Study of the Crystal Structures of Sodium Magnesium and Sodium Nickel Diphosphates

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Single-crystal X-ray crystallography studies have shown that diphosphates $Na_{3.64}Mg_{2.18}(P_2O_7)_2$ and $Na_{3.64}Ni_{2.18}(P_2O_7)_2$ crystallize with the same structural type and the same space group $P\bar{1}$. Their triclinic lattice parameters are equal to $a = 10.901$ (2), $b = 9.765$ (2), $c = 6.382$ (1) Å, $\alpha = 112.43$ (1)°, $\beta = 99.64$ (1)°, $\gamma = 107.53$ (1)°, $Z = 2$ and $a = 10.889$ (5), $b = 9.705$ (4), $c = 6.358$ (4) Å, $\alpha = 112.46$ (4)°, $\beta = 99.92$ (4)°, $\gamma = 107.54$ (4)°, $Z = 2$, respectively. The structure could be regarded as a packing of diphosphate groups $[P_2O_7]^{4-}$ and $[MO_6]$ octahedra (M = Mg, Ni) delimiting cavities and tunnels which host sodium cations. The tunnels are running along [001]. The structure is characterized by mixed (Na, M) sites with an occupation factor ratio equal to ca. 0.82/0.18. Sodium cations are located in five different sites: two cavities (one penta- and the other octa-coordinated) totally occupied and three octahedral interstices, which are partially filled by Na(3), Na(4), and Na(5) according to the respective occupation factors of 0.15, 0.42, and 0.25 for $Na_{3.64}Mg_{2.18}(P_2O_7)_2$ and 0.13, 0.40, and 0.29 in the case of $Na_{3.64}Ni_{2.18}(P_2O_7)_2$. © 2000 Academic Press

I. INTRODUCTION

In the course of a former study we resolved the crystal structures of $Na_2M^{II}P_2O_7$ (M^{II} = Co, Cu) (1–4). Our investigations have also concerned the title compounds in order the predict the structural evolution of the diphosphate family $A_2^I B^{II}P_2O_7$ versus the nature and size of the monovalent and the divalent cations A^I and B^{II}. The study of the binary system $Na_4P_2O_7$–$Mg_2P_2O_7$ has allowed Majling and Hanic to identify only one intermediate nonstoichiometric phase which was found to melt congruently at 823°C (5). Single crystals were grown and their structure was solved by Hanic and Zak who evidenced the nonstoichiometric character of their chemical composition: the ratio Na/Mg $\neq$ 2 in the determined formula $Na_7Mg_{4.5}(P_2O_7)_4$ (6). Furthermore, all our attempts to prepare single crystals of either the latter

compound or its stoichiometric composition $Na_2MgP_2O_7$, have remained unsuccessful (2). In addition, the structure of $Na_7Mg_{4.5}(P_2O_7)_4$, as solved by the former authors, is characterized by both a statistical occupancy of the proper sites of Na^+ and Mg^{2+} ions and the existence of a common site for the two cations. Although these authors have found a low value of R ($R = 0.07$), it was also established that X-ray diffraction technique, used for the structure resolution, could not allow one to distinguish between Na^+ and Mg^{2+} positions since both cations have the same electronic structure and consequently the same values of the atomic scattering factors. It then appeared obvious that the formerly reported cationic distribution within the lattice could not be considered to be highly accurate. To get sound crystallographic data for a better insight into the structural types of the title compounds-like family, we tempted to grow single crystals of the sodium magnesium diphosphate and its nickel equivalent in order to refine their structures on the basis of the new diffraction data recorded for the nickel compound. More accurate cationic distribution and location are expected, because Na^+ and Ni^{2+} atomic scattering factors are rather different. Since Mg^{2+} and Ni^{2+} cations have almost the same size $[r(Mg^{2+}) = 0.72$ Å; $r(Ni^{2+}) = 0.69$ Å] (7) and could easily replace each other, the refinement of nickel structure will normally help to localize precisely all cations in the isotypic Mg-compound lattice.
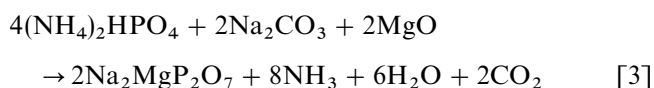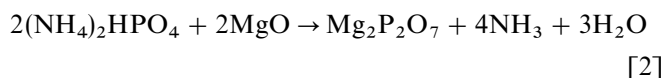
As formerly reported by Hanic and Zak, and confirmed in the course of the present study, mixed diphosphates do not seem to grow readily with the stoichiometric formula $Na_4B_2^{II}P_2O_7$ in neither of the two binary systems $Na_4P_2O_7$–$B_2^{II}P_2O_7$ (with B^{II} = Mg, Ni) investigated. The crystals we have succeded in growing in the Ni system have the nonstoichiometric formula: $Na_{3.64}Ni_{2.18}(P_2O_7)_2$. Chemical analyses, structure refinement, and analogy with the NaNi phosphate indicate a similar nonstoichiometric formula for the NaMg diphosphate. The purpose of the present article is to report on both crystal structure determinations and comparison.

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II. EXPERIMENTAL

A. Crystal Growth

The sodium magnesium diphosphate crystals. Two routes were used for the growth of single crystals of the sodium magnesium mixed diphosphate. Primarily, pulverulent starting materials were prepared by regular solid state reaction, according to one of the following chemical equations:

$$2(NH_4)_2HPO_4 + 2Na_2CO_3 \rightarrow Na_4P_2O_7 + 4NH_3$$
$$+ 3H_2O + 2CO_2 \quad [1]$$

