Synthesis and Crystal Structure Determination of Cs₃Mg₂P₆O₁₇N: The First Example of a Nitrido-Oxo-Cyclohexaphosphate

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The synthesis of a new nitrido-oxo-phosphate, $Cs_3Mg_2P_6O_{17}N$, has been performed by thermal ammonolysis of a mixture of $CsPO_3$, MgO, and $NH_4H_2PO_4$, and its crystal structure was determined from single-crystal data. The unit cell is cubic [space group $Pa\bar{3}$ ($Z = 4$)] with $a = 12.239(1)$ Å. The structure consists of discrete cyclic arrangements of six $P(O,N)_4$ tetrahedra sharing two corners, thus forming large $[P_6O_{17}N]^{7-}$ macroanions. These independent cyclic units are linked together through octahedrally coordinated magnesium atoms, while cesium atoms occupy large cavities of the cyclohexaphosphate network and insure the electrical neutrality. Nitrogen atoms are randomly distributed with oxygen in a bridging P-(O,N)-P anionic position. $Cs_3Mg_2P_6O_{17}N$ is a first term of a series of nitrogen-containing cyclohexaphosphates including the isotypic cesium oxynitrides $Cs_3Fe_2P_6O_{17}N$ and $Cs_3Co_2P_6O_{17}N$. © 2000 Academic Press

Key Words: cyclohexaphosphate; oxynitride; structure.

INTRODUCTION

A new class of oxynitrides, the nitrido-oxo-phosphates, results from partial substitution of nitrogen (N^{3-}) for oxygen (O^{2-}) within a phosphate anionic network, with formation of $P(O,N)_4$ tetrahedra. Different categories of compounds are concerned, which can be either X-ray-amorphous nitrided metallophosphate compositions, as vitreous phases or high specific surface area powders, or crystalline oxynitrides. In this latter case, two types of compounds have to be distinguished depending on the number of phosphorus atoms coordinated by nitrogen in the structural arrangement:

When the nitrogen atoms are bridging between two tetrahedra (two P atoms), they play the same structural role as bridging $-O-$ oxygen atoms, the only difference being their higher negative charge. The corresponding oxynitrides, as pseudo-oxides, are directly comparable to phosphates, and

also to silicates or alumino-silicates, and the structures, like those of phosphates, are built up from tetrahedral units. The phosphorus oxynitride PON gives an illustration all the more evident of this parallelism because of the isoelectronic character of the P^{+V}/N^{-III} and Si^{+IV}/O^{-II} couples: PON is a SiO_2 analog and it crystallizes with the cristobalite-type (1, 2), quartz-type (1, 3), or moganite-type (1, 4, 5) structure.

The trivalent nitrogen atoms may also be bridging between three tetrahedra. An example is given by the nitrido-oxo-phosphate $Na_3AlP_3O_9N$ (6), in which nitrogen bonded to three P forms discrete $N(PO_3)_3$ groups. In this way, the presence of nitrogen instead of oxygen contributes to a higher degree of condensation between tetrahedra.

In the present study, we report the synthesis and structure determination of a new nitrido-oxo-phosphate, $Cs_3Mg_2P_6O_{17}N$, which belongs to the first above-mentioned category of crystalline oxynitrides. It is a first example of a nitrogen-containing cyclohexaphosphate (7).

EXPERIMENTAL PROCEDURES

$Cs_3Mg_2P_6O_{17}N$, in powder form, was commonly prepared by heating at 600°C in flowing ammonia a stoichiometric mixture of $CsPO_3$, MgO, and $NH_4H_2PO_4$. The starting polyphosphate $(CsPO_3)_n$ was obtained by reacting $CsNO_3$ with concentrated H_3PO_4 (1:1), the temperature being slowly increased up to 700°C. Instead of NH_3 as the nitriding agent, it was also possible to use a solid derivative of carbonic acid, such as melamine $(NCNH_2)_3$. Whatever procedure and proportions of the starting products, by-products were always present which were easily eliminated by dissolution in 1 N HCl. The composition $Cs_3Mg_2P_6O_{17}N$ was undoubtedly established by complete chemical analysis of a purified oxynitride powder which was brought into solution by boiling with concentrated hydrochloric acid. The results are gathered in Table 1. Figure 1 displays the corresponding X-ray diffraction powder pattern, and the observed and calculated interreticular distances

