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Crystal Chemistry of $M^{II}Ag(PO_3)_3$ Polyphosphates for M^{II} = Zn, Co, Ni, Mg and $M^{II}_4Na_4(P_4O_{12})_3$ Tetrametaphosphates for M^{II} = Zn, Co, Ni: Crystal Structures of $ZnAg(PO_3)_3$ and $Zn_4Na_4(P_4O_{12})_3$

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The crystal chemistry of $M^{II}M^{I}(PO_3)_3$ for M^I = Na, Ag and M^{II} = Ni, Co, Mg, Zn, Mn is reexamined. All these compounds, previously described as orthorhombic pseudo-cubic salts, in fact belong to (at least) two different structural types. A first form corresponds to a cubic ($I\bar{4}3d$) tetrametaphosphate $M^{I}_4M^{II}_4(P_4O_{12})_3$; a second form is an orthorhombic long chain polyphosphate which has a unit cell closely related to the cubic one. We describe the crystal structure of the zinc–sodium salt $Na_4Zn_4(P_4O_{12})_3$ which has the cubic form with a = 14.570(Å) and Z = 4. The second structure type has been solved with the silver–zinc salt $ZnAg(PO_3)_3$, with a = 13.921, b = 10.718, c = 9.925(Å), and Z = 8; space group *Pcca*. Final R values are, respectively, 0.045 and 0.024. Chemical preparations and crystal data are given for $AgM^{II}(PO_3)_3$ with M^{II} = Zn, Co, Ni, Mg and for $Na_4M^{II}_4(P_4O_{12})_3$ with M^{II} = Zn, Co, Ni. The close relationship between the atomic arrangement of $Zn_4Na_4(P_4O_{12})_3$ and $Al_4(P_4O_{12})_3$ is discussed. The crystal structure of the long chain polyphosphate corresponds to a new type of infinite $(PO_3)_n$ chain with a period of 12 tetrahedra.

Introduction

Many papers have been written about $M^{II}M^{I}(PO_3)_3$ condensed phosphates in which M^I is Na or Ag and M^{II} is Mn, Ni, Co, Zn, Mg, Cd.

$MgAg(PO_3)_3$, $MgNa(PO_3)_3$, and the corresponding cobalt salts have been investigated by Thonnerieux *et al.* (*1*) and Rakotamahanina (*2*), $NiAg(PO_3)_3$ and $NiNa(PO_3)_3$ by Pontcharra (*3*), $CdNa(PO_3)_3$[1] and $ZnNa(PO_3)_3$ by Averbuch-Pouchot (*4, 5*). According to these authors all these compounds appear to be isotypic, crystallizing with a pseudo-cubic orthorhombic unit cell ($a \sim 14.3$ Å), the space group being $P2_12_12_1$. A crystal structure of this type of compound has never been determined. A more careful study, principally in the P_2O_5–ZnO–Na_2O and P_2O_5–ZnO–Ag_2O systems, shows the truth to be very different.

For a compound like $ZnNa(PO_3)_3$, for example, at least two crystallographic forms exist:

(a) cubic: ($I\bar{4}3d$) a_c = 14.5(Å)
(b) orthorhombic: *Pcca* (D^8_{2h}) $a \sim a_c$, $b \sim a_c/\sqrt{2}$, $c \sim a_c/\sqrt{2}$.

Thus the confusion reported in the early literature concerning these compounds can be easily explained by the close relationship

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[1] $CdAg(PO_3)_3$ has a well-established Benitoite structure type (*6*).

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between the unit cell dimensions of these two forms. It is very probable that most of the samples, mainly investigated by powder methods, were mixtures of these two forms and possibly of a third one, not yet well characterized.

The present work deals with the crystal structures of the cubic form of $ZnNa(PO_3)_3$ and the orthorhombic form of $ZnAg(PO_3)_3$. The first one appears to be a tetrametaphosphate and consequently will be denoted as $Zn_4Na_4(P_4O_{12})_3$ in this work.

Chemical Preparations

Cubic $Zn_4Na_4(P_4O_{12})_3$, $Ni_4Na_4(P_4O_{12})_3$, $Co_4Na_4(P_4O_{12})_3$, and orthorhombic $Zn\,Ag(PO_3)_3$, $CoAg(PO_3)_3$, $NiAg(PO_3)_3$ and $MgAg(PO_3)_3$ have been prepared. The chemical preparation may vary considerably from one compound to another one.

$Zn_4Na_4(P_4O_{12})_3$

The first occurrence of this salt was observed during dehydration of an hydrated form of $Na_2ZnP_4O_{12}$. At 623 K one observes the formation of a centered cubic phase coexisting with $Na_3P_3O_9$:

$$4Na_2ZnP_4O_{12} \rightarrow Zn_4Na_4(P_4O_{12})_3 + \tfrac{4}{3}\, Na_3P_3O_9.$$

Later a method for the preparation of pure samples was developed and is described below. A water solution of $Na_4P_4O_{12} \cdot 4H_2O$ is slowly passed through an ion exchange resin column. Amberlite IR.120 is commonly used. The tetrametaphosphoric acid so produced is immediately neutralized by a mixture of Na_2CO_3 and $ZnCO_3$ according to the equation

$$3\ H_4P_4O_{12} + 2\ Na_2CO_3 + 4\ ZnCO_3$$
$$Zn_4Na_4(P_4O_{12})_3 + 6\ CO_2 + 6\ H_2O$$

A large excess of ethanol is then added to the resulting solution. The precipitate is then heated for some days between 573 and 623 K. The same process has been used for the corresponding salts of nickel and cobalt.

TABLE 1

EXPERIMENTAL CONDITIONS FOR PREPARATION OF $ZnAg(PO_3)_3$, $CoAg(PO_3)_3$, AND $NiAg(PO_3)_3$ CRYSTALS

Compounds	$AgNO_3$ (mole)	$M^{II}CO_3$[a]	H_3PO_4 (mole)	T (K)	Duration (hr)
$ZnAg(PO_3)_3$	0.03	0.004	0.12	623	24
$CoAg(PO_3)_3$	0.03	0.004	0.10	623	20
$NiAg(PO_3)_3$	0.03	0.007	0.11	673	20

[a] Zinc, cobalt, and nickel carbonates are never well characterized chemically; here we report their metal equivalents, found by analysis.