$$2(NH_4)_2HPO_4 + 2MgO \rightarrow Mg_2P_2O_7 + 4NH_3 + 3H_2O$$
$$[2]$$

$$4(NH_4)_2HPO_4 + 2Na_2CO_3 + 2MgO$$
$$\rightarrow 2Na_2MgP_2O_7 + 8NH_3 + 6H_2O + 2CO_2 \quad [3]$$
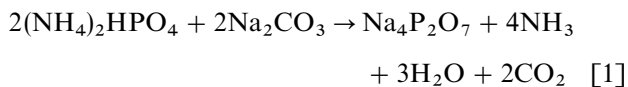
The main difference between the two procedures consists of the bath preparation: (a) in one process, a mixture of pulverulent $Na_4P_2O_7$ and $Mg_2P_2O_7$ (molar ratio of $Na_4P_2O_7/Mg_2P_2O_7 = 1$) was thoroughly ground before melting during 12 h at 800°C in a platinum crucible. The bath is then slowly cooled down to 200°C (with a rate of 5°C per hour) prior to turning off the furnace and letting the system normally reach the ambient temperature; (b) in the second method, the starting mixture consists of pulverulent $Na_2MgP_2O_7$ and $(NH_4)_2HPO_4$ (equivalent to P_2O_5 excess, acting as a flux) taken in the molar ratio $[(NH_4)_2HPO_4/Na_2MgP_2O_7] = 12.5$. These raw materials were first intimately mixed and ground in an agate mortar before being transfered into a platinum crucible for melting at 800°C over night. The bath is then slowly cooled (with a rate of $5°C\,h^{-1}$) down to room temperature.

Single crystals were found to be of a better quality when elaborated by the second procedure. An excess of diphosphorous pentaoxide seems then to improve the quality of the crystals grown from the stoichiometric composition $Na_2MgP_2O_7$, dissolved in P_2O_5 flux.

The sodium nickel diphosphate single crystals. Good quality crystals of sodium nickel diphosphate were grown from a direct melt of appropriate amounts of Na_2CO_3, NiO, $(NH_4)_2HPO_4$, corresponding to the stoichiometric formula $Na_2NiP_2O_7$. The bath is maintained during 12 h at 800°C, before proceeding to a slow cooling with a rate of $10°C\,h^{-1}$ to room temperature. The chemical formula deduced from the crystal structure resolution, $Na_{3.64}Ni_{2.18}(P_2O_7)_2$, corresponds to a nonstoichiometric compound.

The chemical analysis of the single crystals. Elemental chemical analyses were conducted using single crystals grown in both Na–Mg and Na–Ni systems (2). For each preparation, a number of crystals selected under microscope were thoroughly ground and weighed before being dissolved in acidic solutions for elemental cationic analyses:

— phosphorus amount was determined using colorimetric technique with solutions resulting from single crystals dissolved in HNO_3 (6N);

— Na and Mg (or Ni) concentrations were determined using flame spectroscopy and atomic absorption methods, respectively. The liquor analyzed in this way was obtained by dissolving another lot of crystals in HCl (20%).

— oxygen ratio is calculated theoretically by completing the cationic and anionic percentages to 100%.

These analyses give rise to the compositions $Na_{3.6}Ni_{2.3}(P_2O_7)_2$ and $Na_{3.6}Mg_{2.2}(P_2O_7)_2$, very close to the crystal chemical formulas obtained from the crystal structure refinements (Table 1).

B. X-Ray Diffraction Data Collection

Primary identification of pure phases was achieved thanks to powder X-ray diffraction patterns. The crystal structures were determined using single crystals limited by (100), (010), and (001) faces with dimensions $0.026 \times 0.080 \times 0.300$ mm³ in the case of NaMg-compound and $0.070 \times 0.0124 \times 0.0360$ mm³ for the NaNi diphosphate. Intensities of X-ray diffraction patterns were collected with a Philips PW1100 four-circle automated diffractometer using a graphite monochromatized Mo($K\alpha$) radiation ($\lambda_{Mo(K\alpha)} = 0.7107$ Å). Table 1 recapitulates the conditions of the data collection and the structure refinement results for both compounds investigated. A "Peakhunting" program has allowed to identify the unit cell from 25 independent reflections. The structure parameters were refined from 3928 and 4251 independent reflections for the sodium magnesium and sodium nickel diphosphates, respectively. Absorption corrections were performed using the analytical method of De Meulenaer and Tompa (8) while atomic scattering factors were taken from the "International Tables for X-ray Crystallography" (9). The full-matrix least-square refinements were performed using an adapted version of the SFLS-program (10). Anomalous dispersion corrections were made according to the data of Cromer and Liberman (11). Atomic coordinates and selected interatomic distances and bond angles are recapitulated in Tables 2, 3, and 4.

III. RESULTS AND DISCUSSION

A. Structure Determination

The crystal structures of the title compounds were refined with the centrosymmetric $P\bar{1}$ space group. Atomic positions given by Hanic and Zak for the sodium magnesium diphosphate (6) were used as a starting model. Concerning the sodium nickel compound, the first cycles of refinement of

TABLE 1
Crystal Data, Intensity Measurements, and Structure Refinement Parameters

Compound	$Na_{3.64}Mg_{2.18}(P_2O_7)_2$	$Na_{3.64}Ni_{2.18}(P_2O_7)_2$
Crystal data		
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Cell dimensions:		
a (Å)	10.901 (2)	10.889 (5)
b (Å)	9.765 (2)	9.705 (4)
c (Å)	6.382 (1)	6.358 (4)
α (°)	112.43 (1)	112.46 (4)
β (°)	99.64 (1)	99.92 (4)
γ (°)	107.53 (1)	107.54 (4)
Cell volume (Å^3)	567.2	555.7
Z	2	2
$D_{calc.}$ (g/cm^{-3})	2.84	3.36
D_{exp} (g/cm^{-3})	2.79 (4)	3.38 (6)
Data collection		
Equipment	Philips PW 1100	Philips PW 1000
λ [MoKα (graphite monochromator)] (Å)	0.7107	0.7107
Temperature (K)	295	295
Scan mode	ω–2Θ	ω–2Θ
Scan width (°)	1.2	1.2
θ range (°)	2–35	2–35
Standard reflections measured every 2 h (no decay)	$(1\bar{3}0)$; $(3\bar{2}\bar{1})$; $(2\bar{2}1)$	$(\bar{1}\bar{1}1)$; $(1\bar{1}1)$; $(0\bar{2}0)$
Recording reciprocal space	$-17 \le h \le +17$; $-9 \le k \le +9$; $0 \le l \le 9$	$-17 \le h \le +17$; $-9 \le k \le +9$; $0 \le l \le 9$
No. of reflections measured	4720	5104
No. of reflections [$I > 3\sigma(I)$]	4218	4566
No. of independent reflections	3928	4251
Refinement		
No. of parameters refined	235	236
$R = \sum [|F_o| - |F_c|]/\sum|F_o|$	0.030	0.025
$R_w = [\sum w(|F_o| - |F_c|)^2/\sum F_o^2]^{1/2}$ with w = 1/σ (F_o)	0.033	0.028