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TABLE 1
$Cs_3Mg_2P_6O_{17}N$: Analytical Results

	Calculated (wt%)	Observed (wt%)
Cs	43.38	43.3_5
Mg	5.29	5.3_4
P	20.22	20.1_7
N	1.52	1.5_8
Cs:Mg:P:N	3:2:6:1	3.00:2.02:6:1.04

Note. Cs, precipitated as $CsB(C_6H_5)_4$;
Mg, precipitated as $MgNH_4PO_4 \cdot 6H_2O$, then transformed at 900°C into $Mg_2P_2O_7$;
P, precipitated as quinolinium phosphomolybdate;
N, Kjeldahl method.

are gathered in Table 2. The value of the refined cubic parameter $a = 12.2344(6)$ Å is very close to that resulting from the single-crystal analysis.

Single crystals of $Cs_3Mg_2P_6O_{17}N$ were obtained after the powder was heated in pure nitrogen at higher temperature (800°C), where melting was observed. After slow cooling to 400°C, X-ray powder diffraction pattern showed very sharp peaks with a background increase around a Bragg angle of 12° (Cu$K\alpha$), characteristic of a mixture of crystalline and amorphous phases. A single crystal was selected from the powder and mounted on a goniometer head for structural investigation. A SEM micrograph of this crystal is shown in Fig. 2.

The unit cell determination and the intensity data collection were carried out on an Enraf-Nonius CAD 4 four-circle diffractometer with the conditions summarized in Table 3. After averaging out, 1508 unique reflections (agreement factor: 0.021) were used for the structure determination. The observed intensities were corrected for Lorentz and polarization effects. No absorption correction was applied on account of the small crystal size. The observed systematic extinctions ($0kl$: $k = 2n + 1$) were consistent with the cubic space group $Pa\bar{3}$ (No. 205).