Single crystals of $Zn_4Na_4(P_4O_{12})_3$ have been obtained by heating a saturated solution of this salt in monophosphoric acid at 523 K for 6 hr. After that, the excess of the phosphoric acid flux is washed out with warm water. Crystals appear as rhombic dodecahedra.

$M^{II}Ag(PO_3)_3$: $M^{II} = Zn, Ni, Co, Mg$

The Zn, Ni, and Co salts have been prepared as single crystals by using various flux concentrations. Table 1 reports details for these experiments.

The magnesium salt has been obtained in powder form by heating a stoichiometric mixture of magnesium carbonate, silver nitrate, and monohydrogeno diammonium monophosphate at 823 K.

Crystal Chemistry

For most of the title compounds, approximate unit cells, and possible space groups have been determined by single crystal film techniques. Later on unit cell dimensions were refined by using the angular data obtained from low scan speed powder diffractograms. These refined values are reported in Table 2 with some other crystal chemical data. It should be noted that unit cell dimensions reported in this table for $ZnAg(PO_3)_3$ and $Zn_4Na_4(P_4O_{12})_3$ are slightly

TABLE 2

CRYSTALLOGRAPHIC AND PHYSICAL DATA FOR $M^{II}Ag(PO_3)_3$ WITH M^{II} = Zn, Co, Ni, Ag, AND FOR $M_4^{II}Na_4(P_4O_{12})_3$ WITH M^{II} = Zn, Co, Ni.

	a(Å)	b(Å)	c(Å)	$V(Å)^3$	Z	M(g)	d_x
$ZnAg(PO_3)_3$	13.950	10.735	9.951	1490.19	8	410.15	3.656
$CoAg(PO_3)_3$	13.986	10.772	9.958	1500.24	8	403.71	3.574
$NiAg(PO_3)_3$	13.852	10.712	9.874	1465.13	8	403.49	3.658
$MgAg(PO_3)_3$	13.888	10.730	9.973	1486.16	8	369.09	3.299
$Zn_4Na_4(P_4O_{12})_3$	14.580			3099.36	4	1309.09	2.805
$Co_4Na_4(P_4O_{12})_3$	14.593			3107.66	4	1275.34	2.725
$Ni_4Na_4(P_4O_{12})_3$	14.446			3014.69	4	1274.45	2.807

different from those obtained during the four circle diffractometer data collection. These last values are given in the summary and have been used throughout the crystal structure determination, including the final calculations of interatomic distances and bond angles.

For the tetrametaphosphate series $M_4^{II}Na_4(P_4O_{12})_3$, the observed existence conditions

$$h\,k\,l \quad \text{with } h + k + l = 2n$$

$$h\,h\,l \quad \text{with } 2h + l = 4n$$

lead unambiguously to the cubic space group $I\bar{4}3d$.

For the polyphosphate series $AgM^{II}(PO_3)_3$, the conditions are

$$0\,k\,l \quad \text{with } l = 2n$$

$$h\,0\,l \quad \text{with } l = 2n$$

$$h\,k\,0 \quad \text{with } h = 2n$$

and correspond unambiguously to the orthorhombic space group *Pcca* (D_{2h}^8).

Indexed powder data for $ZnAg(PO_3)_3$ and $Ni_4Na_4(P_4O_{12})_3$ are reported in Tables 3 and 4.

TABLE 3

INDEXED POWDER DIAGRAM OF $ZnAg(PO_3)_3$

h k l	$d_{cal.}$	$d_{obs.}$	$I_{obs.}$	h k l	$d_{cal.}$	$d_{obs.}$	$I_{obs.}$
0 1 1	7.30	—	—	3 3 1	2.727	2.726	3
2 0 0	6.97	—	—	0 4 0	2.684	2.682	2
1 1 1	6.47	6.46	8	2 3 2	2.682		
2 1 0	5.85	5.85	20	3 1 3	2.619	2.618	2
0 2 0	5.37	5.37	2	2 2 3	2.616		
2 1 1	5.04	5.04	30	5 1 1	2.606	—	—
0 0 2	4.98	4.97	62	1 4 1	2.548	—	—
1 0 2	4.69	4.69	13	4 2 2	2.521	2.522	79
1 2 1	4.47	—	—	2 4 0	2.505	—	—
1 1 2	4.29	4.29	2	4 3 0	2.497	—	—
2 2 0	4.25	—	—	0 0 4	2.488	2.488	17
2 0 2	4.05	—	—	3 3 2	2.464	2.464	1
3 1 1	3.922	3.917	2	1 0 4	2.449	—	—
2 2 1	3.911			5 0 2	2.433		
2 1 2	3.790	3.789	100	0 3 3	2.433	2.432	3
0 2 2	3.649	3.649	80	2 4 1	2.429		
1 2 2	3.530	3.529	13	4 3 1	2.422	—	—
4 0 0	3.487	3.487	26	3 2 3	2.412	—	—
3 0 2	3.397	3.398	10	5 2 1	2.402	—	—
0 3 1	3.367	—	—	1 3 3	2.396	—	—
4 1 0	3.317	3.315	2	1 1 4	2.388	2.388	1
3 2 1	3.314			5 1 2	2.373	—	—
1 3 1	3.273	3.274	9	0 4 2	2.362	2.361	26
3 1 2	3.239	3.241	7	4 1 3	2.345	—	—
2 2 2	3.233	—	—	2 0 4	2.343	—	—
2 3 0	3.184	3.185	4	1 4 2	2.329	—	—
0 1 3	3.169	—	—	6 0 0	2.325	—	—
4 1 1	3.147	—	—	2 3 3	2.297	2.296	14
1 1 3	3.090	3.091	3	2 1 4	2.289	—	—
2 3 1	3.032	3.033	6	6 1 0	2.272	—	—
4 2 0	2.924	2.926	20	3 4 1	2.263	—	—
2 1 3	2.885	2.886	15	0 2 4	2.257	—	—
3 2 2	2.871	—	—	2 4 2	2.237	—	—
4 0 2	2.856	—	—	4 3 2	2.232	—	—
1 3 2	2.844	—	—	1 2 4	2.228	2.227	7
4 2 1	2.806	—	—	5 2 2	2.216	2.217	14
1 2 3	2.766	—	—	6 1 1	2.215		
4 1 2	2.760	—	—				

Notes. The X-ray data have been run on a Philips–Norelco diffractometer operating with copper $K\alpha$-radiation at a low scan speed ($\frac{1}{8}$°(Θ)/min). Reported intensities are peak heights above the background.