the nickel and phosphorus atoms, led to an R value of 0.317. Fourier difference calculations evidenced a peak whose intensity value is intermediate between those of Na and Ni. This peak is located at the site having the following coordinates: $x = 0.52$, $y = 0.21$, and $z = 0.68$. Such a site could also be attributed either to Na^+ or Ni^{2+}. At first, it was considered a mixed site (Na/Ni). Subsequent cycles of refinement of the atomic coordinates allowed the R factor to drop to 0.29. A second series of Fourier difference calculations permitted us to localize part of the sodium cations [Na (1) at $x = 0.66$, $y = 0.02$, $z = 0.09$]; Na (2) at $x = 0.89$, $y = 0.54$, $z = 0.83$] and the 14 oxygen atoms O(1) to O(14). The corresponding R value is thus found to be equal to 0.084. The remaining sodium cations were located in the same manner at the following positions: Na(3) at $(0, 0, 0)$, Na(4) at $(0.96, 0.94, 0.25)$, and Na(5) at $(0.98, 0.96, 0.10)$. Nevertheless, the occupation of all these sites could be achieved only on a statistical basis. These results are compatible with high incertitude values and large temperature factors for the partially occupied sites Na(4) and Na(5). Furthermore, the

refinement of the mixed positions of Na and Ni led to an occupancy factor of 0.18 (1) for Ni and 0.82 for Na, assuming a total occupancy of the site which astonishingly corresponds to the values required by the charge neutrality of the lattice: 0.82 Na/0.18 Ni. The chemical formula resulting from these atomic positions could then be written: $Na_{3.64}Ni_{2.18}(P_2O_7)_2$. When the anisotropic thermal factors were introduced into the refinement, R dropped to a final value of $R = 0.025$ ($Rw = 0.028$).

The same procedure was followed for the refinement of the structure of the sodium magnesium diphosphate crystal, using atomic positions of $Na_{3.64}Ni_{2.18}(P_2O_7)_2$ as starting data. The magnesium cations were located at the nickel positions. Since sodium and magnesium cations have the same electronic configuration, it was not possible to directly refine their ratio within the mixed site and the ratio was fixed as the Na/Ni refined value. After refining all atomic positions deduced from the nickel compound, the resulting chemical formula was found to be very close to that obtained from the elemental analysis of the grown crystals

Atoms	Occupancy ratio	x	y	z	B_{iso} (Å)^2
Ni (1)	1	0.21976 (2)	0.61028 (3)	0.83379 (4)	0.63 (3)
Ni (2)	1	0.26356 (2)	0.26410 (3)	0.40259 (4)	0.60 (3)
P (1)	1	0.45391 (5)	0.65644 (6)	0.73107 (9)	0.58 (2)
P (2)	1	0.68389 (5)	0.63869 (6)	0.01975 (9)	0.65 (2)
P (3)	1	0.21379 (5)	0.89342 (6)	0.31767 (10)	0.90 (2)
P (4)	1	0.96376 (5)	0.27235 (6)	0.48185 (9)	0.67 (2)
(Na; Ni)	0.82; 0.18 (1) = 1	0.5209 (1)	0.2109 (1)	0.6840 (1)	1.41 (5)
Na (1)	1	0.6623 (1)	0.0175 (2)	0.0976 (3)	2.64 (7)
Na (2)	1	0.8929 (2)	0.5441 (2)	0.8311 (3)	3.52 (9)
Na (3)	0.13 (3)	0	0	0	2.2 (6)
Na (4)	0.40 (4)	0.9520 (6)	0.9413 (4)	0.2487 (25)	5.0 (4)
Na (5)	0.29 (4)	0.9705 (7)	0.9543 (15)	0.0878 (47)	4.1 (4)
O (1)	1	0.7014 (2)	0.4813 (2)	0.9634 (3)	1.28 (8)
O (2)	1	0.4319 (2)	0.7879 (2)	0.9309 (3)	1.00 (7)
O (3)	1	0.7759 (2)	0.7439 (2)	0.9342 (4)	1.15 (8)
O (4)	1	0.1645 (2)	0.7231 (2)	0.1127 (4)	1.92 (9)
O (5)	1	0.5305 (2)	0.5770 (2)	0.8545 (3)	1.05 (7)
O (6)	1	0.1990 (2)	0.0128 (2)	0.2261 (3)	1.03 (7)
O (7)	1	0.6946 (2)	0.7376 (2)	0.2758 (3)	1.56 (7)
O (8)	1	0.0390 (2)	0.4269 (2)	0.7159 (3)	1.47 (7)
O (9)	1	0.8390 (2)	0.2723 (2)	0.3367 (3)	1.46 (7)
O (10)	1	0.0556 (2)	0.2246 (2)	0.3416 (3)	1.27 (7)
O (11)	1	0.5414 (2)	0.7231 (2)	0.6050 (3)	1.11 (7)
O (12)	1	0.3139 (1)	0.5182 (2)	0.5716 (3)	0.77 (2)
O (13)	1	0.9020 (2)	0.1245 (2)	0.5466 (3)	1.08 (7)
O (14)	1	0.3494 (2)	0.9511 (3)	0.4997 (4)	2.36 (7)

Note. $B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} \alpha_i \alpha_j$.

(Section IIA) and to that given by Hanic and Zak (6). Furthermore, Tables 3 and 5 show the correspondence between the results of our present investigations and those formerly published by these authors (6).

