

Crystal data and structure of $\text{Nb}_2\text{Co}(\text{P}_2\text{O}_7)_3$ and $\text{Nb}_2\text{Mg}(\text{P}_2\text{O}_7)_3$

M. T. Averbuch-Pouchot and A. Durif

Laboratoire de Cristallographie, Centre National de la Recherche Scientifique,
Laboratoire associé à l'U.S.T.M.G. 166X, 38042 Grenoble Cedex, France

Received: March 13, 1987

Inorganic dipolyphosphates / $\text{Nb}_2\text{Co}(\text{P}_2\text{O}_7)_3$ / $\text{Nb}_2\text{Mg}(\text{P}_2\text{O}_7)_3$ / Crystal structure

Abstract. Chemical preparations and crystal structures of two new diphosphates $\text{Nb}_2\text{Co}(\text{P}_2\text{O}_7)_3$ and $\text{Nb}_2\text{Mg}(\text{P}_2\text{O}_7)_3$ are reported. These two salts are isotypic, space group $P2_1/n$, $Z = 2$, cell constants: $a = 15.36(1)$, $b = 7.930(5)$, $c = 6.487(5)$ Å, $\beta = 90.51(1)^\circ$ for the magnesium salt and $a = 15.32(1)$, $b = 7.890(5)$, $c = 6.490(5)$, $\beta = 90.76(1)^\circ$ for the cobalt salt.

The crystal structures of the two compounds have been solved and refined to $R = 0.043$ with 1289 hkl for $\text{Nb}_2\text{Co}(\text{P}_2\text{O}_7)_3$ and $R = 0.023$ with 1590 hkl for $\text{Nb}_2\text{Mg}(\text{P}_2\text{O}_7)_3$. Independent NbO_6 and MgO_6 octahedra are interconnected by the P_2O_7 groups. For the magnesium salt, one observes the existence of a partial disorder between niobium and divalent atoms. This new type of structure derives clearly from that of the well-known $\text{M}^{\text{IV}}\text{P}_2\text{O}_7$ series.

Introduction

This study is part of a systematic investigation of the compounds appearing in the $\text{P}_2\text{O}_5 - \text{Nb}_2\text{O}_5 - \text{M}^{\text{II}}\text{O}$ systems. Up to now, $\text{CaNb}_2\text{O}(\text{P}_2\text{O}_7)(\text{P}_4\text{O}_{13})$ is the only example of such a phosphate. The crystal structure of this salt has been reported (Averbuch-Pouchot, 1987).

In the present work, we describe the atomic arrangements of the isotypic diphosphates $\text{Nb}_2\text{Co}(\text{P}_2\text{O}_7)_3$ and $\text{Nb}_2\text{Mg}(\text{P}_2\text{O}_7)_3$.

Chemical preparation

Crystals of $\text{Nb}_2\text{Mg}(\text{P}_2\text{O}_7)_3$ or $\text{Nb}_2\text{Co}(\text{P}_2\text{O}_7)_3$ have been prepared by introducing 0.6 g of MgCO_3 or 1.5 g of CoCO_3 and 0.75 g of Nb_2O_5 into

10 cm³ of H₃PO₄ (85%). The mixtures are heated to 773 K for a week. Crystals of the two compounds are extracted by washing out the excess of the phosphoric acid flux with hot water. The Nb₂Mg(P₂O₇)₃ crystals are colourless prisms while Nb₂Co(P₂O₇)₃ crystals are orange-coloured, a non-common colour for a cobalt salt.

Crystal data

A preliminary study of single crystals by a film technique shows the space group is $P2_1/n$ ($h0l$ with $h + l = 2n$ and $0k0$ with $k = 2n$).

Unit-cell dimensions (reported in Table 1) have been refined by a least-squares method using angular data measured with four-circle diffractometers [18 values used for Nb₂Mg(P₂O₇)₃ and 23 for Nb₂Co(P₂O₇)₃].

