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Sodium silver tricobalt bis(diphosphate) and sodium silver copper(II) diphosphate

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The crystal structures of two new diphosphates, sodium silver tricobalt bis(diphosphate), $(Na_{1.42}Ag_{0.58})Co_3(P_2O_7)_2$, and sodium silver copper(II) diphosphate, $(Na_{1.12}Ag_{0.88})CuP_2O_7$, provide examples of the effect of mixing Na and Ag in the same site of known host phosphate compounds. The small differences in ionic radii of the two monocations do not lead to significant differences in the structural details. In the latter compound, the Cu atom lies on an inversion center.

Comment

Our recent studies of transition metal phosphate complexes of the formula $A^{II}B^{II}P_2O_7$ (Amroussi *et al.*, 1997), $A^{I}_2B^{II}P_2O_7$ (Dridi *et al.*, 2001; Bennazha, Zahouily *et al.*, 2001; Dridi *et al.*, 2000; Bennazha *et al.*, 1999; Erragh *et al.*, 1998*a*,*b*) and $A^{I}_2B^{II}_3(P_2O_7)_2$ (Bennazha, Erragh *et al.*, 2001) have established the identities of a number of new compounds of these three types.

We have now synthesized several new complexes in which Ag has partially replaced Na in a sodium compound of known structure. The solid-state form $(Ag_{0.58}Na_{1.42})Co_3(P_2O_7)_2$, (I), may be compared with the parent compound $Ag_2Co_3(P_2O_7)_2$ (Bennazha, Erragh *et al.*, 2001), and the structure of $(Na_{1.12}Ag_{0.88})CuP_2O_7$, (II), may be compared with that of $Na_2CuP_2O_7$ (Erragh *et al.*, 1995; Etheredge & Hwu, 1995).

The effective ionic radii for six-coordinate Ag and Na (1.15 and 1.02 Å, respectively; Shannon, 1976) are similar, so it is not unexpected to find them sharing a site in a solid matrix. There are precedents for this shared occupancy in an oxide environment. There are several examples of minor quantities of Ag in a site predominately occupied by Na, such as $Ag_{4.6}Al_{12}Na_{7.4}O_{48}Si_{12}$ and $Ag_{3.6}Al_{12}Na_{7.4}O_{48}Si_{12}$ (Kim & Self, 1987, 1985), both of which show six-coordinate Na/Ag sites with average Na/Ag—O distances of 2.606 Å. $NaAgMoO_4$ (Na 0.94/Ag 0.06) contains six-coordinate metal sites, with average Na/Ag—O distances of 2.490 and 2.621 Å (Rulmont *et al.*, 1988).

There are other examples in which Na and Ag share a site more equally. $Ag_{0.40}Na_{1.60}Te_5O_{14}$ (Loeksmanto *et al.*, 1980), with Na/Ag 0.60/0.40 in a single site, has eight O atoms about that site at an average distance of 2.568 Å. $Ag_{0.4}Na_{2.3}Ca_{4.3}RuO_8$, with Na/Ag 0.5904/0.4906 (Mueller-Buschbaum & Frenzen, 1996), also has an eight-coordinate mixed-metal site, with an average *M*—O distance of 2.462 Å. $Ag_9Na(P_8O_{24})(NO_3)_2(H_2O)_4$, with Na and Ag sharing a six-coordinate position in a ratio of 0.50/0.50, has an average *M*—O distance of 2.500 Å (Averbuch-Pouchot & Durif, 1992). Thus, the literature does not present a totally consistent record of increased amounts of Ag leading to increased average bond lengths.

In the first title structure, $(Na_{1.42}Ag_{0.58})Co_3(P_2O_7)_2$, (I), Na and Ag share two sites, with occupancies for Na/Ag of 0.66/0.34 and 0.77/0.23, and with average distances to the eight surrounding O atoms of 2.630 (3) and 2.632 (3) Å. In the parent structure, $Ag_2Co_3(P_2O_7)_2$, Ag—O distances of up to 3.089 (13) Å were considered significant, leading to two eight-coordinate sites, with an average Ag—O distance of 2.685 (5) Å, a slightly larger value, consistent with total occupancy of both sites by the larger Ag atom.

The structure of (I) is isostructural with the structures of $Ag_2Co_3(P_2O_7)_2$ (the parent structure) and $Ag_2Mn_3(P_2O_7)_2$, previously reported by Bennazha, Erragh *et al.* (2001). In (I), as in these structures, layers of P_2O_7 groups are separated by layers of metal atoms (Fig. 1). Two of the Co atoms (Co1 and Co3) display distorted octahedral geometry, with average Co—O distances of 2.123 (3) and 2.098 (3) Å, respectively. Atom Co2, with an average *M*—O distance of 2.055 (3) Å, is pseudo-square-pyramidal. The Co—O averages for atoms Co1, Co2 and Co3 in the parent structure are 2.138 (4), 2.070 (4) and 2.111 (4) Å, respectively. Edge-sharing Co1 and Co2 polyhedra form chains, from which project edge-sharing