STRUCTURE DETERMINATION

The positions of the two independent cesium atoms were determined from a Patterson map. Successive Fourier calculations allowed to locate the phosphorus, the magnesium and the three different anionic positions, all the anions being considered, in a first approach, as oxygen atoms. Refinements carried out with isotropic thermal factors for all atoms converged to $R = 0.13$ and $R_\omega = 0.20$, with high B values for the cesium position Cs1 and for one oxygen position, denoted O3. Whereas O1 and O2 correspond to terminal atoms in the PO_4 tetrahedra, this O3 position is
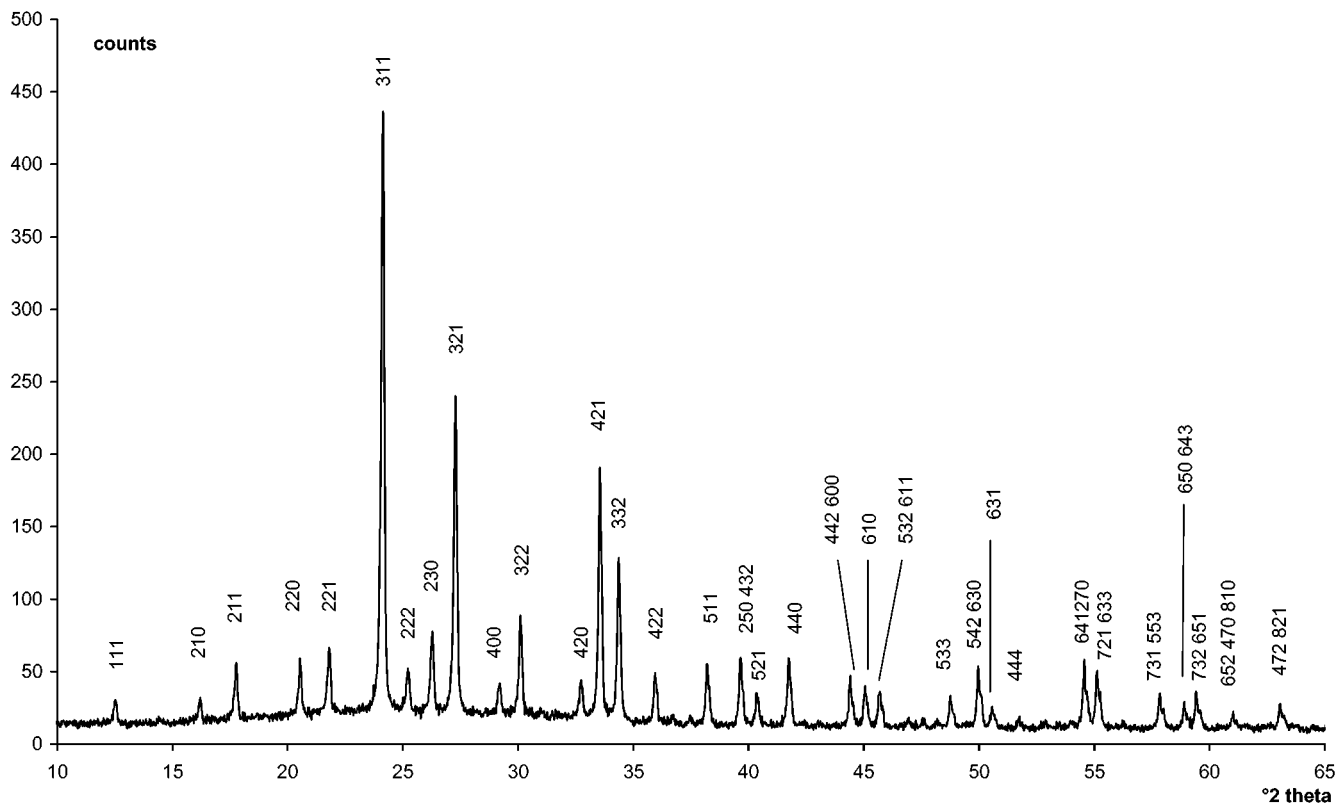
FIG. 1. X-ray diffraction diagram of $Cs_3Mg_2P_6O_{17}N$.

TABLE 2
X-Ray Powder Diffraction Data for $Cs_3Mg_2P_6O_{17}N$

h	k	l	d_{obs} (Å)	d_{calc} (Å)	I/I_0
1	1	1	7.068	7.064	4
2	1	0	5.469	5.471	4
2	1	1	4.993	4.995	9
2	2	0	4.324	4.326	9
2	2	1	4.076	4.078	11
3	1	1	3.688	3.689	100
2	2	2	3.531	3.532	6
2	3	0	3.392	3.393	13
3	2	1	3.269	3.270	53
4	0	0	3.057	3.059	5
3	2	2	2.968	2.967	17
4	2	0	2.736	2.736	6
4	2	1	2.670	2.670	42
3	3	2	2.609	2.608	27
4	2	2	2.498	2.497	8
3	3	3	2.355	2.355	10
4	3	2	2.272	2.272	11
5	2	1	2.234	2.234	5
4	4	0	2.163	2.163	11
4	4	2	2.040	2.039	8
6	1	0	2.011	2.011	7
5	3	2	1.985	1.985	5
5	3	3	1.866	1.866	5
5	4	2	1.824	1.824	10
6	3	1	1.804	1.804	4
4	4	4	1.765	1.766	2
6	4	1	1.681	1.681	11
5	5	2	1.665	1.665	9
5	5	3	1.593	1.593	6
6	4	3	1.567	1.566	5
6	5	1	1.554	1.554	6
6	5	2	1.518	1.518	2
7	4	2	1.473	1.473	4

FIG. 2. SEM micrograph of the single crystal of $Cs_3Mg_2P_6O_{17}N$ used in this study.

of this atomic position remained unsuccessful; consequently, an occupancy of 1.0 was kept. The first six oxygen neighbors are located at 3.382 Å, thus delimiting a large cage around this cesium atom; the next-shortest Cs–O distances are higher than 4.0 Å.