B. Description of the Structures

Both diphosphates $Na_{3.64}Mg_{2.18}(P_2O_7)_2$ and $Na_{3.64}Ni_{2.18}(P_2O_7)_2$ crystallize with the same structural type. Since magnesium and nickel ions play exactly the same role in both structures, our discussion will be mainly centered on the nickel compound. Some slight differences must be noticed (Tables 2 and 3) at the level of the apportionment ratios in some sites like Na(3), Na(4), and Na(5) for example. However, astonishingly the sum of the Na(3), Na(4), and Na(5) occupancy factors is the same (0.82) for the two compounds. This could be considered a clear confirmation of both the equivalent roles played by Mg(II) and Ni(II) cations in this structural type and the similar stoichiometry of the two diphosphates.

Figure 1 represents the projection of the lattice on (001). The structure could be regarded as a packing of $[P_2O_7]^{4-}$ diphosphate groups and $[MO_6]^{10-}$ octahedra, delimiting large interstices where sodium cations are located. Diphosphate anions $[P_2O_7]^{4-}$ are associated by pairs, related by inversion centers of the space group $P\bar{1}$. Owing to their orientation within the lattice, these anions could be ranged in two categories: the first type is built up from P(1) and P(2) while the second one is made of P(3) and P(4). As shown in Fig. 2a, diphosphate groups $[P(1)P(2)O_7]^{4-}$ are related through the symmetry center, located at the position (1/2, 1/2, 0). The corresponding $[PO_4]$ tetrahedra are arranged in an almost eclipsed position: dichromate structural type (12, 13). Figure 1 shows also that they tend to align along [100]. Diphosphate anions of the second type, located around the origin (0, 0, 0), have their $[PO_4]$ tetrahedra in a staggered configuration as in the thortveitite structure (12, 13).

The diphosphate groups $[P(3)P(4)O_7]^{4-}$ are packed with $[M(2)O_6]$ octahedra (M = Mg, Ni), which build up tunnels (Fig. 1) centered around the position (0, 0, 0) running along [001]. As can be seen from Fig. 2b, only Ni(2) cations are involved in the delimitation of the tunnels. The role of $[Ni(1)O_6]$ octahedra is more likely to connect two adjacent tunnels within the planes (010), through the bonds O(8)–Ni(1)–O(9) (Fig. 1). Moreover, these tunnels are hosting three types of sodium cations: Na(3), Na(4), and Na(5), all located in octahedral interstices. As shown in Tables 2, 3, and 4, the sites allotted to these cations are not totally occupied. Furthermore, Table 5 recapitulates the differences between atomic occupancy ratios determined from our investigations and those initially reported by Hanic and Zak. They represent the main structural discrepancies between our results and those formerly published by these authors for sodium magnesium diphosphates (6). The statistical distribution of Na and Mg, evidenced in the course of our investigations (Tables 3 and 5), probably result from the delocalization of Na$^+$ cations [Na(3), Na(4), and Na(5)] whose mobility is expected to be rather high in the tunnels where they might hop between many vacant sites. However, preliminary ionic conductivity experiments have not evidenced any significant superionic conductivity in this material at ca. room temperature.

C. Analysis of the Chemical Bond

The analysis of the chemical bond shows that the values of the mean anion–cation distances are compatible with those generally reported for all cations concerned.

The sodium–oxygen bonds. As expected, a close examination of the sodium–oxygen bonds (Table 4), shows that the mean values of Na–O distances are increasing with increasing coordination number of Na$^+$, except for Na(1)–O. As a matter of fact, Na(3), Na(4), and Na(5) located in octahedral sites give rise to almost the same mean

TABLE 3
Atomic Coordinates and Equivalent Isotropic Temperature Factors for the Diphosphate $Na_{3.64}Mg_{2.18}(P_2O_7)_2$

Atoms	Occupancy ratio	x	y	z	B_{iso} (Å)^2	Ions and their occupation ratio (after Ref. 6)
Mg (1)	1	0.21569 (6)	0.60898 (7)	0.8370 (1)	0.72 (3)	Mg (1) 1
Mg (2)	1	0.26377 (6)	0.26235 (7)	0.4054 (1)	0.69 (3)	Mg (2) 1
P (1)	1	0.45370 (4)	0.65669 (5)	0.73369 (7)	0.59 (2)	P (1) 1
P (2)	1	0.68356 (4)	0.63893 (5)	0.01800 (7)	0.67 (2)	P (2) 1
P (3)	1	0.21645 (5)	0.89454 (6)	0.32451 (9)	0.97 (2)	P (3) 1
P (4)	1	0.96253 (4)	0.27051 (5)	0.47758 (8)	0.70 (2)	P (4) 1
(Na; Mg)	(0.82; 0.18) = 1	0.5239 (1)	0.210 (1)	0.6798 (2)	1.54 (5)	Na (1) 1
Na (1)	1	0.6602 (1)	0.0165 (1)	0.0942 (2)	2.74 (7)	Na (3) 1
Na (2)	1	0.8842 (2)	0.5356 (2)	0.8137 (3)	4.64 (11)	Na (2) 1
Na (3)	0.15 (2)	0	0	0	3.2(7)	Mg (3) 0.5
Na (4)	0.42 (1)	0.9531 (5)	0.9396 (7)	0.2440 (20)	4.8 (4)	Na (4) 0.5
Na (5)	0.25 (3)	0.9711 (6)	0.9490 (14)	0.0951 (43)	3.9 (9)	— —
O (1)	1	0.7028 (2)	0.4842 (2)	0.9659 (3)	1.29 (8)	O (22) 1
O (2)	1	0.4319 (1)	0.7863 (2)	0.9332 (3)	1.09 (7)	O (12) 1
O (3)	1	0.7742 (1)	0.7415 (2)	0.9302 (3)	1.23 (8)	O (24) 1
O (4)	1	0.1739 (2)	0.7277 (2)	0.1243 (4)	2.46 (11)	O (31) 1
O (5)	1	0.5310 (1)	0.5779 (2)	0.8547 (3)	1.10 (7)	O (23) 1
O (6)	1	0.2005 (2)	0.0122 (2)	0.2335 (3)	1.07 (7)	O (32) 1
O (7)	1	0.6933 (2)	0.7362 (2)	0.2725 (3)	1.75 (9)	O (21) 1
O (8)	1	0.0366 (2)	0.4257 (2)	0.7074 (3)	1.39 (8)	O (41) 1
O (9)	1	0.8403 (1)	0.2710 (2)	0.3286 (1)	1.47 (8)	O (43) 1
O (10)	1	0.0560 (1)	0.2222 (2)	0.3437 (3)	1.31 (8)	O (44) 1
O (11)	1	0.5406 (1)	0.7233 (2)	0.6077 (3)	1.18 (7)	O (11) 1
O (12)	1	0.3149 (1)	0.5192 (2)	0.5768 (2)	0.81 (7)	O (13) 1
O (13)	1	0.9004 (2)	0.1255 (2)	0.5445 (3)	1.10 (7)	O (42) 1
O (14)	1	0.3509 (2)	0.9552 (3)	0.5099 (4)	2.67 (12)	O (33) 1