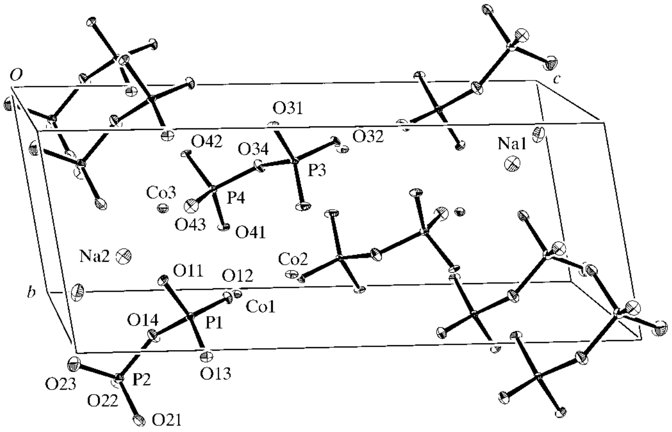

Figure 1
A projection view of (I) down the *a* axis. Displacement ellipsoids are shown at the 50% probability level.

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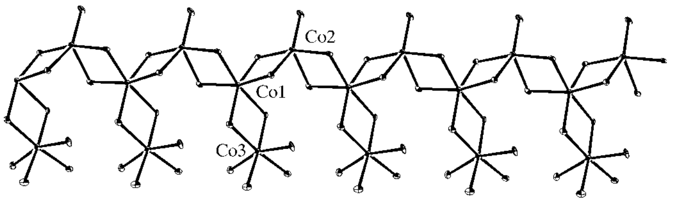

Figure 2
A view of the oxygen-bridged cobalt polymer of (I). Displacement ellipsoids are shown at the 50% probability level.

Co3 octahedra (Fig. 2). The Co—Co distances along these polymeric linkages are 3.113, 3.238 and 3.331 Å, respectively. The P_2O_7 groups in (I) display different conformations, one being eclipsed and the other staggered, with average O—P—P—O torsion angles of 9.9 and 57.5°, compared with angles of 10.0 and 57.1° in $Ag_2Co_3(P_2O_7)_2$.

Comparison of these and other details shows that the introduction of Na into the Ag site has caused little observable change in the solid-state structure, except for decreases in the density [4.009 Mg m^{-3} in (I) and 4.649 Mg m^{-3} in the parent structure] and cell volume [513.5 (2) $Å^3$ in (I) and 528.9 (6) $Å^3$ in the parent].

$(Na_{1.12}Ag_{0.88})CuP_2O_7$, (II), is unlike (I), primarily due to the square-planar geometry seen for the Cu^{II} atom, which changes the packing parameters (Fig. 3). Of the form $A^{I}_{2}B^{II}P_2O_7$ with A = Na/Ag, (II) appears isostructural with both $Na_2CuP_2O_7$ (Erragh *et al.*, 1995; Etheredge & Hwu, 1995) and $Na_2PdP_2O_7$ (Laligant, 1992). In these related structures, the B atom displays square-planar geometry. The P_2O_7 groups share pairs of pseudo-eclipsed O atoms (mean O—P—P—O torsion angle of 12.2°, compared with a value of 14.03° in the parent structure) with each of two adjacent Cu atoms, linking them into a pleated sheet which extends in the z direction. The Ag/Na sites are located between these sheets.

In (II), with Na/Ag occupancy 0.56 (5)/0.43 (5), the six-coordinate metal site has an average A^{I}—O distance of 2.417 (7) Å. In the parent structure, the Na—O distances average 2.423 Å. The Cu—O distances average 1.931 (7) Å in (II) and 1.936 Å in the parent structure. The Cu1 atom lies on an inversion center.

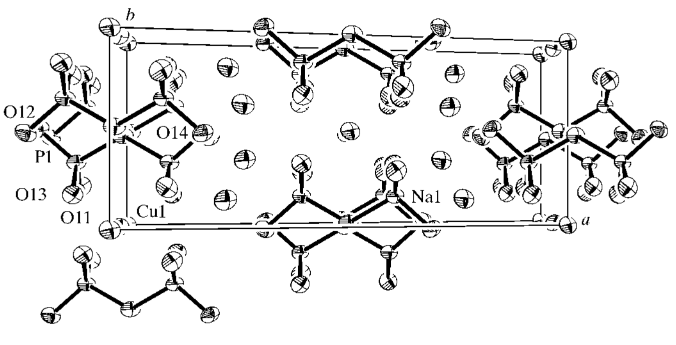

Figure 3
A projection view of (II) down the c axis. Displacement ellipsoids are shown at the 50% probability level.

Thus, for (II), observable changes in the structural details related to the substitution of Ag for Na in the $Na_2CuP_2O_7$ parent structure are limited to differences in cell volume [624.48 (16) $Å^3$ in (II) *versus* 612.8 $Å^3$ in the parent structure] and density [3.811 Mg m^{-3} in (II) *versus* 3.07 Mg m^{-3} in the parent structure].

In conclusion, for (II) as for (I), mixing Na and Ag in the same site results only in changes in mass and density consistent with changes in the atomic masses of the two elements, and not in significant structural changes.