TABLE 3
Crystal Data, Data Collection, and Refinement Details

Formula	$Cs_3Mg_2P_6O_{17}N$
F_w (g)	919.18
Symmetry	Cubic
Space group	$Pa\bar{3}$ (No. 205)
Unit cell parameter (Å)	12.239(1)
V (Å^3)	1833.32 (6)
Data collection temperature (K)	293
Z	4
Crystal size (mm)	$0.15 \times 0.15 \times 0.17$
Radiation	$MoK\alpha$ ($\lambda = 0.71069$ Å)
Monochromator	graphite
Absorption coefficient (cm^{-1})	65.58
Scan mode	ω–2θ
Scan width (deg)	$1.0 + 0.35 \tan \theta$
Aperture (mm)	$2.0 + 0.50 \tan \theta$
θ limits (deg)	$1 < \theta < 35$
h, k, l limits	0–19
Period of intensity control (sec)	3600
No. of measured reflections	4498
No. of unique data	1508 ($831 > 3\sigma(I)$)
No. of variables	48
Extinction coefficient	2.15×10^{-7}
R	0.029
R_ω	0.042
Weighting scheme	$\omega = 4F_o^2/[\sigma^2 F_o^2 + (0.06F_o^2)^2]$
G-O-F	1.06
Max shift	0.02
Max and min residual electron density (e Å^{-3})	1.31–1.25

occupied by bridging atoms which are common to two tetrahedra.

Several solutions were possible for the location of the nitrogen atoms. They could be, in particular, either delocalized over all the three anionic positions, or located in a given position. The best convergence results of the final refinement were obtained when the four nitrogen atoms per unit cell were introduced together with oxygen in the O3 bridging position, with respective site occupancies of 0.167 for nitrogen and 0.833 for oxygen (position 24d of the space group). The position was then denoted ON. This solution is in agreement with a slight decrease in the electron site occupancy consistent with a better resolution of the site thermal factor. The last refinement cycles carried out with anisotropic thermal factors for all atoms converged to the final values $R = 0.029$ and $R_\omega = 0.042$.

The equivalent thermal factor B_{eq} of the cesium atom Cs1 remains unusually high. This fact might be due to a partial site occupancy; however, attempts at refining the occupancy

TABLE 4
Final Atomic Coordinates, B_{eq} Values,[a] and Anisotropic Displacement Parameters

Atom	Position		x	y	z	B_{eq} (Å^2)
Cs1	4b	$\bar{3}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	10.29(1)
Cs2	8c	3	0.12737(2)	x	x	1.977(2)
P	24d	1	0.18144(7)	0.54241(7)	0.34843(7)	1.19(1)
Mg	8c	3	0.30790(9)	x	x	1.242(8)
O1	24d	1	0.1418(2)	0.2798(2)	0.3283(3)	2.05(5)
O2	24d	1	0.2797(2)	0.4731(2)	0.3351(3)	1.92(5)
ON	24d	1	0.0743(3)	0.4734(3)	0.3264(5)	6.4(1)

Anisotropically Refined Displacement Parameters

Atom	$U(1,1)$	$U(2,2)$	$U(3,3)$	$U(1,2)$	$U(1,3)$	$U(2,3)$
Cs1	0.1303(4)	$U(1,1)$	$U(1,1)$	$-0.0491(3)$	$U(1,2)$	$U(1,2)$
Cs2	0.02504(7)	$U(1,1)$	$U(1,1)$	$-0.00660(7)$	$U(1,2)$	$U(1,2)$
P	0.0149(3)	0.0129(3)	0.0173(3)	$-0.0050(2)$	0.0073(3)	$-0.0071(3)$
Mg	0.0157(3)	$U(1,1)$	$U(1,1)$	$-0.0029(4)$	$U(1,2)$	$U(1,2)$
O1	0.021(1)	0.020(1)	0.037(1)	$-0.0048(9)$	$-0.006(1)$	0.004(1)
O2	0.0139(9)	0.018(1)	0.041(1)	$-0.0021(8)$	$-0.002(1)$	$-0.001(1)$
ON	0.011(1)	0.023(1)	0.212(5)	$-0.007(1)$	0.010(2)	$-0.048(2)$

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(\frac{4}{3})\sum_i\sum_j a_i a_j B_{ij}$.