Note. $B_{eq} = \frac{4}{3}\sum_i\sum_j \beta_{ij}\alpha_i\alpha_j$.

bond length (equal to 2.432, 2.471, and 2.484 Å, respectively), shorter than the Na(2)–O distance of 2.625 Å. The corresponding Na(2) cation is located in an eightfold coordination sphere. The distance Na(1)–O of 2.502 Å, related to a pentacoordinated site of Na(1), seems to be exceptionnally high, although it is expected to be lower than that of an octahedral cavity. This is probably due to the fact that within the octahedral interstices, encountered in the structure (Table 4), some Na–O distances are much shorter than the ideal length (d_0[Na–O] = 2.42 Å), representing the sum of the ionic radii (r[Na$^+$] = 1.02 Å; r[O^{2-}] = 1.40 Å) given by Shannon for sodium and oxygen ions (7). As a matter of fact, the analysis of the coordination sphere of the three sodium sites concerned shows that:

— for Na(3): two Na(3)–O(10) and two Na(3)–O(6) distances are equal to 2.229 and 2.326 Å, respectively;

— for Na(4): three distances involving O(3) and O(13) are shorter than d_0[Na–O];

— for Na(5): three distances involving O(3), O(6), and O(10) are also concerned,

It should also be noted that Na–O distances shorter than the ideal length (d_0[Na–O] = 2.42 Å) are not exceptionnal. Actually, such short distances have been reported in various

compounds like $Na_4P_2O_7$, $Na_2PdP_2O_7$, α- and β-$Na_2CuP_2O_7$, and $NaLa(SeO_3)_2$ for example (4, 14–16). Moreover, all sodium coordination spheres are highly distorted, as could be deduced from the dipersion of Na–O distance values (Table 4). In that respect, the Na(3) environment seems to be more symmetrical, since there are only three different values for the six bond lengths.

For the mixed sites (Na, Ni), where the atom occupation factor is equal to the actual values of 0.82 for Na and 0.18 for Ni, the main distance (Na, Ni)–O = 2.418 Å is considered to be identical to the ideal length (d_0[Na–O] = 2.42 Å). This is compatible with the predominent occupation of this site by Na$^+$ cations (Tables 4 and 5). Furthermore, although the nickel (or magnesium) proportion in these mixed sites is rather small, the occupation of the same crystallographic sites by sodium and nickel (or Mg) is unusual. To our knowledge, the title compounds are the first diphosphate materials that evidence this type of mixed sites, statistically occupied by Na and Ni or Na and Mg cations.

b. Nickel (or magnesium)–oxygen bonds. Two different sites were evidenced for both Ni(II) and Mg(II) cations in the resolved structures. Although, Ni(1) and Ni(2) seem to

TABLE 4
Main Interatomic Distances (Å) and Bond Angles (°) for $Na_{3.64}Ni_{2.18}(P_2O_7)_2$

P(1)–O(2) = 1.533 (1)	P(2)–O(1)$_{00\bar{1}}$ = 1.510 (2)	P(3)–O(4) = 1.516 (1)	P(4)–O(8)$_{100}$ = 1.506 (1)
P(1)–O(5) = 1.585 (2)	P(2)–O(3)$_{00\bar{1}}$ = 1.530 (2)	P(3)–O(6)$_{010}$ = 1.518 (2)	P(4)–O(9) = 1.506 (2)
P(1)–O(11) = 1.503 (2)	P(2)–O(5)$_{00\bar{1}}$ = 1.604 (1)	P(3)–O(13)$_{111}$ = 1.651 (2)	P(4)–O(10)$_{100}$ = 1.511 (2)
P(1)–O(12) = 1.533 (1)	P(2)–O(7) = 1.503 (2)	P(3)–O(14) = 1.501 (1)	P(4)–O(13) = 1.627 (2)
⟨P(1)–O⟩=**1.538**	⟨P(2)–O⟩=**1.537**	⟨P(3)–O⟩=**1.546**	⟨P(4)–O⟩=**1.537**