Experimental

$(Na_{1.42}Ag_{0.58})Co_3(P_2O_7)_2$, (I), was prepared from a mixture of $AgNO_3$, Na_2CO_3, $Co(NO_3)_2{\cdot}6H_2O$ and $(NH_4)_2HPO_4$ in the ratio 1:0.5:3:4, in the expectation of preparing $AgNaCo_2P_2O_7$. The reactants were heated, with intermittent grinding, to 773 K to allow degassing to occur. A quantity of $(NH_4)_2HPO_4$ equal to 10% of the mass was added as a flux. The mixture was then heated to 1223 K, where fusion occurred, and then cooled at a rate of 6 K h^{-1} to ambient temperature. Violet crystals of (I) were isolated. For the preparation of $(Na_{1.12}Ag_{0.88})CuP_2O_7$, (II), $AgNO_3$, Na_2CO_3, CuO and $(NH_4)_2HPO_4$ were mixed in the stoichiometry 1:0.5:1:2. These materials were ground together and heated successively to 1173 K with intermittent grinding. After 1 h at 1173 K, the molten mass was cooled at a rate of 5 K h^{-1} to ambient temperature. Dark-blue crystals of (II) with rounded faces were observed to form.

Compound (I)

Crystal data

$(Na_{1.42}Ag_{0.58})Co_3(P_2O_7)_2$
M_r = 619.88
Triclinic, $P\overline{1}$
a = 5.296 (2) Å
b = 6.3590 (10) Å
c = 16.238 (4) Å
α = 80.93 (1)°
β = 81.80 (3)°
γ = 72.92 (2)°
V = 513.5 (2) $Å^3$
Z = 2
D_x = 4.009 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 21 reflections
θ = 5.8–10.1°
μ = 6.64 mm^{-1}
T = 293 (2) K
Chunk, violet
0.1 × 0.1 × 0.1 mm

Table 1
Selected interatomic distances (Å) for (I).

Co1—$O42^{i}$	2.062 (3)	Na1—$O23^{vi}$	2.483 (4)
Co1—$O41^{ii}$	2.073 (3)	Na1—$O11^{vii}$	2.506 (3)
Co1—$O31^{iii}$	2.086 (3)	Na1—$O23^{vii}$	2.460 (4)
Co1—$O32^{iv}$	2.096 (3)	Na1—$O22^{viii}$	2.397 (3)
Co1—$O12^{i}$	2.117 (3)	Na1—$O21^{vi}$	2.614 (3)
Co1—$O13^{iii}$	2.306 (3)	Na1—$O21^{v}$	2.725 (3)
Co2—O33	1.992 (3)	Na1—$O22^{ix}$	2.866 (3)
Co2—$O32^{v}$	2.052 (3)	Na1—$O23^{viii}$	2.994 (3)
Co2—$O31^{iii}$	2.070 (3)	Na2—$O23^{x}$	2.329 (4)
Co2—$O41^{ii}$	2.079 (3)	Na2—$O11^{xi}$	2.421 (3)
Co2—$O12^{iii}$	2.081 (3)	Na2—O21	2.433 (3)
Co3—$O11^{iii}$	2.057 (3)	Na2—$O14^{iii}$	2.642 (3)
Co3—O13	2.081 (3)	Na2—O43	2.655 (4)
Co3—O43	2.077 (3)	Na2—$O13^{xi}$	2.708 (3)
Co3—O21	2.092 (3)	Na2—O22	2.856 (3)
Co3—$O42^{ii}$	2.107 (3)	Na2—$O11^{iii}$	3.013 (4)
Co3—$O22^{ii}$	2.174 (3)		

Symmetry codes: (i) $1+x, 1+y, z$; (ii) $1+x, y, z$; (iii) $x, 1+y, z$; (iv) $2-x, 1-y, 1-z$; (v) $1-x, 1-y, 1-z$; (vi) $x-1, y, 1+z$; (vii) $1-x, -y, 1-z$; (viii) $x, y, 1+z$; (ix) $-x, 1-y, 1-z$; (x) $1-x, 1-y, -z$; (xi) $x-1, 1+y, z$.

Data collection

Syntex $P4$ four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (*XEMP*; Siemens, 1991)
$T_{min} = 0.467$, $T_{max} = 0.515$
3887 measured reflections
2995 independent reflections
2534 reflections with $I > 2\sigma(I)$

$R_{int} = 0.021$
$\theta_{max} = 30°$
$h = -1 \rightarrow 7$
$k = -8 \rightarrow 8$
$l = -22 \rightarrow 22$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.040$
$wR(F^2) = 0.107$
$S = 1.05$
2995 reflections
213 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0663P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.06$ e Å^{-3}
$\Delta\rho_{min} = -0.07$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0048 (11)

Compound (II)

Crystal data

$(Na_{1.12}Ag_{0.88})CuP_2O_7$
$M_r = 358.12$
Monoclinic, $C2/c$
$a = 15.088$ (2) Å
$b = 5.641$ (1) Å
$c = 8.171$ (1) Å
$\beta = 116.11$ (1)°
$V = 624.48$ (16) Å^3
$Z = 4$