Crystal Structure Determinations

Technical parameters concerning the X-ray diffraction data collections are reported

TABLE 4

INDEXED POWDER DIAGRAM OF $Zn_4Na_4(P_4O_{12})_3$ (EXPERIMENTAL CONDITIONS ARE SIMILAR TO THOSE DESCRIBED IN TABLE 3)

h k l	$d_{cal.}$	$d_{obs.}$	$I_{obs.}$	*h k l*	$d_{cal.}$	$d_{obs.}$	$I_{obs.}$
2 1 1	5.90	5.91	68	6 2 0	2.284	2.287	6
2 2 0	5.11	5.12	100	5 4 1	2.229	2.233	12
3 1 0	4.57	4.58	20	6 3 1	2.130	—	—
3 2 1	3.861	3.867	28	4 4 4	2.085	2.086	4
4 0 0	3.612	3.615	44	5 4 3 7 1 0	2.043	2.043	16
4 2 0	3.230	3.235	<1	6 4 0	2.003	—	—
3 3 2	3.080	3.084	12	6 3 3 5 5 2 7 2 1	1.966	1.966	20
4 2 2	2.949	2.952	54	6 4 2	1.931	1.931	12
4 3 1 5 1 0	2.833	2.836	16	7 3 0	1.897	—	—
5 2 1	2.638	—	—	7 3 2 6 5 1	1.835	1.835	16
4 4 0	2.554	2.557	44				
5 3 0	2.478	2.480	48				
6 1 1 5 3 2	2.343	2.346	12				

in Table 5. Lorentz and polarization corrections were applied but in view of the short wavelengths, no absorption correction was applied. In both cases a unitary weighting scheme has been used throughout the process of crystal structure determination.

(A) $Zn_4Na_4(P_4O_{12})_3$

Before starting the structure determination, we noticed the strong analogy between this salt and aluminium tetrametaphosphate, studied earlier by Pauling *et al.* (*7*). This structure type was later refined by Bagieu-Beucher *et al.* (*8*) on the isotypic scandium salt $Sc_4(P_4O_{12})_3$. Their common space group is $I\bar{4}3d$ and their cubic unit cell dimensions are close to 14 Å:

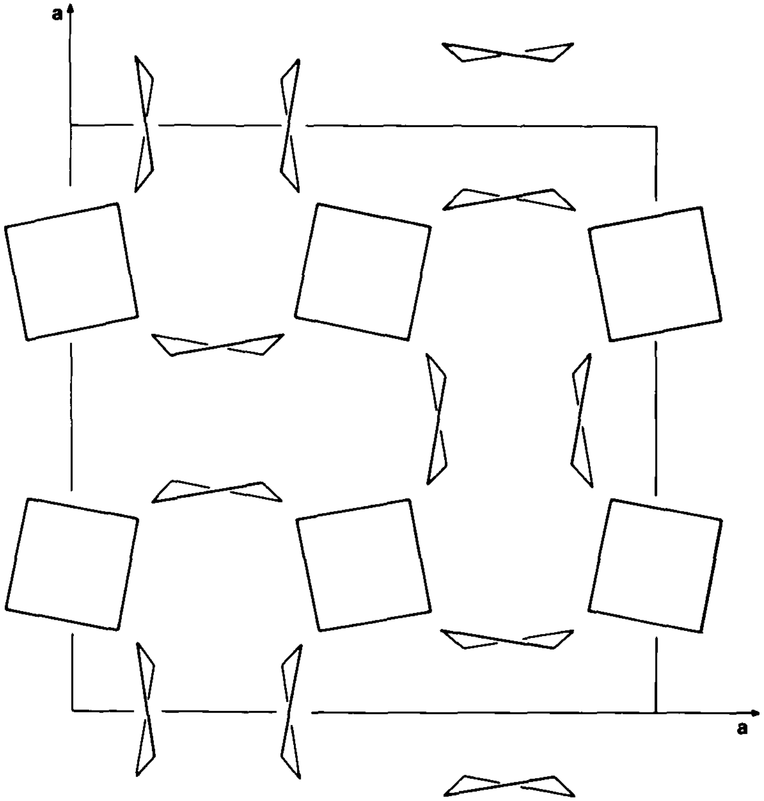

FIG. 1. Schematic representation of the P_4O_{12} ring anions in $Zn_4Na_4(P_4O_{12})_3$. Only P–P bonds are figurated.

TABLE 5

EXPERIMENTAL CONDITIONS USED DURING THE X-RAY DATA COLLECTIONS FOR $ZnAg(PO_3)_3$ AND $Zn_4Na_4(P_4O_{12})_3$

	$Zn_4Na_4(P_4O_{12})_3$	$ZnAg(PO_3)_3$
Apparatus	Philips PW 1100	Enraf Nonius CAD 4
Monochromator	Graphite plate	Graphite plate
Wavelength	Mo*Kα* (0.7107)	Ag*Kα* (0.5608)
Scan mode	$\omega/2\theta$	ω
Scan speed (°/sec)	0.02	from 0.01 to 0.03
Total background measurement (sec)	20	from 20 to 60
Scan width (°)	1.20	1.20
Theta range (°)	3–30	3–25
Intensity reference reflections	080; 008	$12.\bar{2}.0$; 840
Number of collected reflections	485	2649
Crystal size (mm)	0.16 × 0.16 × 0.21	0.13 × 0.13 × 0.13
μ(cm^{-1})	39.7	33.9

$a = 13.730$ Å for $Al_4(P_4O_{12})_3$

$a = 14.363$ Å for $Sc_4(P_4O_{12})_3$

$a = 14.570$ Å for $Zn_4Na_4(P_4O_{12})_3$.

These analogies suggest that the two atomic arrangements could be very similar, the zinc atoms having the same location as the aluminium atoms, while the sodium atoms might occupy the octahedral vacancies observed in the crystal structure of $Al_4(P_4O_{12})_3$.

The crystal structure determination only partly confirms these assumptions. Direct least squares refinements using as initial coordinates those found for the scandium salt did not converge, so that the structure determination was resumed by using the classical method of successive Fourier syntheses.