Crystal structure determination

All the experimental conditions used during the intensity data collections are given in Table 2.

The intensities have been corrected for Lorentz and polarization effects but no absorption correction has been applied. The crystal structure of the cobalt salt has been solved using classical methods: three-dimensional Patterson function for the localization of the niobium atoms and successive Fourier syntheses giving all the remaining atomic positions. For the magnesium salt we used for the refinement the atomic positions found for the isotopic cobalt salt. Refinements run in these conditions lead to anomalies for the thermal parameters of magnesium and niobium atoms. The temperature factor of magnesium is smaller than usually while that of niobium is slightly stronger. These results suggest that there is partial disorder between these cations whose evidence has been shown by refining the populations of the two sites.

After some refinement cycles we find the following occupancy rates

in 2(c) 1.84 Mg + 0.16 Nb

in 4(e) 3.88 Nb + 0.12 Mg

Table 1. Crystal data.

Nb ₂ Co(P ₂ O ₇) ₃	Nb ₂ Mg(P ₂ O ₇) ₃
$a = 15.32(1) \text{ \AA}$	$a = 15.36(1) \text{ \AA}$
$b = 7.890(5)$	$b = 7.930(5)$
$c = 6.490(5)$	$c = 6.487(5)$
$\beta = 90.76(1)^\circ$	$\beta = 90.51(1)^\circ$
$Z = 2$	$Z = 2$
$V = 784.4 \text{ \AA}^3$	$V = 790.0 \text{ \AA}^3$
$d_x = 3.245 \text{ g} \cdot \text{cm}^{-3}$	$d_x = 3.077 \text{ g} \cdot \text{cm}^{-3}$

Table 2. Experimental conditions used for the X-ray data collections.

	Nb ₂ Co(P ₂ O ₇) ₃	Nb ₂ Mg(P ₂ O ₇) ₃
Apparatus	Philips PW 1100	Enraf Nonius CAD4
Monochromator	graphite plate	graphite plate
Wavelength	AgK α (0.5608 \AA)	MoK α (0.7109 \AA)
Crystal size	0.16 × 0.08 × 0.08 mm ³	0.16 × 0.11 × 0.11 mm ³
Scan mode	$\Omega/2\theta$	Ω
θ -range	3–25°	3–30°
Scan width	1.20°	1.20°
Scan speed	0.02°/s	from 0.02 to 0.04°/s
Total background measurement	10 s	from 8 to 17 s
Number of independent collected reflexions	1690	2298
Intensity reference reflexions	314 and $\bar{3}\bar{1}\bar{4}$	031 and 0 $\bar{3}\bar{1}$
Orientation reference reflexions	314 and $\bar{3}\bar{1}\bar{4}$	800 and $\bar{8}00$
μ	58.16 cm ⁻¹	21.81 cm ⁻¹
$F(000)$	734	704

Under these conditions, the last refinement cycles, using anisotropic thermal parameters for all the atoms lead to a R factor of 0.023 for 1590 reflexions such that $F_{\text{obs}} > 3\sigma_F$ and of 0.042 for the complete set of 2298 data. The extinction coefficient was refined to the value of 4.3×10^{-7} .

In the case of Nb₂Co(P₂O₇)₃, 1289 reflexions have been used for the last refinement cycles ($I > 3.5\sigma_I$) leading to a final R value 0.043.

For the complete set of 1690 data this factor is 0.057. The extinction coefficient was refined to the value of 7.7×10^{-8} .

For the two structures, the formula used for the extinction correction is taken from Stout and Jensen's book (1968). All the calculations have been done using the SDP system (1977). Atomic scattering factors for neutral atoms were taken from International Tables for X-ray Crystallography, Table 2-2B (Cromer and Waber, 1974). Anomalous dispersion has been taken into account. Full-matrix refinements on F have been run using a unitary weighting scheme. Tables 3 and 4 report the final atomic coordinates for the two salts. The lists of hkl , F_{obs} , F_{cal} and of the anisotropic thermal parameters have been deposited¹.