$D_x = 3.811$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 17 reflections
$\theta = 4.4$–$9.4°$
$\mu = 6.75$ mm^{-1}
$T = 293$ (2) K
Chunk, dark blue
0.1 × 0.1 × 0.1 mm

Data collection

Syntex $P4$ four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (*XEMP*; Siemens, 1991)
$T_{min} = 0.449$, $T_{max} = 0.509$
1171 measured reflections
892 independent reflections
755 reflections with $I > 2\sigma(I)$

$R_{int} = 0.042$
$\theta_{max} = 30°$
$h = -1 \rightarrow 21$
$k = -7 \rightarrow 1$
$l = -11 \rightarrow 10$
3 standard reflections every 97 reflections intensity decay: none

Table 2
Selected interatomic distances (Å) for (II).

Cu1—O11^{i}	1.916 (5)	Ag1—O12^{vii}	2.591 (5)
Cu1—O13^{ii}	1.951 (4)	P1—O12	1.494 (4)
Ag1—O12^{iii}	2.336 (4)	P1—O11	1.513 (4)
Ag1—O12^{iv}	2.341 (4)	P1—O13	1.527 (4)
Ag1—O11^{v}	2.363 (4)	P1—O14	1.616 (3)
Ag1—O13^{vi}	2.453 (5)		

Symmetry codes: (i) $x-1, y, z$; (ii) $x-1, -y, z-\frac{1}{2}$; (iii) $x, 1-y, \frac{1}{2}+z$; (iv) $\frac{3}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (v) $x, y, 1+z$; (vi) $x, -y, \frac{1}{2}+z$; (vii) $\frac{3}{2}-x, \frac{1}{2}-y, 1-z$.

Refinement

Refinement on F^2
$R(F) = 0.049$
$wR(F^2) = 0.161$
$S = 1.20$
892 reflections
59 parameters

$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.007$
$\Delta\rho_{max} = 0.07$ e Å^{-3}
$\Delta\rho_{min} = -0.01$ e Å^{-3}

For both compounds, data collection: *XSCANS* (Siemens, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1368). Services for accessing these data are described at the back of the journal.

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supporting information

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Sodium silver tricobalt bis(diphosphate) and sodium silver copper(II) diphosphate

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Computing details

For both compounds, data collection: *XSCANS* (Siemens, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997).

(I) Sodium silver tricobalt diphosphate

Crystal data

$Ag_{0.58}Co_3Na_{1.42}O_{14}P_4$
$M_r = 619.88$
Triclinic, $P\bar{1}$
Hall symbol: -P 1
$a = 5.296$ (2) Å
$b = 6.359$ (1) Å
$c = 16.238$ (4) Å
$\alpha = 80.93$ (1)°
$\beta = 81.80$ (3)°
$\gamma = 72.92$ (2)°
$V = 513.5$ (2) Å^3

$Z = 2$
$F(000) = 592$
$D_x = 4.009$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 21 reflections
$\theta = 5.8$–$10.1°$
$\mu = 6.64$ mm^{-1}
$T = 293$ K
Chunk, dark blue
0.1 × 0.1 × 0.1 mm

Data collection

Syntex P4 four-circle diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\theta/2\theta$ scans
Absorption correction: ψ scan (*XEMP*; Siemens, 1991)
$T_{min} = 0.467$, $T_{max} = 0.515$
3887 measured reflections

2995 independent reflections
2534 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 30.0°$, $\theta_{min} = 2.6°$
$h = -1 \rightarrow 7$
$k = -8 \rightarrow 8$
$l = -22 \rightarrow 22$
3 standard reflections every 97 reflections
intensity decay: 0.0%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.107$
$S = 1.05$
2995 reflections
213 parameters
2 restraints

Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
$w = 1/[\sigma^2(F_o^2) + (0.0663P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.06$ e Å^{-3}