The final atomic coordinates and the B_{eq} values, as well as the anisotropic refined displacement parameters, are listed in Table 4. All calculations were carried out using the Enraf-Nonius SDP programs (8). The refinements were run using full-matrix least-squares, and the figures obtained are ORTEP drawings (9).

RESULTS AND DISCUSSION

The structure of $Cs_3Mg_2P_6O_{17}N$ consists of discrete cyclic arrangements of six phosphate tetrahedra sharing two corners, as shown in Fig. 3. As the anionic P–(ON)–P bridging position is randomly occupied by oxygen and nitrogen in the ratio of 5 to 1, these cyclic units form large macroanions exhibiting the formula $[P_6O_{17}N]^{7-}$ which are centered on the 4a position of the space group. They are linked together through the magnesium atoms which are octahedrally surrounded by terminal, often called "external," oxygen atoms: 3 O1 + 3 O2 (Fig. 4). The cesium atoms occupy large cavities within the cyclohexaphosphate network and ensure the electrical neutrality. Selected bond distances and angles are listed in Table 5.

The unit cell contains four $P_6O_{17}N$ rings. The $P(O,N)_4$ tetrahedra are distorted with two short P–O$_1$ and P–O$_2$ bond lengths, 1.482 and 1.480 Å, respectively, and two larger P–ON bond lengths of 1.581 and 1.582 Å. The angles of the tetrahedron around phosphorus range from 104.3 to 118.2°.

The $P_6O_{17}N$ ring has $\bar{3}$ internal symmetry with P–P–P angles of 119.64°, a value very close to 120°. To our knowledge, $Cs_3Mg_2P_6O_{17}N$ is the first example of a cyclohexaphosphate-type compound exhibiting a practically planar ideal ring. This situation is quite different from that encountered with the known purely oxide cyclohexaphosphates in which the spread of the observed values for the P–P–P angles, in P_6O_{18} rings having 3 or $\bar{3}$ symmetry, is very large: 87.5–131.7° (10).

The P–P, P–O, and P–ON interatomic distances in $Cs_3Mg_2P_6O_{17}N$, as well as the bond angles, are similar to the values observed in P_6O_{18} rings. The presence of one nitrogen atom randomly distributed over six equivalent positions involves no extra feature, unless a large anisotropy for the ON position.
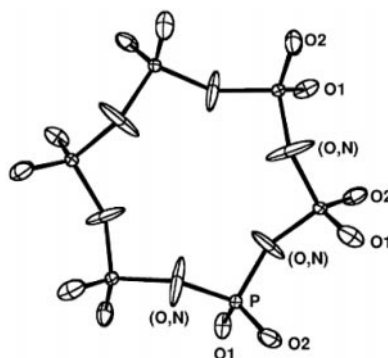

FIG. 3. The $[P_6O_{17}N]^{7-}$ cyclohexaphosphate unit viewed along the threefold axis.
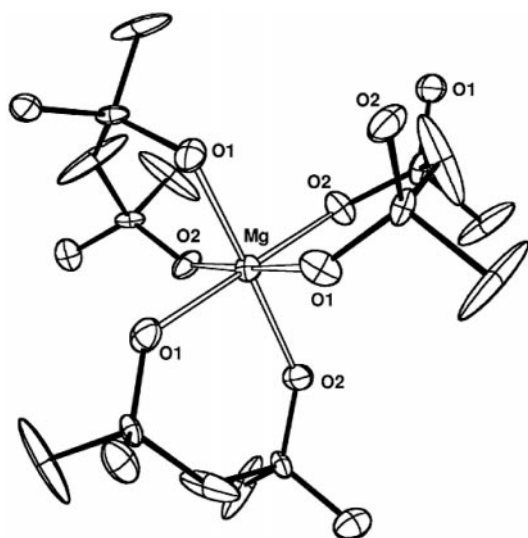
FIG. 4. Environment of the magnesium atoms.