O(2)^i–P(1)–O(5)^i = 107.14 (23)	O(1)$^i_{00\bar{1}}$–P(2)–O(3)$^i_{00\bar{1}}$ = 112.12 (28)	⟨O–P(1)–O⟩=**109.35**
O(2)^i–P(1)–O(11)^i = 113.18 (27)	O(1)$^i_{00\bar{1}}$–P(2)–O(5)$^i_{00\bar{1}}$ = 102.56 (24)	⟨O–P(2)–O⟩=**109.31**
O(2)^i–P(1)–O(12)^i = 107.49 (17)	O(1)$^i_{00\bar{1}}$–P(2)–O(7)^i = 115.99 (26)	⟨O–P(3)–O⟩=**109.23**
O(5)^i–P(1)–O(11)^i = 107.39 (26)	O(3)$^i_{00\bar{1}}$–P(2)–O(5)$^i_{00\bar{1}}$ = 106.69 (13)	⟨O–P(4)–O⟩=**109.30**
O(5)^i–P(1)–O(12)^i = 104.28 (26)	O(3)$^i_{00\bar{1}}$–P(2)–O(7)^i = 110.93 (28)	
O(11)^i–P(1)–O(12)^i = 116.57 (23)	O(5)$^i_{00\bar{1}}$–P(2)–O(7)^i = 107.58 (19)	
O(4)–P(3)–O(6)$_{010}$ = 111.54 (25)	O(8)$^i_{100}$–P(4)–O(9)^i = 112.44 (22)	
O(4)–P(3)–O(13)$^{ii}_{111}$ = 103.03 (22)	O(8)$^i_{100}$–P(4)–O(10)$^i_{100}$ = 113.17 (24)	
O(4)–P(3)–O(14)^i = 114.66 (23)	O(8)$^i_{100}$–P(4)–O(13) = 107.54 (20)	
O(6)$^i_{010}$–P(3)–O(13)$^{ii}_{111}$ = 103.66 (24)	O(9)^i–P(4)–O(10)$^i_{100}$ = 114.43 (30)	
O(6)$^i_{010}$–P(3)–O(14) = 114.91 (32)	O(9)^i–P(4)–O(13)^i = 103.43 (24)	
O(13)$^{ii}_{111}$–P(3)–O(14) = 107.60 (25)	O(10)$^i_{100}$–P(4)–O(13)^i = 104.79 (24)	
⟨P(1)–O(5)^i–P(2)$_{001}$⟩=**133.67 (22)**	⟨P(3)–O(13)^i–P(4)⟩=**125.61 (23)**	

Ni(1)–O(1)$^{ii}_{112}$ = 2.036 (2)	Ni(2)–O(3)$^{ii}_{111}$ = 2.076 (2)	(Na, Ni)–O(1)^i = 2.456 (2)
Ni(1)–O(2)^i = 2.234 (2)	Ni(2)–O(6) = 2.075 (2)	(Na, Ni)–O(2)$^{ii}_{112}$ = 2.408 (2)
Ni(1)–O(4)$^i_{001}$ = 1.996 (2)	Ni(2)–O(7)$^{ii}_{111}$ = 2.024 (2)	(Na, Ni)–O(7)$^{ii}_{111}$ = 2.577 (2)
Ni(1)–O(8)^i = 1.992 (2)	Ni(2)–O(10)^i = 2.120 (2)	(Na, Ni)–O(11)$^{ii}_{111}$ = 2.231 (2)
Ni(1)–O(9)$^{ii}_{111}$ = 2.007 (2)	Ni(2)–O(11)$^{ii}_{111}$ = 2.102 (2)	(Na, Ni)–O(14)$^{ii}_{0\bar{1}0}$ = 2.317 (2)
Ni(1)–O(12)^i = 2.157 (2)	Ni(2)–O(12)^i = 2.120 (2)	(Na, Ni)–O(14)$^{ii}_{111}$ = 2.518 (2)
⟨Ni(1)–O⟩=**2.070**	⟨Ni(2)–O⟩=**2.086**	⟨(Na, Ni)–O⟩=**2.418**

Na(1)–O(2)$^i_{0\bar{1}\bar{1}}$ = 2.510 (2)	Na(2)–O(1)^i = 2.380 (2)	Na(3)–O(3)$^i_{\bar{1}\bar{1}\bar{1}}$ = 2.741 (3) × 2	Na(5)–O(3)$^i_{00\bar{1}}$ = 2.185 (9)
Na(1)–O(2)$^{ii}_{111}$ = 2.454 (3)	Na(2)–O(3)^i = 2.574 (3)	Na(3)–O(6)^i = 2.326 (2) × 2	Na(5)–O(6)$^i_{110}$ = 2.304 (9)
Na(1)–O(6)$^{ii}_{100}$ = 2.736 (3)	Na(2)–O(4)$^i_{101}$ = 2.736 (3)	Na(3)–O(10)^i = 2.229 (2) × 2	Na(5)–O(6)$^i_{110}$ = 2.659 (23)
Na(1)–O(9)^i = 2.320 (2)	Na(2)–O(4)$^{ii}_{111}$ = 2.655 (2)	Na(4)–O(3)$^i_{00\bar{1}}$ = 2.210 (8)	Na(5)–O(10)$^i_{110}$ = 2.265 (23)
Na(1)–O(14)$^{ii}_{111}$ = 2.491 (3)	Na(2)–O(8)$^i_{100}$ = 2.285 (3)	Na(4)–O(6)$^i_{110}$ = 2.614 (9)	Na(5)–O(10)$^{ii}_{110}$ = 2.522 (23)
	Na(2)–O(8)$^i_{112}$ = 2.728 (3)	Na(4)–O(7)$^i_{110}$ = 2.983 (3)	Na(5)–O(13)$^{ii}_{211}$ = 2.967 (26)
	Na(2)–O(10)$^{ii}_{111}$ = 2.810 (3)	Na(4)–O(10)^i = 2.417 (6)	
	Na(2)–O(12)$^{ii}_{111}$ = 2.830 (3)	Na(4)–O(3)$_{110}$ = 2.326 (10)	⟨Na(3)–O⟩=**2.432**
		Na(4)–O(13)$^{ii}_{211}$ = 2.273 (11)	⟨Na(4)–O⟩=**2.471**
⟨Na(1)–O⟩=**2.502**	⟨Na(2)–O⟩=**2.625**		⟨Na(5)–O⟩=**2.484**

[a] Symmetry code (see Table 2 for the values of x, y, z). i: x y z; ii: $\bar{x}$ $\bar{y}$ $\bar{z}$.

