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Disodium Zinc Pyrophosphate and Disodium (Europium) Zinc Pyrophosphate

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Abstract

Comparison of the isotypic solid-state structures of disodium zinc diphosphate ($Na_2ZnP_2O_7$) and disodium zinc diphosphate doped with europium ($Na_{1.94}Eu_{0.02}ZnP_2O_7$) shows the europium to share a sodium site and to exist at the intersection of two mirror planes in the layer-like structure. The emission characteristics of this rare-earth-containing material are reported.

Comment

In the interest of understanding the influence of crystallographic symmetry elements upon the emission of Eu^{III} in an oxide environment, we have prepared $Na_2ZnP_2O_7$, (I), and $Na_2ZnP_2O_7$ doped with Eu^{III}, (II) (refined formula: $Na_{1.94}Eu_{0.02}ZnP_2O_7$).

The doped crystal glows red under excitation with 287 nm radiation, whereas the undoped crystal displays no emission. Both samples crystallize in the tetragonal space group *P*4$_2$/*mnm* and refinement shows the two forms to be isotypic.

The structure of $Na_2ZnP_2O_7$ may be compared with the structures of members of the family $A_2^{I}B^{II}P_2O_7$. Gabelica-Robert (1981) has reported that compounds of this family, with *A* = Na and *B* = Zn or Co, are isotypic and are found in a tetragonal form (a = 7.6 and c = 10.2 Å). We have previously reported the structures of two different forms of $Na_2CoP_2O_7$ (triclinic and orthorhombic space groups; Erragh *et al.*, 1991), distinguished by their differing colors which reflect the presence of octahedral (rose) or tetrahedral (blue) cobalt coordination. The blue form is a layer structure with bands of cobalt and diphosphate groups alternating with planes of Na$^+$ ions.

$Na_2ZnP_2O_7$, (I), is similar to the blue form of $Na_2CoP_2O_7$, with zinc- and phosphate-containing layers alternating with planes of Na$^+$ ions (Fig. 1).

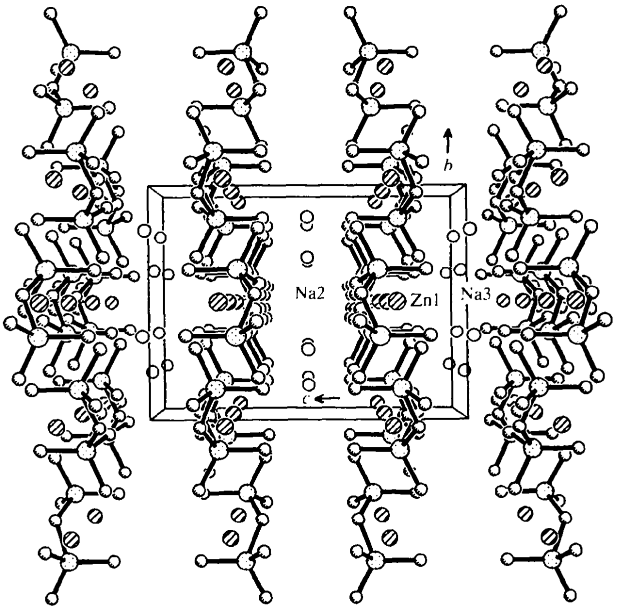

Fig. 1. Projection view of $Na_2ZnP_2O_7$. Open spheres represent Na atoms, whereas spheres with diagonal lines represent Zn atoms. Eu^{III} is localized in the Na2 site in structure (II).

A comparison of the ionic radii of six-coordinate sodium and zinc (Na$^+$ 1.02 and Zn^{2+} 0.74 Å) with that of six-coordinate europium (Eu^{3+} 0.947 Å) (Shannon, 1976) suggests that europium should replace sodium in the structure of $Na_2ZnP_2O_7$.

Refinement of the occupancy factors of sodium and zinc alone in the sites of the doped structure showed an occupancy of greater than 1 for Na2, but occupancies close to 1 for Na3 and Zn1. Europium was introduced into the Na2 site with the restraint of 1 being applied to the charge at the site (final result: 0.97 Na, 0.01 Eu and 0.02 vacancy).

Valence-bond calculations (*VALENCE*; Brown, 1996) show 2.195 for Zn1, 0.982 for Na3 and 1.160 for Na2 in structure (I), and totals of 2.207 for Zn1, 0.981 for Na3 and a weighted value of 1.017 for the Na2/Eu2 site of (II).