Three different configurations occur for the anions:

- O1 is tricoordinated, by a cesium atom (Cs2), a magnesium atom, and a phosphorus atom. The bond lengths around this oxygen atom are in good agreement with ionic bonds as far as cesium and magnesium are concerned, since the values 3.090 Å (Cs2-O1) and 2.076 Å (Mg–O1) are comparable to the sum of the ionic radii: 3.14 and 2.08 Å, respectively (11). The P–O1 distance (1.482 Å) is very close to the average value of 1.481 Å

observed in condensed phosphates for external oxygen atoms (12). The nonplanarity of the O1 configuration has to be related to the sum of the bond angles (331.21°) around this atom, and this value is close to a tetrahedral configuration (328.40°).

- O2 has a distorted tetrahedral environment involving the two cesium atoms, Cs1 and Cs2, a magnesium atom, and a phosphorus atom. The oxygen–cesium distances are in this case longer than the sum of the ionic radii, thus denoting weak interactions between these atoms, while the O2–Mg (2.077 Å) and O2–P (1.480 Å) distances are very close to the values observed for O1.

- ON has a nearly planar configuration with a P–(O,N)–P angle of 137.0° and a normal Cs2–ON ionic bond length of 3.155 Å. Each ON atom connects two adjacent $P[O1O2(ON)_2]$ tetrahedra.

The magnesium atoms are located on threefold axes, and, as shown in Fig. 4, they are coordinated by three O1 and three O2 forming a regular octahedron. Only one oxygen atom per tetrahedron is bonded to a given magnesium atom; in other words, this Mg atom links together six different tetrahedra. They form three pairs of adjacent tetrahedra—each pair sharing one O1 and one O2 with Mg—and, therefore, belong to three different cyclohexaphosphate units.

The three-dimensional network made up by cyclic hexaphosphate units linked by magnesium atoms forms large cavities occupied by the cesium atoms, on threefold axes. Cs1 is surrounded by six O2 at 3.382 Å, forming a triangular

TABLE 5
Main Interatomic Distances (Å) and Bond Angles (Deg)

Atoms	Distances	Atoms	Distances	Atoms	Distances
Cs1–O2 (6×)	3.382(3)	Mg–O1 (3×)	2.076(3)	P–ON	1.582(3)
Cs2–O1 (6×)	3.090(3)	Mg–O2 (3×)	2.077(3)	P–ON[a]	1.581(3)
Cs2–O2 (3×)	3.363(3)	P–O1	1.482(3)	P–P	2.944(4)
Cs2–ON (3×)	3.155(3)	P–O2	1.480(3)		

Atoms	Angles	Atoms	Angles	Atoms	Angles
O2–Cs1–O2 (3×)	180.(0)	O2–Cs2–O2 (3×)	110.99(7)	O1–P–ON	106.0(2)
O2–Cs1–O2 (6×)	52.36(6)	O2–Cs2–ON (3×)	78.1(1)	O1–P–ON	109.9(2)
O2–Cs1–O2 (6×)	127.64(6)	O2–Cs2–ON (3×)	87.23(8)	O2–P–ON	107.3(2)
O1–Cs2–O1 (3×)	55.94(7)	O2–Cs2–ON (3×)	153.3(1)	O2–P–ON	110.4(2)
O1–Cs2–O2 (3×)	73.63(7)	ON–Cs2–ON (3×)	77.3(1)	O1–P–O2	118.2(2)
O1–Cs2–O2 (3×)	101.48(7)	O1–Mg–O2 (3×)	88.8(1)	ON–P–ON	104.3(3)
O1–Cs2–O2 (3×)	46.15(7)	O1–Mg–O1 (3×)	88.6(1)	P–O1–Mg	134.4(2)
O1–Cs2–ON (3×)	105.2(1)	O1–Mg–O2 (3×)	90.7(1)	P–O2–Mg	135.2(2)
O1–Cs2–ON (3×)	159.5(1)	O1–Mg–O2 (3×)	177.3(1)	P–ON–P	137.0(2)
O1–Cs2–ON (3×)	123.2(1)	O2–Mg–O2 (3×)	91.8(1)	P–P–P	119.64(4)