For the final refinement cycles 68 reflections have been rejected of the original set of 485 *hkl*: 64 corresponded to $F_{obs} < \sqrt{5}\sigma_F$ and 4 corresponded to $||F_{obs}| - |F_{cal}|| > 80$ in a F scale ranging from 0 to 2915. The final R value for the remaining 417 reflections is 0.045. The final atomic coordinates are reported in Table 6 while anisotropic thermal factors are given in Table 7. A table of structure factors is available from the author.

(*B*) $ZnAg(PO_3)_3$

Again this structure has been solved by using classical methods; study of the three-dimensional Patterson function followed by successive Fourier syntheses. After some refinement iterations the final R value is 0.024 for a set of 1703 reflections corresponding to the rejection of 946 reflections according to the following criteria: 935 re-

TABLE 6

ATOMIC PARAMETERS AND B_{eq} OF $Zn_4Na_4(P_4O_{12})_3$ ($B_{eq.} = \frac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i\mathbf{a}_j$)

Atoms	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$	$B_{eq.}$
Zn	0.2350(2)	0.2350(2)	0.2350(2)	1.45(8)
P	0.3281(1)	0.3914(1)	0.1140(1)	0.68(4)
Na	0.1097(8)	0.1097(8)	0.1097(8)	0.63(3)
O(E1)	0.0837(4)	0.0532(4)	0.4182(4)	0.94(7)
O(E2)	0.4767(4)	0.1096(4)	0.3838(4)	0.92(7)
O(L)	0.2240(4)	0.4217(4)	0.0984(4)	0.88(6)

TABLE 7

ANISOTROPIC THERMAL PARAMETERS OF $Zn_4Na_4(P_4O_{12})_3$ ($T = \beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl$)

Atoms	$\beta_{11}(\sigma)$	$\beta_{22}(\sigma)$	$\beta_{33}(\sigma)$	$\beta_{12}(\sigma)$	$\beta_{13}(\sigma)$	$\beta_{23}(\sigma)$
Zn	0.00080(5)	0.00080(5)	0.00080(5)	0.0000(1)	0.0000(1)	0.0000(1)
P	0.00082(5)	0.00089(6)	0.00051(5)	−0.0002(1)	−0.0002(1)	0.0001(1)
Na	0.0017(3)	0.0017(3)	0.0017(3)	−0.0007(6)	−0.0007(6)	−0.0007(6)
O(E1)	0.0012(2)	0.0007(2)	0.0014(2)	0.0006(3)	0.0008(4)	0.0007(4)
O(E2)	0.0012(2)	0.0011(2)	0.0010(2)	0.0000(4)	−0.0011(4)	0.0001(3)
O(L)	0.0009(2)	0.0009(2)	0.0013(2)	0.0002(4)	−0.0003(4)	−0.0002(4)

flections with $F_0 < \sqrt{6}\sigma_F$ and 11 with $||F_o| - |F_c|| > 175$ in a F scale ranging from 0 to 4064. For the complete set of 2649 reflections the R value is 0.059. An extinction correction has been applied. Final atomic coordinates and anisotropic thermal factors are reported in Tables 8 and 9. A table of structure factors is available from the author.

Structure Descriptions

(A) $Zn_4Na_4(P_4O_{12})_3$

As presumed when starting this work the atomic arrangement exhibits great similarities with that of the aluminium tetrametaphosphate $Al_4(P_4O_{12})_3$. The location of the P_4O_{12} ring anions is the same but the preliminary assumption of zinc atoms replacing

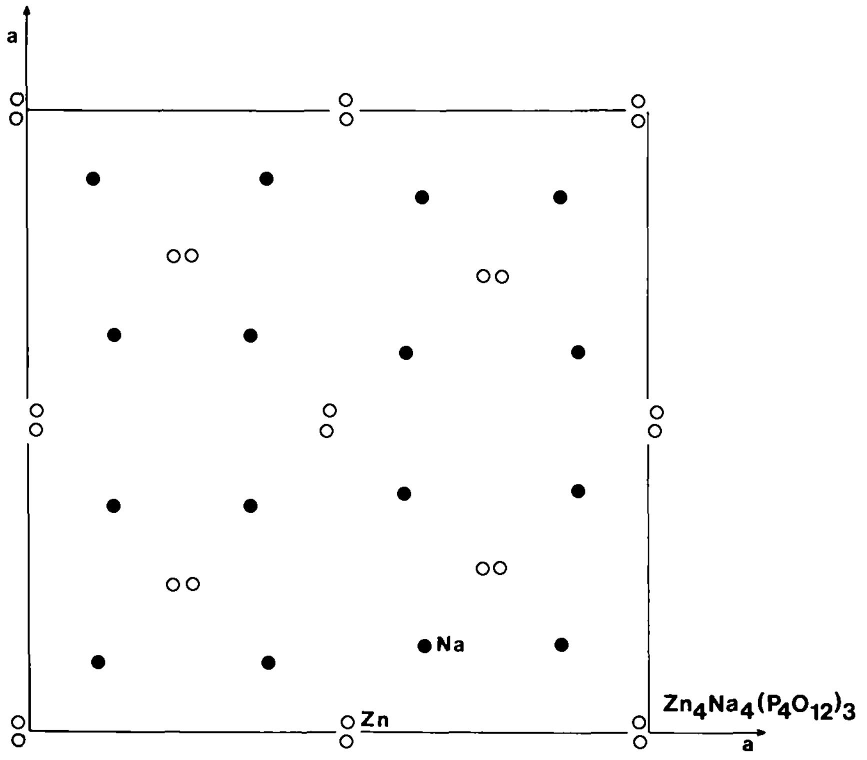

FIG. 2. Location of the associated cations in projection along an a axis.

the trivalent cation appeared to be wrong. In fact the octahedral site occupied by the aluminium in $Al_4(P_4O_{12})_3$ is here filled by the sodium atoms while zinc atoms are located in another octahedral void of the framework. Figure 1 reports the respective locations of the P_4O_{12} ring anions, while Fig. 2 describes the position of the associated cations Zn and Na in the unit cell. ZnO_6 and NaO_6 face sharing octahedra alternate along the threefold axis. Figure 3 gives a representation of this octahedra linkage along a portion of a threefold axis.