The P_2O_7 group shows normal bond angles and distances. The bridging O13 atom is disordered about the mirror plane passing through O11 and the P atoms. In both structures, Na2 shows distances of 2.4–2.9 Å to O13 in both disorder positions. The disorder of the O13 position results in a slight disorder of the O12 position which manifests itself in a somewhat elongated displacement ellipsoid.

Both structures show Zn1 to be on a $\bar{4}$ tetrahedral site, with Zn—O bond lengths of 1.926 (3) Å for (I) and 1.924 (4) Å for (II). The Na3 sites (*mm*) show eightfold coordination to oxygen [average Na—O 2.619 (4) Å in (I) and 2.618 (6) Å in (II)]. The Na2 site (*mm* symmetry) is eightfold coordinated [average Na—O 2.614 (5) Å in (I) and 2.626 (8) Å in (II)].

The literature (Blasse & Grabmaier, 1994) reports that Eu^{III} displays emission bands due to $^5D_0$–^7F_j (j = 0–6) transitions with the greatest intensities for $^5D_0$–$^7F_1$ (three bands, 590 nm) and $^5D_0$–$^7F_2$ (five bands, 610 nm) in the visible region. The relative intensities of these two sets of bands are affected by the crystallographic symmetry at the site of the rare earth ion. If the rare earth ion occupies a crystallographic site with inversion symmetry, the $^5D_0$–$^7F_1$ emission dominates in intensity. For $Na(Lu,Eu)O_2$, for example, Eu^{III} occupies a site with inversion symmetry and the intensity centered at 590 nm dominates, a desirable characteristic for luminescent applications. If Eu^{III} occupies a crystallographic site of no symmetry, the $^5D_0$–$^7F_2$ band dominates. $Na(Gd,Eu)O_2$ is an example of this situation, displaying peaks in the 610 nm region which dominate in intensity.

$Na_{1.94}Eu_{0.02}ZnP_2O_7$, (II), in which Er^{III} exists on an *mm* site, displays a greater emission intensity in the $^5D_0$–$^7F_1$ bands (Fig. 2), inconsistent with the pattern reported in the literature. Further work is underway to examine the effects of mirror planes and rotation axes upon the emission characteristics of rare earth ions in oxide environments.

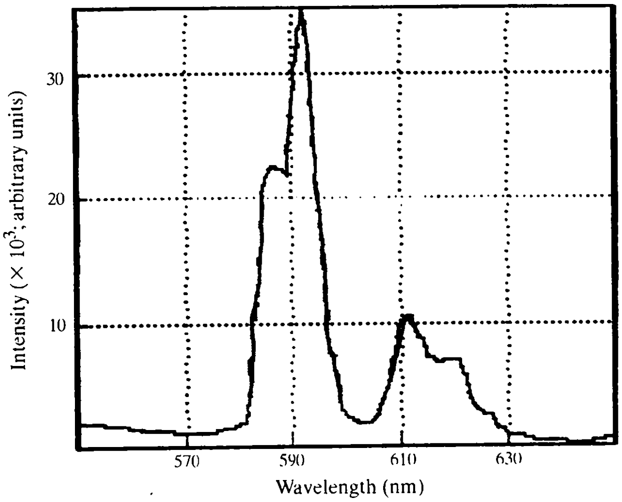

Fig. 2. Emission spectrum of $Na_{1.94}Eu_{0.02}ZnP_2O_7$.

Experimental

A stoichiometric mixture of Na_2CO_3, ZnO and $(NH_4)_2HPO_4$ was ground together and heated to 423 K, followed by further grinding and progressive heating to 1023 K. The molten material was subjected to slow cooling (3 K h^{-1}), whereupon transparent crystalline material was observed. The Eu-doped crystal was prepared in the same manner with the addition of Eu_2O_3 according to the equation:

$$(1-3x/2)Na_2CO_3 + x/2Eu_2O_3 + ZnO + 2(NH_4)2HPO_4 \rightarrow Na_{(2-3x)}Eu_xZn_2P_2O_7 \ (x = 0.05).$$

Compound (I)

Crystal data

$Na_2ZnP_2O_7$
M_r = 285.29
Tetragonal
$P4_2/mnm$
a = 7.656 (1) Å
c = 10.233 (2) Å
V = 599.80 (16) Å^3
Z = 4
D_x = 3.16 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 49 reflections
θ = 5.32–21.78°
μ = 4.762 mm^{-1}
T = 293 (2) K
Chunk
0.2 × 0.2 × 0.2 mm
Transparent

Data collection

Syntex $P4$ four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (*XEMP*; Sheldrick, 1990)
T_{min} = 0.13, T_{max} = 0.39
1293 measured reflections
503 independent reflections