Structure description

Figure 1 represents the projection of the atomic arrangement of Nb₂Co(P₂O₇)₃ along the b axis.

Divalent metals, located on the inversion center (0, $\frac{1}{2}$, 0) and niobium atoms are in octahedral coordinations (Tables 5 and 6). The NbO₆ and

¹ Additional material to the paper can be ordered referring to the no. CSD 52474 name(s) of the author(s) and citation of the paper at the Fachinformationszentrum Energie-Physik-Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, FRG.

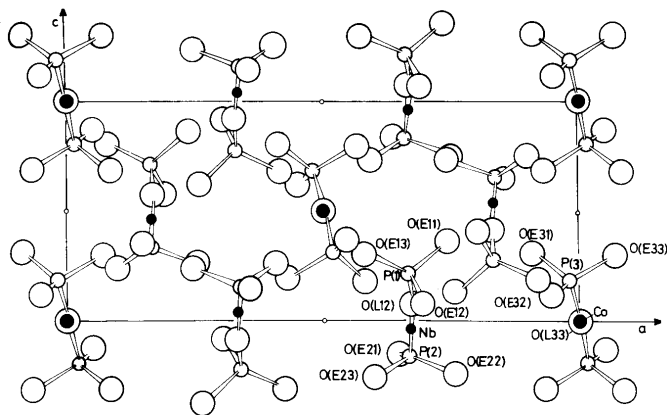
Table 3. Atomic coordinates for Nb₂Co(P₂O₇)₃. B_{eq} is defined as $B_{eq} = 4/3 \sum_i \sum_j a_i a_j \beta_{ij}$.

Atom	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$	$B_{eq}(\sigma)$
Nb	0.16612(5)	0.0227(1)	0.4611(1)	0.696(9)
Co	0	1/2	0	0.85(3)
P(1)	0.1668(2)	0.3916(3)	0.7188(4)	0.84(4)
P(2)	0.1607(2)	0.6035(3)	0.3437(4)	0.79(4)
P(3)	0.0181(2)	0.8863(3)	0.8140(4)	0.84(4)
O(E11)	0.2589(5)	0.9226(9)	0.627(1)	1.4(1)
O(E12)	0.1943(5)	0.2426(9)	0.579(1)	1.4(1)
O(E13)	0.0809(5)	0.365(1)	0.811(1)	1.5(1)
O(L12)	0.1707(5)	0.5555(8)	0.579(1)	1.4(1)
O(E21)	0.3559(5)	0.2957(9)	0.150(1)	1.6(1)
O(E22)	0.2458(5)	0.076(1)	0.242(1)	1.7(1)
O(E23)	0.0934(5)	0.5029(9)	0.238(1)	1.7(1)
O(E31)	0.4162(5)	0.483(1)	0.813(1)	1.9(1)
O(E32)	0.4521(5)	0.220(1)	0.621(1)	1.8(1)
O(E33)	0.0688(5)	0.112(1)	0.304(1)	2.5(2)
O(L33)	0	0	0	5.0(4)

Table 4. Atomic coordinates for Nb₂Mg(P₂O₇)₃. B_{eq} is defined as $B_{eq} = 4/3 \sum_i \sum_j a_i a_j \beta_{ij}$.