$\Delta\rho_{\min} = -0.07$ e Å^{-3}

Extinction correction: *SHELXL97* (Sheldrick, 1997), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0048 (11)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles. Correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$	Occ. (<1)
Co1	1.23425 (11)	0.96160 (8)	0.34055 (3)	0.00901 (14)	
Co2	0.80340 (12)	0.71808 (9)	0.41125 (4)	0.01018 (14)	
Co3	0.96264 (12)	0.36526 (9)	0.19545 (3)	0.00979 (14)	
Na1	0.09797 (17)	0.25188 (14)	0.97986 (5)	0.0217 (3)	0.659 (3)
Ag1	0.09797 (17)	0.25188 (14)	0.97986 (5)	0.0217 (3)	0.341 (3)
Na2	0.3906 (2)	0.72922 (16)	0.13722 (6)	0.0197 (3)	0.765 (3)
Ag2	0.3906 (2)	0.72922 (16)	0.13722 (6)	0.0197 (3)	0.235 (3)
P1	0.8110 (2)	−0.09808 (16)	0.21710 (6)	0.00766 (19)	
O11	0.9431 (6)	−0.3030 (5)	0.17431 (18)	0.0129 (6)	
O12	0.6445 (6)	−0.1368 (5)	0.29903 (18)	0.0102 (5)	
O13	1.0115 (6)	0.0257 (5)	0.22299 (19)	0.0108 (5)	
O14	0.5943 (6)	0.0482 (5)	0.1573 (2)	0.0150 (6)	
P2	0.5659 (2)	0.25057 (17)	0.08228 (6)	0.0097 (2)	
O21	0.7277 (6)	0.3973 (5)	0.09851 (19)	0.0139 (6)	
O22	0.2705 (6)	0.3568 (5)	0.0910 (2)	0.0153 (6)	
O23	0.6746 (8)	0.1474 (6)	0.0030 (2)	0.0216 (7)	
P3	0.7048 (2)	0.21744 (16)	0.45848 (6)	0.00687 (19)	
O31	0.8802 (6)	0.0146 (4)	0.41945 (18)	0.0092 (5)	
O32	0.5896 (6)	0.1575 (5)	0.54735 (17)	0.0099 (5)	
O33	0.8365 (6)	0.3989 (5)	0.4503 (2)	0.0134 (6)	
O34	0.4405 (6)	0.2999 (5)	0.41178 (18)	0.0132 (6)	
P4	0.3575 (2)	0.42729 (16)	0.32343 (6)	0.00725 (19)	
O41	0.1744 (6)	0.6529 (5)	0.34236 (19)	0.0101 (5)	
O42	0.2019 (6)	0.2891 (4)	0.29514 (18)	0.0103 (5)	
O43	0.5949 (7)	0.4470 (5)	0.2654 (2)	0.0161 (6)	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0097 (3)	0.0065 (2)	0.0105 (3)	−0.00272 (19)	0.0005 (2)	−0.00060 (18)
Co2	0.0103 (3)	0.0064 (2)	0.0132 (3)	−0.00295 (19)	0.0018 (2)	−0.00095 (18)
Co3	0.0109 (3)	0.0082 (2)	0.0106 (3)	−0.0033 (2)	−0.0015 (2)	−0.00055 (18)

Na1	0.0231 (5)	0.0296 (5)	0.0156 (4)	−0.0115 (3)	0.0004 (3)	−0.0062 (3)
Ag1	0.0231 (5)	0.0296 (5)	0.0156 (4)	−0.0115 (3)	0.0004 (3)	−0.0062 (3)
Na2	0.0161 (5)	0.0215 (5)	0.0209 (5)	−0.0039 (4)	−0.0012 (4)	−0.0046 (3)
Ag2	0.0161 (5)	0.0215 (5)	0.0209 (5)	−0.0039 (4)	−0.0012 (4)	−0.0046 (3)
P1	0.0088 (4)	0.0068 (4)	0.0078 (4)	−0.0032 (3)	0.0006 (3)	−0.0017 (3)
O11	0.0178 (15)	0.0103 (12)	0.0102 (13)	−0.0041 (11)	0.0027 (11)	−0.0037 (10)
O12	0.0084 (13)	0.0135 (13)	0.0080 (12)	−0.0036 (11)	0.0026 (10)	−0.0013 (10)
O13	0.0106 (14)	0.0085 (12)	0.0141 (13)	−0.0042 (10)	−0.0012 (11)	−0.0008 (10)
O14	0.0130 (15)	0.0162 (14)	0.0160 (14)	−0.0070 (12)	−0.0043 (12)	0.0059 (11)
P2	0.0097 (5)	0.0099 (4)	0.0091 (4)	−0.0023 (4)	−0.0007 (4)	−0.0010 (3)
O21	0.0152 (15)	0.0133 (13)	0.0146 (14)	−0.0065 (12)	−0.0038 (12)	0.0015 (11)
O22	0.0107 (14)	0.0166 (14)	0.0172 (15)	−0.0020 (12)	−0.0016 (12)	−0.0009 (11)
O23	0.030 (2)	0.0205 (16)	0.0161 (15)	−0.0106 (15)	0.0030 (14)	−0.0068 (12)
P3	0.0074 (4)	0.0057 (4)	0.0070 (4)	−0.0016 (3)	0.0006 (3)	−0.0008 (3)
O31	0.0084 (13)	0.0065 (12)	0.0123 (13)	−0.0011 (10)	0.0001 (10)	−0.0027 (10)
O32	0.0111 (14)	0.0117 (12)	0.0060 (12)	−0.0040 (11)	0.0012 (10)	0.0009 (10)
O33	0.0143 (14)	0.0082 (12)	0.0182 (14)	−0.0059 (11)	0.0023 (12)	−0.0008 (11)
O34	0.0110 (14)	0.0148 (13)	0.0115 (13)	−0.0017 (11)	−0.0034 (11)	0.0033 (11)
P4	0.0078 (4)	0.0058 (4)	0.0078 (4)	−0.0017 (3)	0.0001 (3)	−0.0011 (3)
O41	0.0099 (13)	0.0066 (12)	0.0145 (13)	−0.0025 (10)	−0.0016 (11)	−0.0027 (10)
O42	0.0138 (14)	0.0080 (12)	0.0119 (13)	−0.0069 (11)	−0.0022 (11)	−0.0014 (10)
O43	0.0149 (15)	0.0175 (14)	0.0163 (14)	−0.0077 (12)	0.0078 (12)	−0.0056 (11)