403 reflections with $I > 2\sigma(I)$
R_{int} = 0.045
θ_{max} = 29.99°
$h = -10 \rightarrow 1$
$k = -10 \rightarrow 1$
$l = -1 \rightarrow 14$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.102
S = 1.113
503 reflections
45 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0534P)^2 + 0.4146P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.041

$\Delta\rho_{max}$ = 0.728 e Å^{-3}
$\Delta\rho_{min}$ = −0.995 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0000 (13)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (I)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Zn1	0	1/2	1/4	0.0187 (3)
Na2	0.6977 (3)	0.6977 (3)	1/2	0.0287 (7)
Na3	0.6404 (3)	0.6404 (3)	0	0.0251 (7)
P1	0.13630 (12)	0.13630 (12)	0.21145 (11)	0.0169 (3)
O11	0.1348 (3)	0.1348 (3)	0.3575 (3)	0.0235 (8)
O12	0.0776 (5)	0.3029 (4)	0.1485 (3)	0.0543 (12)
O13†	0.5319 (6)	0.5319 (6)	0.6580 (6)	0.024 (2)

† Site occupancy = 0.50.

Table 2. *Selected bond distances (Å) for (I)*

Zn1—O12^{i}	1.926 (3)	Na3—O11^{xi}	2.563 (3)
Zn1—O12	1.926 (3)	Na3—O11^{xii}	2.563 (3)
Zn1—O12^{ii}	1.926 (3)	Na3—O11^{i}	2.563 (3)
Zn1—O12^{iii}	1.926 (3)	Na3—O11^{ix}	2.563 (3)
Na2—O11^{iv}	2.328 (4)	Na3—O12^{xiii}	2.675 (4)
Na2—O11^{v}	2.328 (4)	Na3—O12^{v}	2.675 (4)
Na2—O13^{vi}	2.416 (7)	Na3—O12^{xiv}	2.675 (4)
Na2—O13	2.416 (7)	Na3—O12^{xv}	2.675 (4)
Na2—O12^{vii}	2.720 (4)	P1—O11	1.494 (3)
Na2—O12^{viii}	2.720 (4)	P1—O12	1.498 (3)
Na2—O12^{ix}	2.720 (4)	P1—O12^{xvi}	1.498 (3)
Na2—O12^{x}	2.720 (4)	P1—O13^{xvii}	1.611 (3)
Na2—O13^{iv}	2.965 (7)	P1—O13^{xviii}	1.611 (3)
Na2—O13^{v}	2.965 (7)		

Symmetry codes: (i) $\frac{1}{2}-y, \frac{1}{2}+x, \frac{1}{2}-z$; (ii) $-x, 1-y, z$; (iii) $y-\frac{1}{2}, \frac{1}{2}-x, \frac{1}{2}-z$; (iv) $1-x, 1-y, 1-z$; (v) $1-x, 1-y, z$; (vi) $x, y, 1-z$; (vii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (viii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$; (ix) $\frac{1}{2}+y, \frac{1}{2}-x, \frac{1}{2}-z$; (x) $\frac{1}{2}+y, \frac{1}{2}-x, \frac{1}{2}+z$; (xi) $\frac{1}{2}-y, \frac{1}{2}+x, z-\frac{1}{2}$; (xii) $\frac{1}{2}+y, \frac{1}{2}-x, z-\frac{1}{2}$; (xiii) $1-y, 1-x, z$; (xiv) $1-y, 1-x, -z$; (xv) $1-x, 1-y, -z$; (xvi) y, x, z; (xvii) $\frac{1}{2}-y, x-\frac{1}{2}, z-\frac{1}{2}$; (xviii) $y-\frac{1}{2}, \frac{1}{2}-x, z-\frac{1}{2}$.

Compound (II)

Crystal data

$Na_{1.94}Eu_{0.02}ZnP_2O_7$
$M_r = 286.72$
Tetragonal
$P4_2/mnm$
$a = 7.664$ (2) Å
$c = 10.241$ (2) Å
$V = 601.5$ (3) Å^3
$Z = 4$
$D_x = 3.168$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 64 reflections
$\theta = 5.68$–$23.45°$
$\mu = 4.92$ mm^{-1}
$T = 293$ (2) K
Chunk
0.2 × 0.2 × 0.2 mm
Transparent

Data collection

Syntex $P4$ four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (*XEMP*; Sheldrick, 1990)
$T_{min} = 0.15$, $T_{max} = 0.37$
1222 measured reflections
482 independent reflections