Note. Numbers in parentheses are estimated standard deviations in the least-significant digits.
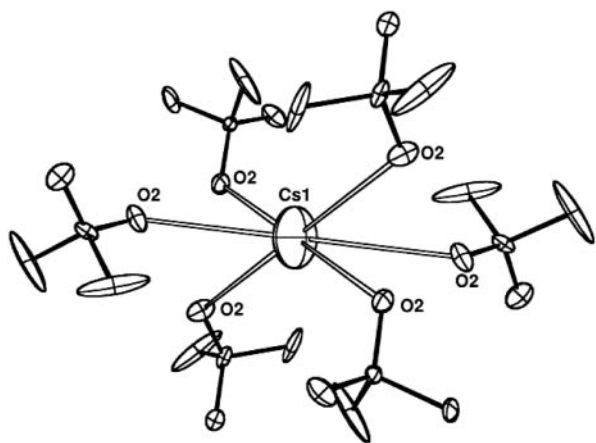[a] Denotes ON in $\frac{1}{2} - z, \frac{1}{2} + x, y$.

FIG. 5. Environment of the cesium atom Cs1.

based antiprism (Fig. 5). The next anions are located at distances higher than 4.0 Å. This large site probably allows some delocalization for this atom, in agreement with the large unusual values of the atomic thermal factor.

Cs2, also located on a threefold axis, is 9-coordinated (Fig. 6) by three ON of a cyclic unit situated at 3.155 Å under its position, according to a view along the threefold axis, three O2 at 3.363 Å, at nearly the same level, and three O1 situated above at 3.090 Å. The O1 and O2 atoms form three couples, each of which belongs to the same tetrahedron.

For large-sized cations such as cesium which often have a more or less well-defined coordination, Hoppe and Mehlhorn [13] have proposed a formula to determine the "effective coordination number" or ECoN. In $Cs_3Mg_2P_6O_{17}N$, the effective coordination number of the Cs1 atom is clearly 6, while the value calculated for the Cs2 atom is 8.28 when
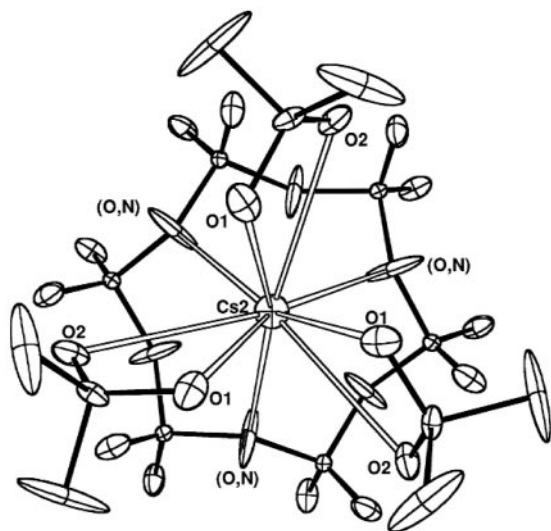
considering the 9 surrounding atoms and 8.33 if one takes into account the twelve closest neighbors. The ECoN contribution for the three extra O1 atoms located at 3.835(3) Å is very weak (0.02 each) and may be withdrawn.