[b] O(n)$^X_{pqr}$ represents the oxygen O(n), concerned by the above symmetry code X and the translation vector: $p\vec{a} + q\vec{b} + r\vec{c}$.

play different roles in the structure, the mean values of both Ni(1)–O and Ni(2)–O length are almost identical to the ideal distance d_0[Ni–O], representing the sum of the ionic radii (r[Ni^{2+}] = 0.69 Å; r[O^{2-}] = 1.40 Å), reported by Shannon for the two ions (7). As expected, almost the same values are found for the Mg–O bond length. The Ni–O distances are found to vary within the range [1.992–2.234] and [2.024–2.120] Å for Ni(1)–O and Ni(2)–O, respectively. Such values are close to those formerly reported for $Ni_2P_2O_7$ polymorphs (17–19). However, the mean value of Ni(2)–O bond lengths is higher than that of Ni(1)–O. This probably results from the involvement of Ni(2)–O bonds in the building of the tunnel walls while Ni(2)–O bonds, only concerned with the connection of the tunnels, are sustaining less mechanical tensions. The magnesium–oxygen bond

strengths, found in the present study are also comparable to those reported for both varieties α and β of magnesium disphosphates (20, 21).

c. Phosphorus–oxygen bonds. Due to the peculiar structure of the diphosphate anions, two types of phosphorus–oxygen bonds must be distinguished: bridging and nonbridging P–O bonds. In all tetrahedra, bridging P–O bonds are longer than the nonbridging equivalent bonds (Fig. 1; Table 4). However, it should be noted that the mean values of the P–O bonds are almost identical in the four types of tetrahedra encountered in the structure. Although the bond angles within the [PO$_4$] tetrahedra have almost the same mean value of a regular tetrahedron, perceptible distorsions of these sites are evidenced from P–O distances

TABLE 5
Atomic Occupancy Ratios for Sodium and Mixed Sites
in the Diphosphate $Na_{3.64}Mg_{2.18}(P_2O_7)_2$

Chemical formula considered Selected sites (see Table 3)	Present work $Na_{3.64}Mg_{2.18}(P_2O_7)_2$	Results reported by Hanic and Zak (Ref. 6) $Na_{3.5}Mg_{2.25}(P_2O_7)_2$
	Atom occupancy ratio	
(Na, Mg)	0.82 Na + 0.18 Mg	Na (1) : 1
Na (3)	0.15	Mg (3) : 0.5
Na (4)	0.42	Na (4) : 0.5
Na (5)	0.25	

ranging within the intervals [1.503–1.585], [1.503–1.604], [1.501–1.651], and [1.506–1.627] Å, for $[P(1)O_4]$, $[P(2)O_4]$, $[P(3)O_4]$, and $[P(4)O_4]$ tetrahedra, respectively (Table 4).

The analysis of the crystal structures of various diphosphates and their polymorphs shows a uniformity in the values of the O–P–O angles and a significant spread for the
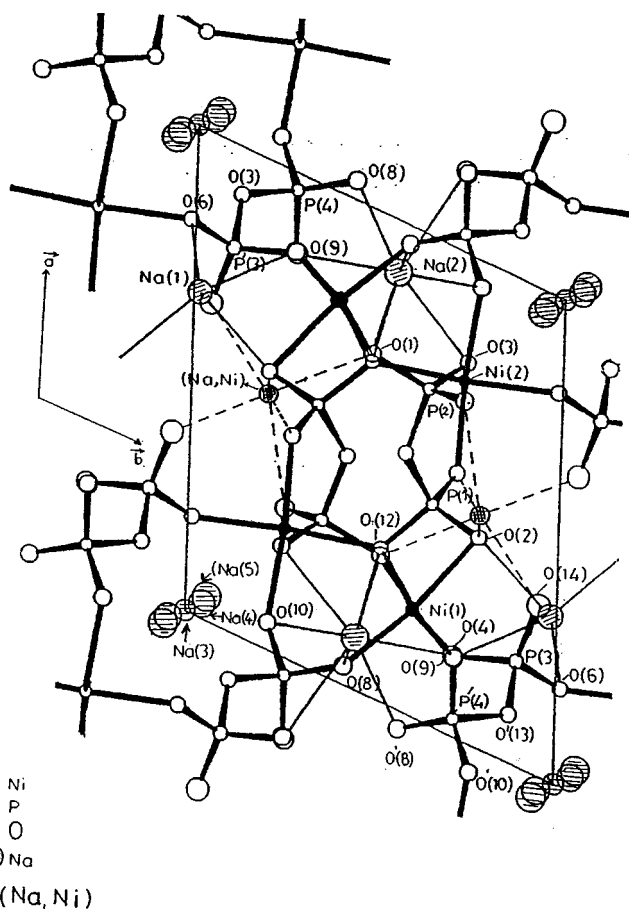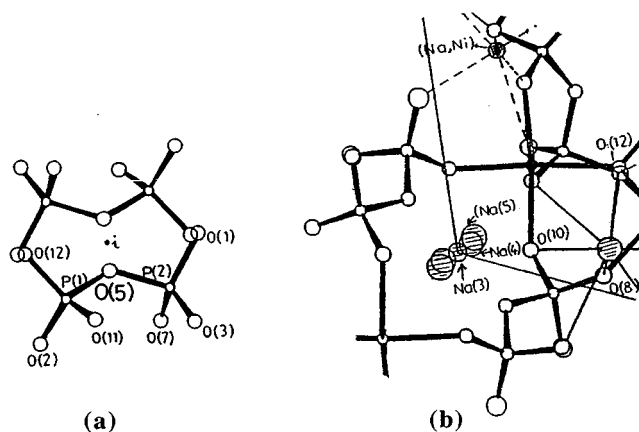

FIG. 2. Environment of different diphosphate anions $[P_2O_7]^{4-}$ in $Na_{3.64}M_{2.18}(P_2O_7)_2$ (M = Mg, Ni) structure as projected on (001): (a) symmetrical relation between diphosphate groups around the (1/2, 1/2, 0) position; (b) diphosphate groups and $[MO_6]$ octahedra (M = Mg, Ni), delimiting tunnel walls near the origin.

bridging P–O–P angles versus composition (Table 6). As discussed for the $Na_2CuP_2O_7$ compound, the chemical formula and the structural type seem to play a key role in the predetermination of the values of these angles (Table 6, Ref. 4).