Atom	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$	$B_{eq}(\sigma)$
(Nb,Mg)	0.16598(2)	0.02093(4)	0.46321(5)	0.632(4)
(Mg,Nb)	0	1/2	0	0.89(2)
P(1)	0.16720(6)	0.3920(1)	0.7168(1)	0.75(1)
P(2)	0.16048(6)	0.6038(1)	0.3404(1)	0.75(1)
P(3)	0.01625(6)	0.8865(1)	0.8141(1)	0.73(1)
O(E11)	0.2573(2)	0.9228(4)	0.6338(5)	1.66(5)
O(E12)	0.1918(2)	0.2425(4)	0.5786(4)	1.39(5)
O(E13)	0.0828(2)	0.3712(4)	0.8167(5)	1.65(5)
O(L12)	0.1691(2)	0.5538(4)	0.5746(4)	1.47(5)
O(E21)	0.3534(2)	0.2949(4)	0.1500(5)	1.62(5)
O(E22)	0.2480(2)	0.0727(4)	0.2468(5)	1.74(5)
O(E23)	0.0919(2)	0.5091(4)	0.2330(5)	1.78(5)
O(E31)	0.4172(2)	0.4789(4)	0.8158(5)	2.14(6)
O(E32)	0.4551(2)	0.2183(4)	0.6218(5)	1.87(6)
O(E33)	0.0706(2)	0.1105(4)	0.3007(6)	2.49(6)
O(L33)	0	0	0	5.9(2)

M^{II}O₆ octahedra are independent. The Co—O and Mg—O mean distances are 2.062 and 2.037 Å, respectively. The means of the distances Nb—O are very close for the two salts: 1.945 Å for Nb₂Co(P₂O₇)₃ and 1.946 Å for Nb₂Mg(P₂O₇)₃. The Co—O mean distance being clearly higher than the Mg—O one can explain that for the cobalt salt, the disorder does not exist or is so small that it cannot be detected in the structure refinements.

**Fig. 1.** Projection of the atomic arrangement of Nb₂Co(P₂O₇)₃ along the *b* axis.**Table 5.** Main interatomic distances and bond angles in cation coordinations for Nb₂Co(P₂O₇)₃.

NbO ₆ octahedron						
Nb	O(E11)	O(E12)	O(E21)	O(E22)	O(E31)	O(E33)
O(E11)	1.940(4)	2.728(6)	2.690(6)	2.783(6)	2.756(6)	3.866(6)
O(E12)	89.3(2)	1.942(4)	3.898(6)	2.677(6)	2.753(6)	2.802(6)
O(E21)	87.3(2)	176.5(2)	1.957(4)	2.803(6)	2.803(6)	2.764(6)
O(E22)	91.9(2)	87.4(2)	92.2(2)	1.934(5)	3.901(6)	2.760(7)
O(E31)	89.7(2)	89.5(2)	91.1(2)	176.5(2)	1.969(4)	2.691(6)
O(E33)	176.3(2)	92.8(2)	90.7(2)	91.2(2)	87.3(2)	1.928(4)
CoO ₆ octahedron						
Co—O(E13)	2.051(4) (× 2) Å					
Co—O(E23)	2.091(4) (× 2) Å					
Co—O(E32)	2.044(4) (× 2) Å					
O(E13)—Co—O(E23)	91.9(2) and 88.1(2)°					
O(E13)—Co—O(E32)	90.8(2) and 89.2(2)°					
O(E23)—Co—O(E32)	88.3(2) and 91.7(2)°					
O(E13)—O(E23)	2.978(6) and 2.879(6) Å					
O(E13)—O(E32)	2.916(6) and 2.876(6) Å					
O(E23)—O(E32)	2.880(6) and 2.968(6) Å					

Table 6. Main interatomic distances and bond angles in cation coordinations for $\text{Nb}_2\text{Mg}(\text{P}_2\text{O}_7)_3$.