Table 10 reports the main interatomic distances and bond angles in this structure.

TABLE 8

ATOMIC PARAMETERS AND $B_{eq.}$ OF $ZnAg(PO_3)_3$

($B_{eq.} = \frac{4}{3} \Sigma_i \Sigma_j \beta_{ij} \mathbf{a}_i \mathbf{a}_j$)

Atoms	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$	$B_{eq.}$
Ag	0.37690(3)	0.24870(4)	0.02445(4)	2.25(1)
Zn(1)	0.2500(0)	0.5000(0)	0.46555(5)	0.69(1)
Zn(2)	0.0000(0)	0.0000(0)	0.00000(0)	0.72(1)
P(1)	0.14898(6)	0.04610(8)	0.23865(9)	0.60(2)
P(2)	0.12635(7)	0.25085(8)	0.04840(8)	0.58(2)
P(3)	0.10061(6)	0.47006(7)	0.21442(9)	0.59(2)
O(L11)	0.2500(0)	0.0000(0)	0.2937(3)	0.85(8)
O(E11)	0.0919(2)	0.0833(2)	0.3579(3)	0.93(6)
O(E12)	0.3927(2)	0.0443(2)	0.1420(3)	1.05(6)
O(L12)	0.1808(2)	0.1692(2)	0.1590(3)	0.99(6)
O(E21)	0.2980(2)	0.3173(2)	0.4726(3)	0.95(6)
O(E22)	0.0558(2)	0.1740(2)	0.9737(3)	0.89(6)
O(L23)	0.0660(2)	0.3476(2)	0.1355(3)	0.93(6)
O(E31)	0.3487(2)	0.4451(2)	0.1200(3)	0.97(6)
O(E32)	0.1499(2)	0.4312(3)	0.3380(3)	1.23(7)
O(L33)	0.5000(0)	0.4686(3)	0.2500(0)	0.92(8)

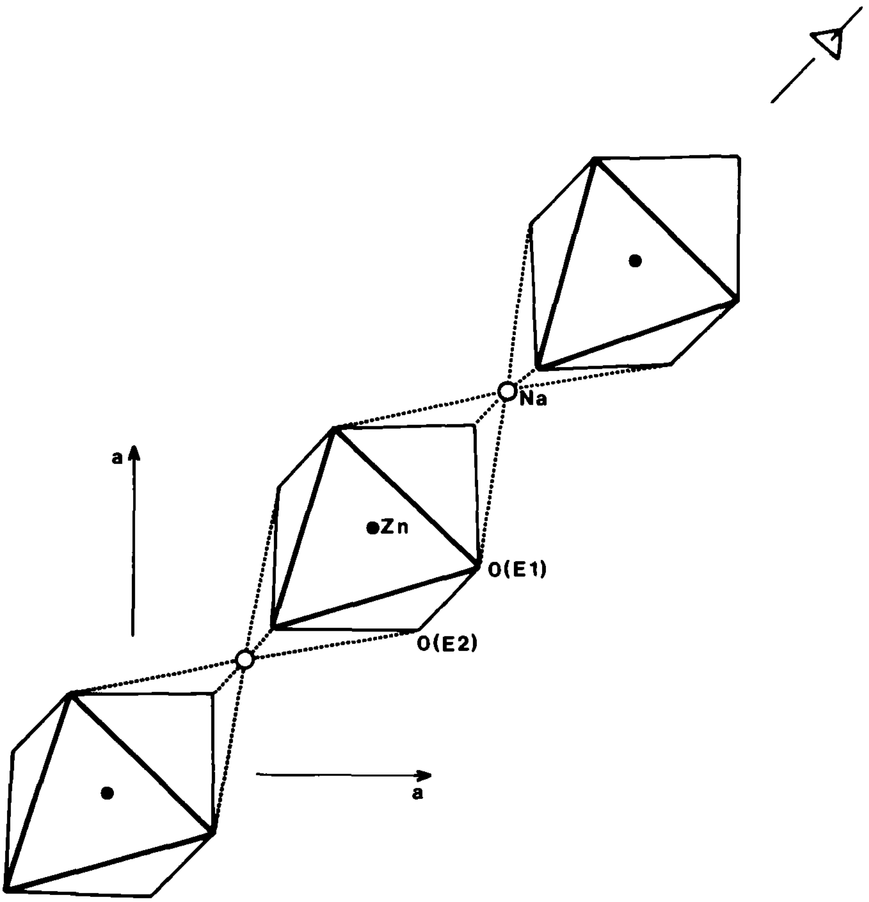

FIG. 3. Linkage of the ZnO_6 and NaO_6 octahedra along a portion of the threefold axis.

TABLE 9

ANISOTROPIC THERMAL PARAMETERS OF $ZnAg(PO_3)_3$ ($T = \beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl$)

	$\beta_{11}(\sigma)$	$\beta_{22}(\sigma)$	$\beta_{33}(\sigma)$	$\beta_{12}(\sigma)$	$\beta_{13}(\sigma)$	$\beta_{23}(\sigma)$
Ag	0.00259(1)	0.00232(2)	0.00929(4)	0.00231(3)	0.00024(5)	−0.00193(5)
Zn(1)	0.00088(2)	0.00127(3)	0.00201(4)	0.00015(6)	0.00000(0)	0.00000(0)
Zn(2)	0.00090(2)	0.00102(3)	0.00257(4)	−0.00015(6)	−0.00022(5)	−0.00038(8)
P(1)	0.00074(3)	0.00127(5)	0.00164(6)	0.00018(8)	0.00005(8)	−0.0001(1)
P(2)	0.00075(3)	0.00087(4)	0.00193(6)	−0.00043(7)	0.00011(8)	0.0002(1)
P(3)	0.00070(3)	0.00127(5)	0.00162(6)	−0.00012(7)	0.00025(8)	0.0000(1)
O(L11)	0.0007(1)	0.0024(2)	0.0023(3)	0.0009(4)	0.0000(0)	0.0000(0)
O(E11)	0.0012(1)	0.0018(2)	0.0026(2)	0.0004(2)	0.0009(3)	−0.0005(3)
O(E12)	0.0014(1)	0.0016(2)	0.0033(2)	0.0002(3)	0.0015(3)	0.0004(3)
O(L12)	0.0012(1)	0.0016(2)	0.0032(2)	−0.0005(2)	−0.0006(3)	0.0018(3)
O(E21)	0.0011(1)	0.0014(2)	0.0033(2)	0.0008(2)	−0.0012(3)	0.0001(3)
O(E22)	0.0011(1)	0.0015(2)	0.0027(2)	−0.0012(2)	−0.0007(3)	−0.0004(3)
O(L23)	0.0009(1)	0.0019(2)	0.0031(2)	−0.0006(2)	0.0006(3)	−0.0021(3)
O(E31)	0.0014(1)	0.0017(2)	0.0027(2)	−0.0002(2)	−0.0017(3)	−0.0012(3)
O(E32)	0.0014(1)	0.0030(2)	0.0031(2)	−0.0005(3)	−0.0017(3)	0.0008(4)
O(L33)	0.0008(1)	0.0015(2)	0.0037(3)	0.0000(0)	−0.0013(4)	0.0000(0)