352 reflections with $I > 2\sigma(I)$
$R_{int} = 0.097$
$\theta_{max} = 29.96°$
$h = -10 \rightarrow 1$
$k = -1 \rightarrow 10$
$l = -14 \rightarrow 1$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.137$
$S = 1.229$
482 reflections
47 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0534P)^2 + 0.4146P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.092$

$\Delta\rho_{max} = 0.304$ e Å^{-3}
$\Delta\rho_{min} = -0.595$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.000 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (II)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Zn1	0	1/2	1/4	0.0176 (4)
Na2†	0.6979 (4)	0.6979 (4)	1/2	0.0323 (16)
Eu2‡	0.6979 (4)	0.6979 (4)	1/2	0.0323 (16)
Na3	0.6406 (4)	0.6406 (4)	0	0.0233 (10)
P1	0.13641 (17)	0.13641 (17)	0.21157 (17)	0.0154 (5)
O11	0.1351 (6)	0.1351 (6)	0.3564 (5)	0.0239 (12)
O12	0.0800 (10)	0.3042 (6)	0.1489 (4)	0.0523 (18)
O13§	0.5310 (9)	0.5310 (9)	0.6573 (10)	0.020 (3)

† Site occupancy = 0.948 (14). ‡ Site occupancy = 0.017 (5). § Site occupancy = 0.50.

Table 4. *Selected bond distances (Å) for (II)*

Zn1—O12^{i}	1.924 (4)	Na3—O11^{xi}	2.575 (5)
Zn1—O12	1.924 (4)	Na3—O11^{xii}	2.575 (5)
Zn1—O12^{ii}	1.924 (4)	Na3—O11^{i}	2.575 (5)
Zn1—O12^{iii}	1.924 (4)	Na3—O11^{ix}	2.575 (5)
Na2/Eu2—O11^{iv}	2.331 (7)	Na3—O12^{xiii}	2.662 (7)
Na2/Eu2—O11^{v}	2.331 (7)	Na3—O12^{v}	2.662 (7)
Na2/Eu2—O13^{vi}	2.422 (10)	Na3—O12^{xiv}	2.662 (7)
Na2/Eu2—O13	2.422 (10)	Na3—O12^{xv}	2.662 (7)
Na2/Eu2—O12^{vii}	2.743 (7)	P1—O11	1.484 (5)
Na2/Eu2—O12^{viii}	2.743 (7)	P1—O12	1.501 (4)
Na2/Eu2—O12^{ix}	2.743 (7)	P1—O12^{xvi}	1.501 (4)
Na2/Eu2—O12^{x}	2.743 (7)	P1—O13^{xvii}	1.615 (4)
Na2/Eu2—O13^{iv}	2.958 (10)	P1—O13^{xviii}	1.615 (4)
Na2/Eu2—O13^{v}	2.958 (10)		

Symmetry codes: (i) $\frac{1}{2}-y, \frac{1}{2}+x, \frac{1}{2}-z$; (ii) $-x, 1-y, z$; (iii) $y-\frac{1}{2}, \frac{1}{2}-x, \frac{1}{2}-z$; (iv) $1-x, 1-y, 1-z$; (v) $1-x, 1-y, z$; (vi) $x, y, 1-z$; (vii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (viii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$; (ix) $\frac{1}{2}+y, \frac{1}{2}-x, \frac{1}{2}-z$; (x) $\frac{1}{2}+y, \frac{1}{2}-x, \frac{1}{2}+z$; (xi) $\frac{1}{2}-y, \frac{1}{2}+x, z-\frac{1}{2}$; (xii) $\frac{1}{2}+y, \frac{1}{2}-x, z-\frac{1}{2}$; (xiii) $1-y, 1-x, z$; (xiv) $1-y, 1-x, -z$; (xv) $1-x, 1-y, -z$; (xvi) y, x, z; (xvii) $\frac{1}{2}-y, x-\frac{1}{2}, z-\frac{1}{2}$; (xviii) $y-\frac{1}{2}, \frac{1}{2}-x, z-\frac{1}{2}$.

For both compounds, a variable scan rate was used, with a $\theta/2\theta$ scan mode and a scan width of 0.6° below $K\alpha_1$ and 0.6° above $K\alpha_2$ to a maximum 2θ value of 60°. Refinement was completed using full-matrix least-squares methods.

For both compounds, data collection: *XSCANS* (Siemens, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structures: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1990); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1194). Services for accessing these data are described at the back of the journal.