(Nb,Mg)	O(E11)	O(E12)	O(E21)	O(E22)	O(E31)	O(E33)
O(E11)	1.942(2)	2.750(4)	2.693(3)	2.780(4)	2.739(4)	3.872(6)
O(E12)	89.9(1)	1.949(2)	3.907(6)	2.687(3)	2.768(4)	2.784(4)
O(E21)	87.3(1)	176.9(1)	1.959(2)	2.783(4)	2.798(4)	2.779(4)
O(E22)	91.5(1)	87.5(1)	91.1(1)	1.939(3)	3.895(3)	2.766(4)
O(E31)	89.3(1)	90.3(1)	91.2(1)	177.6(1)	1.957(3)	2.703(4)
O(E33)	176.9(1)	91.7(1)	91.2(1)	91.2(1)	88.1(1)	1.932(3)

(Mg,Nb) O_6 octahedron

(Mg,Nb)—O(E13) 2.025(2) ($\times 2$) Å
(Mg,Nb)—O(E23) 2.060(2) ($\times 2$)
(Mg,Nb)—O(E32) 2.027(3) ($\times 2$)

O(E13)—(Mg,Nb)—O(E23) 91.1(1) and 88.9(1)
O(E13)—(Mg,Nb)—O(E32) 90.9(1) and 89.1(1)
O(E23)—(Mg,Nb)—O(E32) 88.7(1) and 91.3(1)

O(E13)—O(E23) 2.916(4) and 2.861(4) Å
O(E13)—O(E32) 2.888(4) and 2.842(4)
O(E23)—O(E32) 2.857(4) and 2.923(4)

Table 7. Main interatomic distances and bond angles in the P_2O_7 anions for $\text{Nb}_2\text{Co}(\text{P}_2\text{O}_7)_3$.

The P(1)P(2) O_7 group P(1) O_4 tetrahedron				
P(1)	O(E11)	O(E12)	O(E13)	O(L12)
O(E11)	1.525(5)	2.478(5)	2.522(6)	2.417(6)
O(E12)	107.5(2)	1.548(4)	2.511(6)	2.495(6)
O(E13)	114.8(2)	112.7(2)	1.468(4)	2.541(6)
O(L12)	102.2(2)	105.8(2)	112.9(3)	1.580(4)

P(2) O_4 tetrahedron

P(2)	O(E21)	O(E22)	O(E23)	O(L12)
O(E21)	1.538(4)	2.495(6)	2.542(6)	2.439(6)
O(E22)	107.4(3)	1.558(5)	2.533(6)	2.465(6)
O(E23)	115.6(3)	113.8(3)	1.465(4)	2.532(6)
O(L12)	102.9(2)	103.5(2)	112.4(2)	1.580(4)

P(1)—P(2) 2.954(2) Å P(1)—O(L12)—P(2) 138.3(3)°

The P(3) O_7 group
P(3) O_4 tetrahedron

P(3)	O(E31)	O(E32)	O(E33)	O(L33)
O(E31)	1.518(4)	2.489(6)	2.458(6)	2.423(6)
O(E32)	113.9(3)	1.451(5)	2.511(6)	2.462(6)
O(E33)	107.7(3)	114.9(3)	1.527(5)	2.393(6)
O(L33)	105.2(3)	111.2(3)	102.9(3)	1.532(5)

P(3)—O(L33)—P(3) 180° P(3)—P(3) 3.064(3) Å

Table 8. Main interatomic distances and bond angles in the P_2O_7 anions for $\text{Nb}_2\text{Mg}(\text{P}_2\text{O}_7)_3$.

The P(1)P(2) O_7 group P(1) O_4 tetrahedron				
P(1)	O(E11)	O(E12)	O(E13)	O(L12)
O(E11)	1.524(2)	2.472(3)	2.507(3)	2.428(3)
O(E12)	107.8(2)	1.536(2)	2.506(3)	2.493(3)
O(E13)	114.1(2)	113.3(2)	1.464(2)	2.522(3)
O(L12)	102.9(1)	106.3(1)	111.8(2)	1.581(2)