TABLE 10

MAIN INTERATOMIC DISTANCES AND BOND ANGLES IN $Zn_4Na_4(P_4O_{12})_3$

P	O(E1)	O(E2)	O(L)	O(L)
O(E1)	1.488(3)	2.571(4)	2.516(5)	2.497(5)
O(E2)	119.6(2)	1.487(4)	2.469(5)	2.535(5)
O(L)	109.2(2)	106.3(2)	1.597(3)	2.500(5)
O(L)	107.6(2)	110.1(2)	102.7(2)	1.605(4)

P–P 2.887(1)

P–O(L)–P 128.8(2)

P–P–P 88.44(2)

Na	O(E1)	O(E1)	O(E1)	O(E2)	O(E2)	O(E2)
O(E1)	2.438(8)	2.801(6)	2.801(6)	3.973(4)	4.887(4)	4.035(4)
O(E1)	70.1(2)	2.438(8)	2.801(6)	4.035(4)	3.973(4)	4.887(4)
O(E1)	70.1(2)	70.1(2)	2.438(8)	4.887(4)	4.035(4)	3.973(4)
O(E2)	108.8(2)	111.3(2)	177.9(3)	2.450(8)	2.808(6)	2.808(6)
O(E2)	177.9(3)	108.8(2)	111.3(2)	69.9(2)	2.450(8)	2.808(6)
O(E2)	111.3(2)	177.9(3)	108.8(2)	69.9(2)	69.9(2)	2.450(8)

Zn	O(E1)	O(E1)	O(E1)	O(E2)	O(E2)	O(E2)
O(E1)	2.090(3)	2.801(6)	2.801(6)	3.125(4)	3.081(4)	4.182(4)
O(E1)	84.2(1)	2.090(3)	2.801(6)	4.182(4)	3.125(4)	3.081(4)
O(E1)	84.2(1)	84.2(1)	2.090(3)	3.081(4)	4.182(4)	3.125(4)
O(E2)	96.7(1)	178.7(2)	94.9(1)	2.093(3)	2.808(6)	2.808(6)
O(E2)	94.9(1)	96.7(1)	178.7(2)	84.3(1)	2.093(3)	2.808(6)
O(E2)	178.7(2)	94.9(1)	96.7(1)	84.3(1)	84.3(1)	2.093(3)

Na–Zn 3.160(3)
3.149(3)

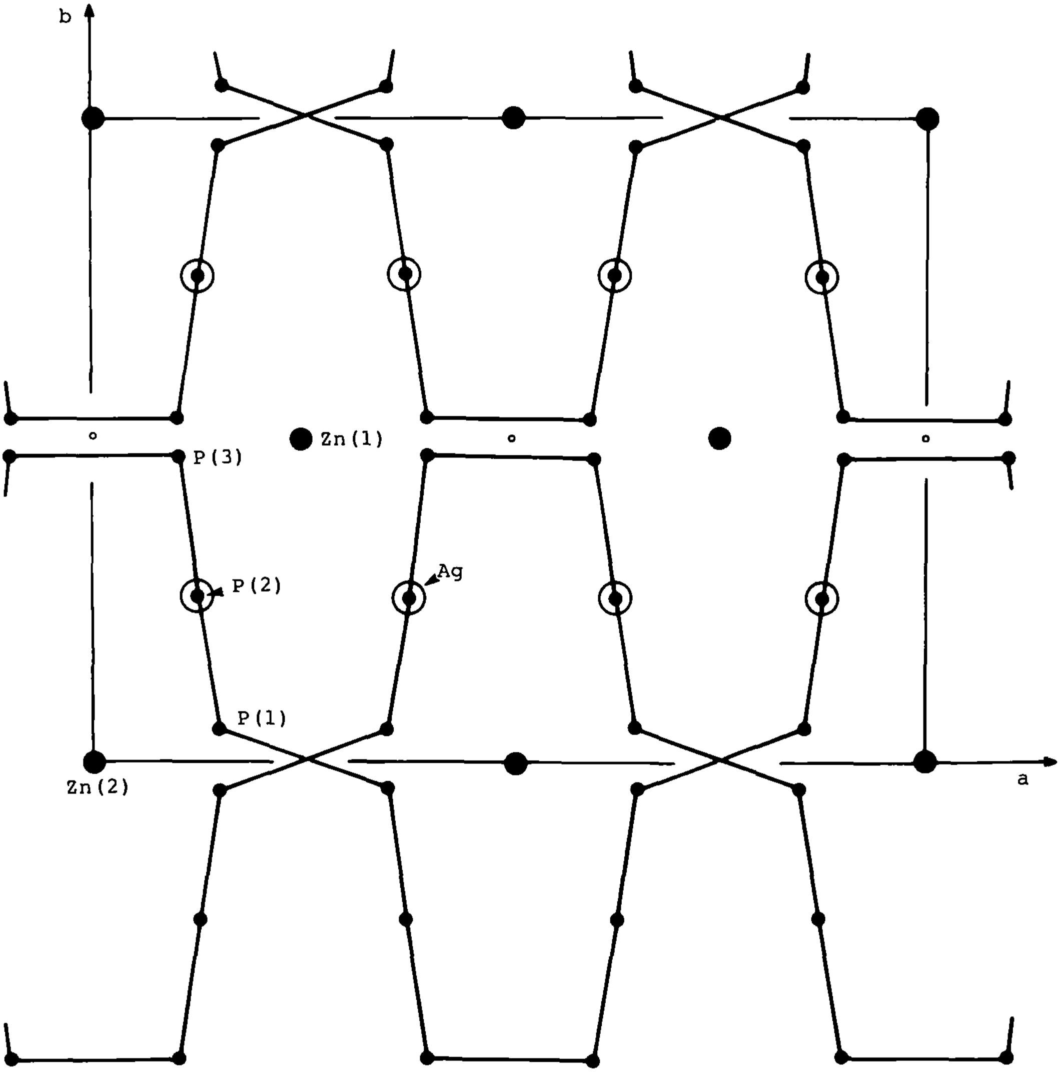

FIG. 4. Schematic representation of the repartition of the $(PO_3)_x$ infinite chain inside the unit cell of $ZnAg(PO_3)_3$. Oxygen atoms are not represented. The projection is made along the **c** axis.

