)	O(1)—O(2 ^{ix})	2.331 (3)
O(3)	1.452 (4)	O(1)—O(5)	2.386 (3)
O(4)	1.483 (4)	O(5)—O(2 ^{ix})	2.381 (3)
Mean	1.476	Mean	2.366
B(2)—O(3)	1.454 (4)	B(4) triangle	
O(5)	1.503 (4)	O(4)—O(6)	2.390 (3)
O(6)	1.465 (4)	O(4)—O(8)	2.372 (3)
O(7)	1.463 (4)	O(6)—O(8)	2.353 (3)
Mean	1.471	Mean	2.372
B(3)—O(1)	1.374 (4)	B(1)—B(2)	2.356 (5)
O(2 ^{ix})	1.362 (4)	B(1)—B(3)	2.449 (5)
O(5)	1.363 (4)	B(1)—B(4)	2.425 (5)
Mean	1.366	B(1)—B(3 ^{viii})	2.535 (5)
B(4)—O(4)	1.356 (4)	B(2)—B(3)	2.490 (5)
O(6)	1.361 (4)	B(2)—B(4)	2.422 (5)
O(8)	1.392 (4)	B(3)—B(1 ^{ix})	2.535 (5)
Mean	1.372		

Symmetry code

None	x, y, z	(v)	1 - x, $\frac{1}{2} + y$, $\frac{1}{2} - z$
(i)	1 - x, 1 - y, -z	(vi)	1 - x, $-\frac{1}{2} + y$, $\frac{1}{2} - z$
(ii)	$\frac{1}{2} + x$, $\frac{1}{2} - y$, -z	(vii)	$\frac{1}{2} - x$, 1 - y, $\frac{1}{2} + z$
(iii)	$-\frac{1}{2} + x$, $\frac{1}{2} - y$, -z	(viii)	$\frac{1}{2} + x$, y, $\frac{1}{2} - z$
(iv)	$\frac{1}{2} - x$, $\frac{1}{2} + y$, z	(ix)	$-\frac{1}{2} + x$, y, $\frac{1}{2} - z$

there are two triangles and two tetrahedra condensed in a double-ring arrangement (see Fig. 1). According to Christ's (1960) third rule, the hydroxyl O atoms are those linked to only one B: they are O(7) and O(8) and belong to one tetrahedron and one triangle respectively.

Tables 3 and 4 report interatomic distances and angles. The average of the B—O bond distances in the tetrahedra is 1.474 Å as opposed to 1.369 Å for the triangles. This compares very well with the corresponding mean bond lengths observed in many other hydrated or anhydrous borate compounds. As usually happens, there are variations in the individual B—O bond lengths: from 1.452 to 1.503 Å and from 1.356 to 1.392 Å in tetrahedra and triangles respectively. These differences are in the right direction to remove, in part at least, the electrostatic imbalance of some O atoms.

Some of the individual O—B—O angles in triangles as well as in tetrahedra differ significantly from the corresponding ideal values. With regard to the B—O—B angles it is interesting that the angle for the O atom linking the two tetrahedra inside the group, that is B(2)—O(3)—B(1), is very small (108.4°), while the angle for the O atom linking different groups, B(1)—O(2)—B(3^{viii}), has the value 126.8°.

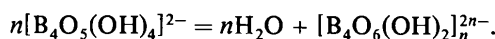
In the unit cell there are four B—O chains. They run parallel to the *a* axis and can be regarded as the first

Table 4. Bond angles (°)

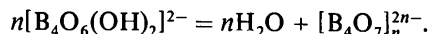
The standard deviations are: for O—Na—O 0.1°; for O—B—O 0.2°.