P(2) O_4 tetrahedron

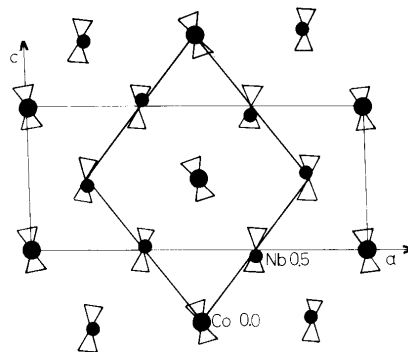
P(2)	O(E21)	O(E22)	O(E23)	O(L12)
O(E21)	1.532(3)	2.477(4)	2.531(4)	2.426(3)
O(E22)	107.5(3)	1.540(3)	2.513(4)	2.457(3)
O(E23)	115.3(2)	113.5(2)	1.465(3)	2.529(3)
O(L12)	102.7(1)	104.2(2)	112.6(2)	1.574(2)

P(1)—P(2) 2.961(1) Å P(1)—O(L12)—P(2) 140.0(2)°

The P(3) O_7 group
P(3) O_4 tetrahedron

P(3)	O(E31)	O(E32)	O(E33)	O(L33)
O(E31)	1.519(3)	2.491(4)	2.464(4)	2.427(3)
O(E32)	113.2(2)	1.464(3)	2.511(4)	2.470(3)
O(E33)	108.2(2)	114.4(2)	1.523(3)	2.390(3)
O(L33)	105.6(1)	111.3(1)	103.2(1)	1.527(3)

P(3)—P(3) 3.054(3) Å P(3)—O(L33)—P(3) 180°

**Fig. 2.** Schematic projection of the $\text{Nb}_2\text{Co}(\text{P}_2\text{O}_7)_3$ structure on the (a, c) plane. The P_2O_7 anions are represented by two triangles.

The atomic arrangements include two kinds of P_2O_7 anions. The first $P(1)P(2)O_7$ group has a common configuration, with normal bond angles and interatomic distances.

The second one $P(3)_2O_7$ has a rarer conformation. The bonding oxygen $O(L33)$ of this anion is on a symmetry center $(0,0,0)$ and so the $P(3)-O(L33)-P(3)$ angle is 180° ; the $P(3)-O(L33)$ distance is shorter and the $P(3)-P(3)$ distance higher than usual [3.064 \AA for $Nb_2Co(P_2O_7)_3$ and 3.054 \AA for $Nb_2Mg(P_2O_7)_3$].

One can remark in Table 3 or 4 that the isotropic thermal parameter of this oxygen atom is larger than those of the other oxygen atoms; this fact expresses a slight dynamic disorder around the inversion center. All the main interatomic distances and bond angles for P_2O_7 groups of the two atomic arrangement are reported in Tables 7 and 8. This structure is to be compared with that of the cubic $M^{IV}P_2O_7$ series of compounds (Levi and Peyronel, 1935). These compounds can, in fact, be considered as an NaCl packing of M^{IV} metals and P_2O_7 groups. In our case, if one refers to Figure 2 one can see clearly that the divalent metals and niobium atoms on one hand and the anionic P_2O_7 groups on the other hand form a very distorted NaCl-type lattice.

References

- Averbuch-Pouchot, M. T.: Crystal structure of a tetrapoly-dipolyphosphate: $CaNb_2O(P_4O_{13})(P_2O_7)$. *Z. Anorg. Allg. Chem.*, to be published, 1987.
- Cromer, D. T., Waber, J. T.: *International Tables for X-ray Crystallography*, Vol. IV, Table 2-2B Birmingham: The Kynoch Press, 1974.
- Levi, G. R., Peyronel, G.: Struttura cristallografica del gruppo isomorfo $(Si^{4+}, Ti^{4+}, Zr^{4+}, Sn^{4+}, Hf^{4+})P_2O_7$. *Z. Kristallogr. (A)* **92** (1935) 190–209.
- Stout, G. H., Jensen, L. H.: *X-Ray Structure Determination*, Mac Millan, 1968.
- Structure Determination Package, version RSX11M, September 1977; Enraf-Nonius.