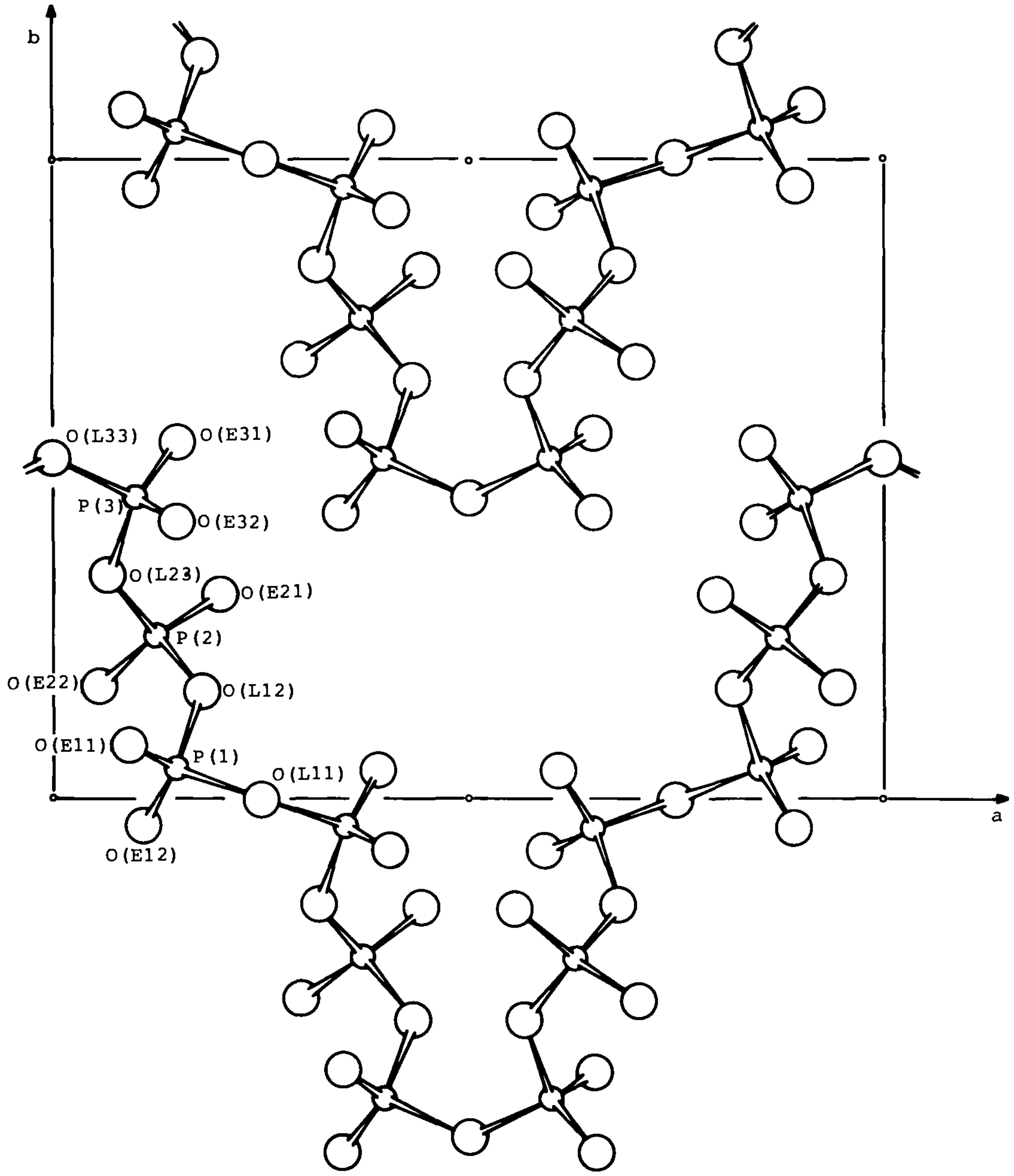

FIG. 5. Details for infinite $(PO_3)_x$ chains in projection along the c axis. Only two chains are represented. Associated cations have been omitted.

TABLE 11

MAIN INTERATOMIC DISTANCES AND BOND ANGLES IN THE $(PO_3)_n$ CHAIN OF $ZnAg(PO_3)_3$

		$P(1)O_4$ tetrahedron		
P(1)	O(L11)	O(E11)	O(E12)	O(L12)
O(L11)	1.588(1)	2.458(2)	2.538(2)	2.451(2)
O(E11)	106.5(1)	1.480(2)	2.551(3)	2.505(3)
O(E12)	111.5(1)	118.9(1)	1.482(2)	2.512(3)
O(L12)	100.47(8)	108.7(1)	109.1(1)	1.601(2)
		$P(2)O_4$ tetrahedron		
P(2)	O(L12)	O(E21)	O(E22)	O(L23)
O(L12)	1.595(2)	2.455(3)	2.533(3)	2.503(2)
O(E21)	106.0(1)	1.477(2)	2.549(2)	2.510(3)
O(E22)	110.8(1)	119.1(1)	1.481(2)	2.462(2)
O(L23)	103.6(1)	109.8(1)	106.5(1)	1.590(2)
		$P(3)O_4$ tetrahedron		
P(3)	O(L23)	O(E31)	O(E32)	O(L33)
O(L23)	1.603(2)	2.524(3)	2.492(3)	2.453(3)
O(E31)	109.6(1)	1.485(2)	2.538(3)	2.483(2)
O(E32)	108.5(1)	118.7(1)	1.466(2)	2.505(2)
O(L33)	100.5(1)	107.8(1)	110.16(9)	1.587(2)
P(1)–P(1)	2.981(1)	P(1)–O(L11)–P(1)	139.7(2)	
P(1)–P(2)	2.912(1)	P(1)–O(L12)–P(2)	131.3(1)	
P(2)–P(3)	2.892(1)	P(2)–O(L23)–P(3)	129.8(1)	
P(3)–P(3)	2.889(1)	P(3)–O(L33)–P(3)	131.0(2)	