O(5 ^v)—Na(1)—O(1 ^{viii})	131.7	O(2)—Na(2)—O(4)	55.7
O(8 ^{vii})	107.5	O(7 ⁱⁱ)	145.4
O(3 ^{iv})	74.4	O(7 ^{iv})	88.2
O(4 ^{viii})	143.1	O(4)—Na(2)—O(7 ⁱⁱ)	112.5
O(7 ^v)	56.6	O(7 ^{iv})	141.5
O(1 ^{viii})—Na(1)—O(8 ^{vii})	120.2	O(7 ⁱⁱ)—Na(2)—O(7 ^{iv})	89.2
O(3 ^{iv})	90.4	O(1)—B(1)—O(2)	108.5
O(4 ^{viii})	55.7	O(3)	110.4
O(7 ^v)	96.5	O(4)	107.3
O(8 ^{vii})—Na(1)—O(3 ^{iv})	116.0	O(2)—B(1)—O(3)	113.1
O(4 ^{viii})	73.0	O(4)	104.5
O(7 ^v)	111.7	O(3)—B(1)—O(4)	112.6
O(3 ^{iv})—Na(1)—O(4 ^{viii})	139.9	O(3)—B(2)—O(5)	108.4
O(7 ^v)	119.1	O(6)	110.7
O(4 ^{viii})—Na(1)—O(7 ^v)	88.3	O(7)	114.7
O(6 ⁱⁱ)—Na(2)—O(3 ^{iv})	132.9	O(5)—B(2)—O(6)	109.2
O(8 ⁱ)	137.4	O(7)	108.9
O(2)	89.2	O(6)—B(2)—O(7)	104.8
O(4)	85.3	O(1)—B(3)—O(2 ^{ix})	116.9
O(7 ⁱⁱ)	56.5	O(5)	121.3
O(7 ^{iv})	81.2	O(5)—B(3)—O(2 ^{ix})	121.8
O(3 ^{iv})—Na(2)—O(8 ⁱ)	83.5	O(4)—B(4)—O(6)	123.2
O(2)	97.9	O(8)	119.3
O(4)	136.2	O(6)—B(4)—O(8)	117.4
O(7 ⁱⁱ)	107.7		
O(7 ^{iv})	52.9		
O(8 ⁱ)—Na(2)—O(2)	190.6		
O(4)	75.7		
O(7 ⁱⁱ)	96.3		
O(7 ^{iv})	135.3		

step in polymerization of the isolated [B₄O₅(OH)₄]²⁻ groups found in borax (Morimoto, 1956; Giese, 1968), in tincalconite (Giacovazzo, Menchetti & Scordari, 1973) and in the compound K₂O.2B₂O₃.4H₂O (Marezio, Plettinger & Zachariasen, 1963), according to the reaction:



The polyanion of the potassium borate is not crossed by a twofold axis as it is in the other two structures. Also in 1:2:1 the double ring does not show internal symmetry. On the other hand the 1:2:1 chains represent a degree of polymerization lower than that found in some anhydrous borates with a ratio metal oxide to boron oxide of 1 to 2. In fact, in the structure of Li₂O.2B₂O (Krogh-Moe, 1962) as well as in CdO.2B₂O₃ (Ihara & Krogh-Moe, 1966) there is a three-dimensional B—O network, with repeat unit [B₄O₇]²⁻, built up by the same polyanion found in 1:2:1. Of course there are no hydroxyl groups and each O atom is linked to two B atoms. Starting from the repeat unit of 1:2:1 the reaction is evidently:



It is interesting to note also in kernite (Giese, 1966; Cialdi, Corazza & Sabelli, 1967; Cooper, Larsen & Coppens, 1973), which has chemical composition Na₂O.2B₂O₃.4H₂O, that there are B—O chains whose repeat unit [B₄O₆(OH)₂]²⁻ is formed by the linkage of two triangles and two tetrahedra, as in 1:2:1. Nevertheless it is easy to observe from Figs. 1 and 2 that these chains are different from those found in the present structure; thus, while the transformation of borax—tincalconite into 1:2:1 involves only a simple polymerization by elimination of water, the transformation of borax—tincalconite into kernite involves a more complicated structural rearrangement, so that in kernite there is no remaining evidence of the typical double ring of borax. With regard to the crystals of 1:2:1 Kemp (1956) wrote: '...they are slowly soluble in water and smoothly rehydrate in moist air to the pentahydrate, giving no indication of the intermediate formation of a dihydrate'. This statement is in good agreement with the structural results which allow one to