D. Analysis of the Nonstoichiometry

The monovalent and divalent cations mixed disphosphates so far known can be classified in two categories: (i) the stoichiometric group identified by the general formula $A_4^I B_2^{II}(P_2O_7)_2$ (A^I = monovalent cation, B^{II} = divalent cation) and (ii) the nonstoichiometric class corresponding to the general formula $A_{4-2x}^I B_{2+x}^{II}(P_2O_7)_2$. In both categories only a few materials are structurally characterized even though many of the known stoichiometric compounds were subject to various investigations by X-ray diffraction (powder patterns or crystal symmetry determination) and vibrational spectroscopy for example (26–28). More recently, some crystal structures were solved on single crystals: e.g., $Li_2CuP_2O_7$ (29), $Li_2PdP_2O_7$ (30), $Na_2PdP_2O_7$ (15), $Na_2CoP_2O_7$ (3), $Na_2CuP_2O_7$ (1–4), and $Na_2MnP_2O_7$ (31).

The three nonstoichiometric phases so far reported are (this work, Refs. 6, 25): $Na_{3.64}Mg_{2.18}(P_2O_7)_2$ [close to the composition $Na_{3.5}Mg_{2.25}(P_2O_7)_2$ formerly reported by Hanic and Zak (6)], $Na_{3.64}Ni_{2.18}(P_2O_7)_2$ and $Na_{3.12}Fe_{2.44}(P_2O_7)_2$. All these compounds have in common a deficit of Na^+ cations and an excess of divalent cations. Their most general formula could probably suggest the existence of solid solutions of the type $A_{4-2x}^I B_{2+x}^{II}(P_2O_7)_2$, expanding over very limited extension domains. It is not yet known why these domains do not seem to encompass the stoichiometric composition $Na_2B^{II}P_2O_7$ (B = Mg, Fe, Ni).

● Ni
○ P
○ O
⊜ Na

⊛(Na, Ni)

FIG. 1. Projection of the structure of $Na_{3.64}Ni_{2.18}(P_2O_7)_2$ along [001]. Identical figure is obtained for $Na_{3.64}Mg_{2.18}(P_2O_7)_2$ when Ni is replaced by Mg in the same drawing.

TABLE 6
**Variation of [PO$_4$] Bond Angles ($^\circ$) Versus Composition and Structural Type of Diphosphate Compounds**

Chemical formula	O–P–O range	$\langle$O–P–O$\rangle$	P–O–P bridge	References
Na$_4$P$_2$O$_7$	102.4–113.5	109.32	127.5	(14)
	102.5–113.2	109.33		
Na$_4$P$_2$O$_7 \cdot$6H$_2$O	103.4–117.7		136.1	(22) (cited in Ref. 14)
Na$_4$P$_2$O$_7 \cdot$10H$_2$O	101.8–115.0		130.2	(23) (cited in Ref. 14)
α-Mg$_2$P$_2$O$_7$	103–112	109.33		
	108–113	109.33	144	(21)
β-Mg$_2$P$_2$O$_7$	103.3–113.3	109	180	(20)
β-Zn$_2$P$_2$O$_7$	102.1–112.6	108.9	180	cited in (20)
KAlP$_2$O$_7$			123	(24) (cited in Ref. 14)
Na$_2$PdP$_2$O$_7$	106.5–113.0	109.40	122	(15)
α-Na$_2$CuP$_2$O$_7$	104.68–113.62	109.34		
	105.16–112.11	109.39	118.66	(4)
β-Na$_2$CuP$_2$O$_7$	105.75–112.84	109.40	120.2	(4)
Na$_{6.24}$Fe$_{4.88}$(P$_2$O$_7$)$_4$	103.4–114.3	109.28		
	103.7–113.2	109.35	125.1	
	103.6–116.3	109.35	132	(25)
	103.0–115.2	109.33		
Na$_7$Mg$_{4.5}$(P$_2$O$_7$)$_4$	103.4–114.5			
	103.7–114.5		126.6	(6)
	104.2–116.6		133.6	
	104.3–114.6			
Na$_{3.64}$Mg$_{2.18}$(P$_2$O$_7$)$_2$	103.23–115.00	109.27		
	103.84–114.27	109.29	126.66	this work
	102.66–116.75	109.34	133.55	
	104.05–116.74	109.34		
Na$_{3.64}$Ni$_{2.18}$(P$_2$O$_7$)$_2$	102.56–116.00	109.23		
	103.03–114.91	109.30	125.61	this work
	103.43–113.17	109.31	133.67	
	104.28–116.57	109.35		

Moreover, due to complex diffraction powder patterns (triclinic symmetry), it was not easy to evidence the expansion domains of the solid solutions related to the title compounds. Although their equimolar compounds do not exist, the nonstoichiometric compositions isolated may melt congruently as reported for the phase belonging to the binary diagram Na$_4$P$_2$O$_7$–Mg$_2$P$_2$O$_7$ (5). In addition, some slight but noticeable differences between the crystal structures of the nonstoichiometric materials are to be reviewed. For example, in the sodium iron mixed diphosphate structure, the Na(3) site is occupied to a ratio of 0.882 while equivalent sodium cations are spread over three sites Na(3), Na(4), and Na(5) in both diphosphates Na$_{3.64}B^{II}_{2.18}$(P$_2$O$_7$)$_2$ (B = Mg, Ni). The randomly occupied site (Na/B) is characterized by a ratio Na/B = 0.82/0.18 for B = Mg, Ni while this ratio is equal to (0.677/0.333) = 2 in iron compound. Therefore, a cationic order Na/Fe is more likely to happen in the latter compound. However, such an order has not been reported by the authors who determined the crystal struc-

ture (25). The peculiarly low values of the room temperature ionic conductivity of the magnesium phase, found in the course of our investigations and also reported by Znasik et al. (32), could be interpreted as a confirmation of the existence of limited structural defects or at least their limited mobility in the nonstoichiometric phases examined.

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