Geometric parameters (Å, º)

Co1—O42^{i}	2.062 (3)	Na2—O23^{x}	2.329 (4)
Co1—O41^{ii}	2.073 (3)	Na2—O11^{xi}	2.421 (3)
Co1—O31^{iii}	2.086 (3)	Na2—O21	2.433 (3)
Co1—O32^{iv}	2.096 (3)	Na2—O14^{iii}	2.642 (3)
Co1—O12^{i}	2.117 (3)	Na2—O43	2.655 (4)
Co1—O13^{iii}	2.306 (3)	Na2—O13^{xi}	2.708 (3)
Co2—O33	1.992 (3)	Na2—O22	2.856 (3)
Co2—O32^{v}	2.052 (3)	Na2—O11^{iii}	3.013 (4)
Co2—O31^{iii}	2.070 (3)	P1—O11	1.510 (3)
Co2—O41^{ii}	2.079 (3)	P1—O12	1.516 (3)
Co2—O12^{iii}	2.081 (3)	P1—O13	1.517 (3)
Co3—O11^{iii}	2.057 (3)	P1—O14	1.591 (3)
Co3—O13	2.081 (3)	O14—P2	1.614 (3)
Co3—O43	2.077 (3)	P2—O23	1.500 (3)
Co3—O21	2.092 (3)	P2—O22	1.506 (3)
Co3—O42^{ii}	2.107 (3)	P2—O21	1.512 (3)
Co3—O22^{ii}	2.174 (3)	P3—O33	1.495 (3)
Na1—O23^{vi}	2.483 (4)	P3—O31	1.521 (3)
Na1—O11^{vii}	2.506 (3)	P3—O32	1.521 (3)
Na1—O23^{vii}	2.460 (4)	P3—O34	1.599 (3)
Na1—O22^{viii}	2.397 (3)	O34—P4	1.585 (3)
Na1—O21^{vi}	2.614 (3)	P4—O43	1.484 (3)
Na1—O21^{v}	2.725 (3)	P4—O41	1.527 (3)

Na1—O22^{ix}	2.866 (3)	P4—O42	1.524 (3)
Na1—O23^{viii}	2.994 (3)		

O42^{i}—Co1—O41^{ii}	155.16 (12)	O23^{viii}—Na1—O11^{vii}	107.9 (11)
O42^{i}—Co1—O31^{iii}	97.19 (11)	O23^{viii}—Na1—O23^{vi}	150.3 (11)
O41^{ii}—Co1—O31^{iii}	82.56 (11)	O23^{viii}—Na1—O23^{vii}	66.3 (11)
O42^{i}—Co1—O32^{iv}	116.49 (12)	O23^{viii}—Na1—O22^{viii}	54.8 (11)
O41^{ii}—Co1—O32^{iv}	88.25 (11)	O23^{viii}—Na1—O22^{ix}	132.3 (11)
O31^{iii}—Co1—O32^{iv}	83.91 (12)	O23^{viii}—Na1—O21^{vi}	121.4 (11)
O42^{i}—Co1—O12^{i}	92.35 (12)	O23^{viii}—Na1—O21^{v}	72.6 (11)
O41^{ii}—Co1—O12^{i}	95.61 (11)	O23^{x}—Na2—O11^{xi}	93.58 (12)
O31^{iii}—Co1—O12^{i}	160.93 (12)	O23^{x}—Na2—O21	90.85 (12)
O32^{iv}—Co1—O12^{i}	77.05 (12)	O11^{xi}—Na2—O21	116.52 (11)
O42^{i}—Co1—O13^{iii}	75.22 (11)	O23^{x}—Na2—O14^{iii}	94.99 (11)
O41^{ii}—Co1—O13^{iii}	79.95 (11)	O11^{xi}—Na2—O14^{iii}	129.73 (10)
O31^{iii}—Co1—O13^{iii}	91.93 (12)	O21—Na2—O14^{iii}	112.77 (11)
O32^{iv}—Co1—O13^{iii}	167.92 (11)	O23^{x}—Na2—O43	155.88 (11)
O12^{i}—Co1—O13^{iii}	106.51 (11)	O11^{xi}—Na2—O43	95.42 (11)
O33—Co2—O32^{v}	98.00 (12)	O21—Na2—O43	65.12 (10)
O33—Co2—O31^{iii}	151.69 (13)	O14^{iii}—Na2—O43	96.34 (10)
O32^{v}—Co2—O31^{iii}	91.45 (11)	O23^{x}—Na2—O13^{xi}	104.47 (11)
O33—Co2—O41^{ii}	93.48 (12)	O11^{xi}—Na2—O13^{xi}	57.62 (10)
O32^{v}—Co2—O41^{ii}	165.02 (11)	O21—Na2—O13^{xi}	163.61 (10)
O31^{iii}—Co2—O41^{ii}	82.81 (11)	O14^{iii}—Na2—O13^{xi}	72.28 (10)
O33—Co2—O12^{iii}	120.02 (13)	O43—Na2—O13^{xi}	99.25 (10)
O32^{v}—Co2—O12^{iii}	78.82 (11)	O23^{x}—Na2—O22	79.92 (11)
O31^{iii}—Co2—O12^{iii}	87.94 (12)	O11^{xi}—Na2—O22	62.20 (9)
O41^{ii}—Co2—O12^{iii}	87.13 (12)	O21—Na2—O22	56.49 (10)
O11^{iii}—Co3—O13	174.79 (13)	O14^{iii}—Na2—O22	167.65 (10)
O11^{iii}—Co3—O43	88.47 (12)	O43—Na2—O22	84.60 (10)
O13—Co3—O43	93.67 (12)	O13^{xi}—Na2—O22	119.80 (10)
O11^{iii}—Co3—O21	91.71 (12)	O23^{x}—Na2—O11^{iii}	112.45 (12)
O13—Co3—O21	93.28 (12)	O11^{xi}—Na2—O11^{iii}	153.97 (13)
O43—Co3—O21	82.35 (13)	O21—Na2—O11^{iii}	65.27 (9)
O11^{iii}—Co3—O42^{ii}	95.68 (12)	O14^{iii}—Na2—O11^{iii}	50.83 (9)
O13—Co3—O42^{ii}	79.33 (11)	O43—Na2—O11^{iii}	60.79 (9)
O43—Co3—O42^{ii}	98.00 (13)	O13^{xi}—Na2—O11^{iii}	112.62 (9)
O21—Co3—O42^{ii}	172.60 (11)	O22—Na2—O11^{iii}	120.70 (9)
O11^{iii}—Co3—O22^{ii}	81.05 (12)	O11—P1—O12	114.78 (17)
O13—Co3—O22^{ii}	98.17 (12)	O11—P1—O13	110.30 (18)
O43—Co3—O22^{ii}	160.78 (13)	O12—P1—O13	113.94 (17)
O21—Co3—O22^{ii}	81.90 (13)	O11—P1—O14	104.36 (18)
O42^{ii}—Co3—O22^{ii}	99.04 (12)	O12—P1—O14	102.70 (17)
O23^{vi}—Na1—O11^{vii}	87.89 (11)	O13—P1—O14	109.96 (17)
O23^{vi}—Na1—O23^{vii}	86.97 (13)	P1—O14—P2	138.5 (2)
O11^{vii}—Na1—O23^{vii}	98.65 (11)	O23—P2—O22	115.2 (2)
O23^{vi}—Na1—O22^{viii}	121.48 (12)	O23—P2—O21	111.1 (2)
O11^{vii}—Na1—O22^{viii}	146.52 (11)	O22—P2—O21	113.94 (19)