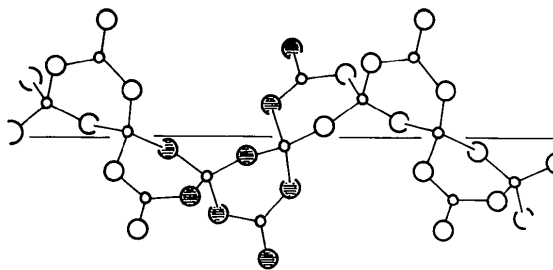


Fig. 2. B—O chain in kernite (Cialdi *et al.*, 1967). Hatched circles mark the repeat unit.

group, on the one hand, the phases 1:2:1, 1:2:5, 1:2:10 and, on the other, 1:2:4 and perhaps 1:2:2 (?). It is also evident that the crystal-chemical formula of the borate polyanion is not sufficient to represent fully the structural features: indeed in spite of the observed differences the chains of 1:2:1 and of kernite are identically formulated as $[B_4O_6(OH)_2]_n^{2n-}$. A similar situation has been recently found in the structural study of the compound $3Na_2O \cdot 5B_2O_3 \cdot 4H_2O$ (Menchetti & Sabelli, 1977). This compound, as well as the mineral heidornite (Burzlaff, 1967), is structurally characterized by B—O sheets whose repeat unit in both instances can be written as $[B_3O_8(OH)_2]^{3-}$; nevertheless in heidornite polymerization takes place in a different way with respect to 3:5:4 (Menchetti & Sabelli, 1977).

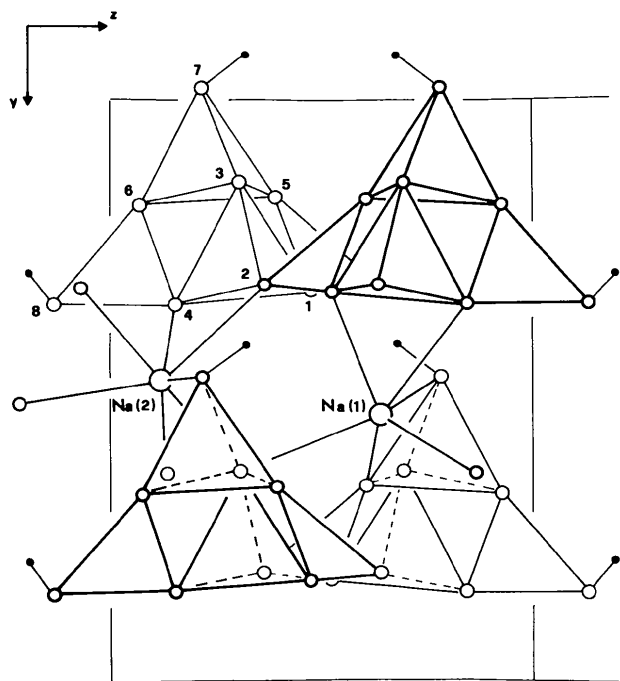


Fig. 3. The structure of $Na_2[B_4O_6(OH)_2]$ projected on (100). For clarity only half the Na atoms are shown. Atoms with numbers only are oxygens. Filled circles represent H atoms.

Both independent Na atoms exhibit an irregular coordination (see Fig. 3). Na(1) is linked to four O atoms and two hydroxyls with cation-anion distances ranging from 2.258 to 2.749 Å with a mean value of 2.529 Å. On the other hand Na(2) has seven neighbours (four O atoms and three hydroxyls) but, while six cation-anion distances form a fairly homogeneous set (2.294–2.585 Å), the seventh, $Na(2)-O(7^{iv}) = 2.981$ Å, is significantly longer than the mean value of 2.535 Å. The Na polyhedra are connected to each other in various ways; each Na(1) shares four O atoms with as many Na(2) atoms while between pairs of centrosymmetric Na(2) polyhedra there is a common edge.