As mentioned by Averbuch-Pouchot and Durif [14], the first evidence for the existence of a P_6O_{18} ring anion was reported by Thilo and Schülke in 1963 [15], and by Jost in 1965 [16] with the structure determination of $Na_6P_6O_{18} \cdot 6H_2O$. A number of cyclohexaphosphates have been since structurally characterized (for example $K_6P_6O_{18}$: space group $Pa\bar{3}$, $a = 15.753$ Å [17]), in particular compounds involving two cations beside phosphorus. Introduction of nitrogen N^{3-} instead of oxygen O^{2-} within the cyclic hexaphosphate unit gives possibilities of new compositions. $Cs_3Mg_2P_6O_{17}N$ is the first term of an oxynitride series of monovalent–divalent cation cyclohexaphosphates in which two isotypic cesium compounds, $Cs_3Fe_2^{II}P_6O_{17}N$ and $Cs_3Co_2^{II}P_6O_{17}N$ (purple-colored), have already been isolated. The cubic unit cell parameter values, a(Fe) = 12.300(1) Å and a(Co) = 12.210(1) Å, vary with respect to that of the magnesium compound, in accordance with the corresponding radii for ions in octahedral coordination [11]. Due to the charge -7 of the ring anion, the 3:2 cation stoichiometry of these oxynitrides is unique for cyclohexaphosphate-type compounds. It is worth noting that a similar stoichiometry is possible in cyclohexasilicates, the structure is made up by a skeleton of similar cyclic macroanions $[Si_6O_{18}]^{12-}$. Let us mention, for example, the beryl $Be_3Al_2Si_6O_{18}$ [18], which has a different crystal structure: the aluminum atoms, like the Mg atoms in $Cs_3Mg_2P_6O_{17}N$, are octahedrally surrounded whereas the beryllium atoms, which are very small as compared to the large cesium atoms, adopt a tetrahedral environment.

REFERENCES

1. A. Le Sauze, J. Haines, C. Chateau, J. M. Léger, and R. Marchand, *Mater. Sci. Forum* **325–326,** 77 (2000).
2. L. Boukbir, R. Marchand, Y. Laurent, P. Bacher, and G. Roult, *Ann. Chim. Fr.* **14,** 475 (1989).
3. J. M. Léger, J. Haines, L. S. de Oliveira, C. Chateau, A. Le Sauze, R. Marchand, and S. Hull, *J. Phys. Chem. Solids* **60,** 145 (1999).
4. C. Chateau, J. M. Léger, J. Haines, A. Le Sauze, and R. Marchand, *Am. Mineral.* **84,** 207 (1999).
5. J. Haines, C. Chateau, J. M. Léger, and R. Marchand, *Acta Crystallogr. B* **55,** 677 (1999).
6. R. Conanec, P. L'Haridon, W. Feldmann, R. Marchand, and Y. Laurent, *Eur. J. Solid State Inorg. Chem.* **31,** 13 (1994).
7. R. Marchand, W. Feldmann, and P. L'Haridon, Proc. 27th GDCh-Hauptversammlung, Berlin, Germany, 1999.
8. B. A. Frenz and Associates, Inc., "SDP Structure Determination Package." College Station, Texas, USA and Enraf-Nonius, Delft, The Netherlands (1985).
9. C. K. Johnson, "ORTEP II," Report ORNL-5138. Oak Ridge National Laboratory, Ridge, TN, 1976.
10. A. Durif, *in* "Crystal Chemistry of Condensed Phosphates," p. 315. Plenum Press, New York, 1995.

FIG. 6. Environment of the cesium atom Cs2.

11. R. D. Shannon, *Acta Crystallogr. A* **32,** 751 (1976).

12. A. Durif, *in* "Crystal Chemistry of Condensed Phosphates," p. 375. Plenum Press, New York, 1995.

13. R. Hoppe and B. Mehlhorn, *Z. Anorg. Allg. Chem.* **425,** 200 (1976).

14. M. T. Averbuch-Pouchot and A. Durif, *Eur. J. Solid State Inorg. Chem.* **28,** 9 (1991).

15. E. Thilo and U. Schülke, *Angew. Chem.* **75,** 1175 (1963); *Angew. Chem., Int. Ed. Engl.* **2,** 742 (1963).

16. K. H. Jost, *Acta Crystallogr.* **19,** 555 (1965).

17. M. T. Averbuch-Pouchot, *Acta Crystallogr. C* **45,** 1273 (1989).

18. W. L. Bragg and J. West, *Proc. R. Soc. London A* **111,** 691 (1926).