O23$^{\rm vii}$—Na1—O22$^{\rm viii}$	98.62 (12)	O23—P2—O14	106.21 (19)
O23$^{\rm vi}$—Na1—O21$^{\rm vi}$	58.27 (10)	O22—P2—O14	101.34 (18)
O11$^{\rm vii}$—Na1—O21$^{\rm vi}$	127.30 (11)	O21—P2—O14	107.97 (17)
O23$^{\rm vii}$—Na1—O21$^{\rm vi}$	116.44 (11)	O33—P3—O31	112.66 (17)
O22$^{\rm viii}$—Na1—O21$^{\rm vi}$	67.69 (11)	O33—P3—O32	113.75 (17)
O23$^{\rm vi}$—Na1—O21$^{\rm v}$	137.10 (11)	O31—P3—O32	112.14 (16)
O11$^{\rm vii}$—Na1—O21$^{\rm v}$	69.25 (10)	O33—P3—O34	110.46 (18)
O23$^{\rm vii}$—Na1—O21$^{\rm v}$	130.79 (12)	O31—P3—O34	106.59 (17)
O22$^{\rm viii}$—Na1—O21$^{\rm v}$	77.75 (10)	O32—P3—O34	100.30 (17)
O21$^{\rm vi}$—Na1—O21$^{\rm v}$	107.41 (8)	P4—O34—P3	136.8 (2)
O23$^{\rm vi}$—Na1—O22$^{\rm ix}$	77.31 (11)	O43—P4—O41	112.21 (18)
O11$^{\rm vii}$—Na1—O22$^{\rm ix}$	61.18 (9)	O43—P4—O42	113.96 (18)
O23$^{\rm vii}$—Na1—O22$^{\rm ix}$	154.43 (11)	O41—P4—O42	110.60 (17)
O22$^{\rm viii}$—Na1—O22$^{\rm ix}$	106.76 (9)	O43—P4—O34	110.84 (19)
O21$^{\rm vi}$—Na1—O22$^{\rm ix}$	71.95 (10)	O41—P4—O34	104.98 (17)
O21$^{\rm v}$—Na1—O22$^{\rm ix}$	59.96 (10)	O42—P4—O34	103.52 (17)

Symmetry codes: (i) $x+1, y+1, z$; (ii) $x+1, y, z$; (iii) $x, y+1, z$; (iv) $-x+2, -y+1, -z+1$; (v) $-x+1, -y+1, -z+1$; (vi) $x-1, y, z+1$; (vii) $-x+1, -y, -z+1$; (viii) $x, y, z+1$; (ix) $-x, -y+1, -z+1$; (x) $-x+1, -y+1, -z$; (xi) $x-1, y+1, z$.