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KAg_5S_3

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Abstract

Potassium pentasilver trisulfide, KAg_5S_3, was synthesized in supercritical ethylenediamine using previously reported techniques [Wood *et al.* (1992). *J. Am. Chem. Soc.* **114**, 9233–9235]. Dark-red crystals of KAg_5S_3 crystallize in the hexagonal space group $P\bar{6}2c$. The compound has an open-channeled structure composed of Ag and S atoms, with K^+ cations sitting in the middle of these channels.

Comment

The anionic framework of KAg_5S_3 crystallizes as infinite columns composed of Ag and S atoms. The channels created by the silver sulfide network contain the K^+ cations. The unit-cell view of this compound is shown in Fig. 1. Ag and S atoms form planar 12-membered rings which reside on mirror planes. The unit cell contains two unique 12-membered rings, with a distance between them of approximately 4 Å. As a result of this, the unit-cell *c*-axis length is approximately 8 Å. As shown in Fig. 2, the Ag1 and Ag4 atoms are coordinated in a distorted trigonal-planar fashion by S atoms. The angles about these Ag atoms range from 142.8 (2) to 101.1 (2)°. The interconnected 12-membered Ag–S rings form layers which stack along the *c* axis. The layers are connected diagonally by Ag atoms between the sheets. These Ag2 and Ag3 atoms are linearly coordinated to S atoms in adjacent silver sulfide sheets. The linear Ag—S bond distances range from 2.397 (3) to 2.403 (3) Å. This is in agreement with the general trend of shorter bond distances with lower coordination number. All close Ag···Ag contacts range from 2.948 (2) to 3.001 (2) Å, but these are probably not indicative of formal single bonds (Jansen, 1987). In this compound, all of the Ag atoms are formally +1, and the S atoms have an oxidation state of −2. All the distances within the anionic framework are very close to those found in the Rb analog (Wood *et al.*, 1994). However, as expected, the average K—S distance of 3.187 (8) Å is shorter than the average Rb—S distance of 3.283 Å, due in large part to the decrease in the radius of the cation on going from Rb^+ to K^+. Each of the two unique K^+ cations sits along threefold rotation axes at the center of the channels created by the 12-membered Ag–S rings. Each K^+ cation is six-coordinate to S atoms, with a slightly distorted octahedral geometry. We wish to note that during the investigation of KAg_5S_3, it was determined that $RbAg_5S_3$ (Wood *et al.*, 1994) can also be successfully refined in $P\bar{6}2c$, not $P\bar{6}$ as reported. Thus, the K and Rb members are isostructural. Details of the heavier analog are available from the authors.

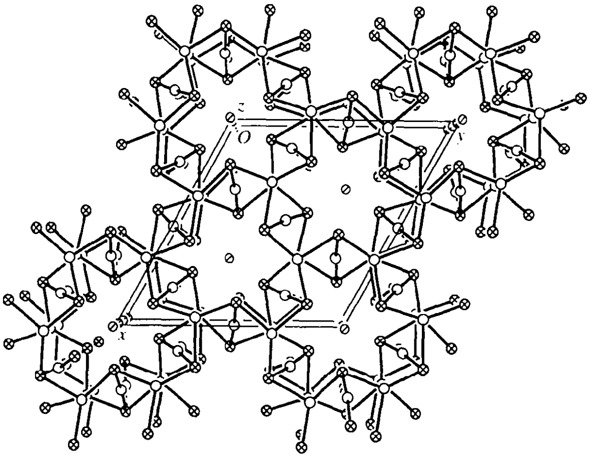

Fig. 1. Unit-cell view of KAg_5S_3. Ag atoms are open circles, S atoms are cross-hatched circles, and K atoms are lined circles.

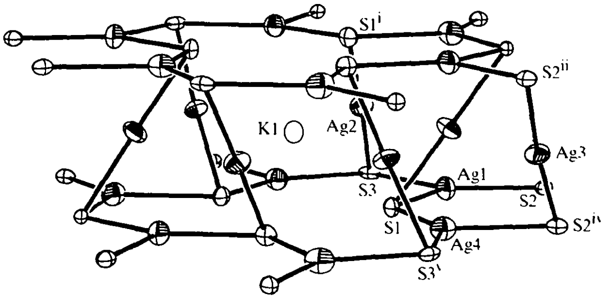

Fig. 2. View of the silver sulfide rings. Ag atoms are full displacement ellipsoids, S atoms are principal ellipsoids, and the K^+ cation is a boundary ellipsoid; all are at the 70% probability level.

The space group $P6_3/mmc$ (No. 194) was also considered. Given the atomic positions reported here in $P\bar{6}2c$, space group No. 194 would result in Ag1 and