(*B*) *$ZnAg(PO_3)_3$*

This compound is a long chain polyphosphate. The infinite $(PO_3)_\infty$ chains run in zigzag along the **a** direction, with a period of 12 tetrahedra. Figure 4 gives a schematic representation of their repartition inside the unit cell. Figure 5 reports details for two of these chains in projection along the **c** axis. Main interatomic distances and bond angles in the chain are reported in Table 11, showing that the infinite anion is built up, with only three crystallographically independent phosphorus atoms. In this chain the P–P distance average is 2.918 Å with large deviations from this value (P(1)–P(1) = 2.981 Å). The average of the bonding angle P–O–P is 132.99° with also a large deviation (P(1)–O–P(1) = 139.71°) in connection with the largest P–P distances (P(1)–P(1)) already noticed. The linkage of the associated cation polyhedra is quite similar to the one observed in the cubic form of $Zn_4Na_4(P_4O_{12})_3$. Chains of face sharing ZnO_6 and AgO_6 octahedra are located in (210) planes with $z \sim 0.50$ and $(\bar{2}10)$ planes with $z \sim 0.0$. Figure 6 reports details for such a chain in projection along the **a** axis. Main interatomic distances and bond angles for ZnO_6 octahedra and AgO_6 polyhedra are reported in Table 12.

Another cubic form with almost the same unit cell ($a \sim 14$ Å) has been characterized as the high temperature form of $Zn_4Na_4(P_4O_{12})_3$ related compounds. Single crystals have been obtained and are under investigation.

At least one other form exists but, up to now, only as polycrystalline sample.

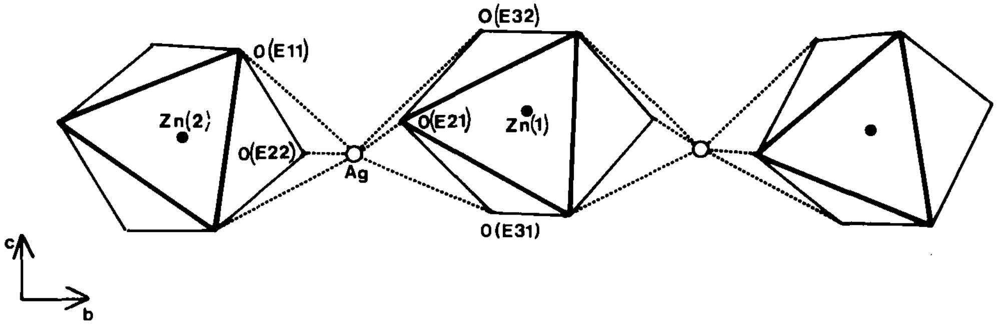

FIG. 6. Linkage of the ZnO_6 octahedra and AgO_6 polyhedra along the **a** axis.

TABLE 12

INTERATOMIC DISTANCES AND BOND ANGLES IN THE ZnO_6 OCTAHEDRA AND AgO_6 POLYHEDRON (SHORTEST DISTANCES Zn–Ag)

$Zn(1)O_6$ octahedron

Zn(1)	O(E21)	O(E21)	O(E31)	O(E31)	O(E32)	O(E32)
O(E21)	2.071(2)	4.139(3)	2.861(3)	3.021(3)	2.743(3)	3.095(3)
O(E21)	176.1(1)	2.071(2)	3.021(3)	2.861(3)	3.095(3)	2.743(3)
O(E31)	85.57(7)	91.64(7)	2.141(2)	2.989(4)	2.802(3)	4.153(3)
O(E31)	91.64(7)	85.57(7)	88.6(1)	2.141(2)	4.153(3)	2.802(3)
O(E32)	84.18(7)	98.28(8)	84.58(8)	172.22(8)	2.022(2)	3.153(4)
O(E32)	98.28(8)	84.18(7)	172.22(8)	84.58(8)	102.5(1)	2.022(2)

$Zn(2)O_6$ octahedron

Zn(2)	O(E11)	O(E11)	O(E12)	O(E12)	O(E22)	O(E22)
O(E11)	2.103(2)	4.206(4)	3.092(3)	2.858(3)	2.823(3)	3.029(3)
O(E11)	180.0(1)	2.103(2)	2.858(3)	3.092(3)	3.029(3)	2.823(3)
O(E12)	94.52(8)	85.48(8)	2.108(2)	4.215(4)	2.963(3)	2.899(3)
O(E12)	85.48(8)	94.52(8)	180.0(1)	2.108(2)	2.899(3)	2.963(3)
O(E22)	85.95(7)	94.05(7)	91.25(7)	88.75(7)	2.037(2)	4.075(3)
O(E22)	94.05(7)	85.95(7)	88.75(7)	91.25(7)	180.0(1)	2.037(2)

AgO_6 polyhedron

Ag	O(E11)	O(E12)	O(E21)	O(E22)	O(E31)	O(E32)
O(E11)	2.462(2)	2.858(3)	3.977(3)	2.823(3)	4.742(4)	3.821(2)
O(E12)	70.45(6)	2.492(2)	4.293(3)	2.899(3)	4.345(3)	5.162(4)
O(E21)	103.67(6)	115.12(6)	2.595(2)	5.186(4)	2.861(3)	2.743(3)
O(E22)	67.47(6)	69.13(6)	168.94(6)	2.615(2)	4.197(3)	4.392(3)
O(E31)	161.54(6)	128.00(6)	70.62(6)	115.58(6)	2.342(2)	2.802(3)
O(E32)	94.91(6)	164.46(6)	62.13(6)	110.84(6)	66.78(6)	2.718(2)

Zn(1)–Ag	3.274(1)
Zn(2)–Ag	3.178(1)

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