Connexions between B—O chains are provided by Na atoms, each of which is linked to O atoms belonging to three different chains, so that a three-dimensional network is formed. Further connexions are also provided by the two independent hydrogen bonds. Donor-acceptor distances (see Table 5) involved in these bonds are rather long: 2.817 and 2.984 Å. However, they lie in the range of values found for hydrogen bonds.

An electrostatic valence balance was computed according to the method of Brown & Shannon (1973). For the H bonds the curve by the same authors, quoted in Donnay & Donnay (1973), was employed. Table 6 reports the contributions of different atoms and the bond-strength sums (v.u.). From these data, confirmation of the general bond system results. Three O atoms do not exhibit fourfold coordination: O(5) and O(6) have a coordination number of 3, while O(7) has five neighbours, one of which, however, makes a very weak contribution.

The computer programs used throughout this work were *MULTAN* (Germain, Main & Woolfson, 1971), *ORFLS* (Busing, Martin & Levy, 1962), *ORTEP*

Table 5. Distances (Å) and angles (°) involving hydrogen bonds

O(7)—O(1 ^{vi})	2.984 (3)	O(8)—O(2 ⁱⁱⁱ)	2.817 (3)
H(1)—O(7)	1.01 (3)	H(2)—O(8)	0.89 (3)
H(1)—O(1 ^{vi})	1.97 (3)	H(2)—O(2 ⁱⁱⁱ)	1.93 (3)
O(7)—H(1)—O(1 ^{vi})	173 (2)	O(8)—H(2)—O(2 ⁱⁱⁱ)	168 (3)

Table 6. The electrostatic valence balance (v.u.)

	Na(1)	Na(2)	B(1)	B(2)	B(3)	B(4)	H	...H	Sums
O(1)	0.20		0.71		0.98			0.13	2.02
O(2)		0.15	0.76		1.00			0.18	2.09
O(3)	0.12	0.17	0.80	0.78					1.87
O(4)	0.10	0.13	0.73			1.04			2.00
O(5)	0.29			0.69	1.02				2.00
O(6)		0.23		0.76		1.02			2.01
O(7)	0.10	0.17		0.77			0.87		1.91
O(8)	0.19	0.15				0.94	0.82		2.10

(Johnson, 1965) and the *BONDLA* bond distances and angles program from the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

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Structure Magnétique du Fluorure Antiferromagnétique MnCrF₅

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Monoclinic MnCrF₅ (*C2/c*) has been studied by neutron diffraction. It is antiferromagnetic ($T_N = 6 \pm 0.5$ K). The magnetic cell is (*a, 2b, c*). Its magnetic structure has been solved with two orthogonal antiferromagnetic sublattices. Mn²⁺ moments ($\mu = 3.9 \mu_B$) are parallel to [010]; Cr³⁺ moments ($\mu = 2.5 \mu_B$) lie along [001]. Anomalous thermal variation of some intensities leads us to propose a slight distortion of the CrF₆ octahedra in the nuclear cell. Under pulsed fields, moments take a ferromagnetic arrangement.

Les fluorures A^{II}A^{III}F₅, contenant deux cations paramagnétiques que l'on connaît actuellement sont peu nombreux: Fe₂F₅ (Brauer & Eichner, 1958), Cr₂F₅ (Sturm, 1962), MnCrF₅ (Férey, Leblanc, Jacoboni & de Pape, 1971), Cr^{III}B^{III}F₅ (Tressaud, Dance, Ravez, Portier, Hagenmuller & Goodenough, 1973) (avec B =

Al, Ti, V), et Mn₂F₅ (Tressaud & Dance, 1974). L'existence de Fe₂F₅ n'a d'ailleurs pu être confirmée (Férey *et al.*, 1971; Dance, 1974).

On sait que Cr^{II}Ti^{III}F₅ et Cr^{II}V^{III}F₅ ont un caractère ferrimagnétique lié à la configuration 3d¹ et 3d² de l'ion trivalent (Tressaud *et al.*, 1973; Dance,