(II) Sodium silver copper(II) diphosphate

Crystal data

$\mathrm{Ag_{0.88}CuNa_{1.12}O_7P_2}$
$M_r = 358.12$
Monoclinic, $C2/c$
Hall symbol: -C 2yc
$a = 15.088$ (2) Å
$b = 5.641$ (1) Å
$c = 8.171$ (1) Å
$\beta = 116.11$ (1)°
$V = 624.48$ (16) Å^3
$Z = 4$

$F(000) = 675$
$D_x = 3.811$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 17 reflections
$\theta = 4.4$–9.4°
$\mu = 6.75$ mm^{-1}
$T = 293$ K
Chunk, violet
0.1 × 0.1 × 0.1 mm

Data collection

Syntex P4 four-circle diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\theta/2\theta$ scans
Absorption correction: ψ scan (*XEMP*; Siemens, 1991)
$T_{\min} = 0.449$, $T_{\max} = 0.509$
1171 measured reflections

892 independent reflections
755 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.042$
$\theta_{\max} = 30.0°$, $\theta_{\min} = 3.0°$
$h = -1 \rightarrow 21$
$k = -7 \rightarrow 1$
$l = -11 \rightarrow 10$
3 standard reflections every 97 reflections
intensity decay: 0.0%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.161$
$S = 1.20$
892 reflections
59 parameters

1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.007
$\Delta\rho_{max}$ = 0.07 e Å^{-3}
$\Delta\rho_{min}$ = −0.01 e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles: correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Cu1	0.0000	0.0000	0.0000	0.0303 (3)	
Ag1	0.76835 (7)	0.14209 (15)	0.70370 (11)	0.0396 (4)	0.438 (3)
Na1	0.76835 (7)	0.14209 (15)	0.70370 (11)	0.0396 (4)	0.562 (3)
P1	0.89677 (11)	0.3398 (2)	0.15609 (16)	0.0268 (4)	
O11	0.8986 (4)	0.2075 (8)	−0.0035 (5)	0.0393 (11)	
O12	0.8145 (4)	0.5159 (7)	0.0995 (5)	0.0343 (10)	
O13	0.8952 (4)	0.1683 (7)	0.2993 (5)	0.0344 (10)	
O14	1.0000	0.4827 (9)	0.2500	0.0318 (13)	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0349 (6)	0.0289 (5)	0.0130 (4)	−0.0027 (4)	−0.0025 (4)	−0.0076 (3)
Ag1	0.0449 (6)	0.0363 (5)	0.0192 (4)	−0.0047 (3)	−0.0028 (4)	−0.0021 (3)
Na1	0.0449 (6)	0.0363 (5)	0.0192 (4)	−0.0047 (3)	−0.0028 (4)	−0.0021 (3)
P1	0.0330 (7)	0.0206 (6)	0.0102 (6)	0.0018 (4)	−0.0056 (5)	0.0006 (4)
O11	0.041 (2)	0.040 (2)	0.0168 (16)	0.0048 (18)	−0.0062 (16)	−0.0137 (16)
O12	0.035 (2)	0.0271 (18)	0.0223 (18)	0.0064 (15)	−0.0041 (16)	0.0010 (13)
O13	0.036 (2)	0.032 (2)	0.0201 (17)	0.0008 (15)	−0.0008 (16)	0.0144 (14)
O14	0.039 (3)	0.025 (2)	0.0093 (18)	0.000	−0.0095 (19)	0.000

Geometric parameters (Å, º)

Cu1—O11^{i}	1.916 (5)	Ag1—O13^{viii}	2.453 (5)
Cu1—O11^{ii}	1.916 (5)	Ag1—O12^{ix}	2.591 (5)
Cu1—O13^{iii}	1.951 (4)	P1—O12	1.494 (4)
Cu1—O13^{iv}	1.951 (4)	P1—O11	1.513 (4)
Ag1—O12^{v}	2.336 (4)	P1—O13	1.527 (4)
Ag1—O12^{vi}	2.341 (4)	P1—O14	1.616 (3)
Ag1—O11^{vii}	2.363 (4)	O14—P1^{x}	1.616 (3)
O11^{i}—Cu1—O11^{ii}	180.0	O12^{v}—Ag1—O12^{ix}	144.41 (16)
O11^{i}—Cu1—O13^{iii}	86.48 (18)	O12^{vi}—Ag1—O12^{ix}	111.93 (16)

O11^{ii}—Cu1—O13^{iii}	93.52 (18)	O11^{vii}—Ag1—O12^{ix}	80.69 (16)
O11^{i}—Cu1—O13^{iv}	93.52 (18)	O13^{viii}—Ag1—O12^{ix}	94.50 (15)
O11^{ii}—Cu1—O13^{iv}	86.48 (18)	O12—P1—O11	112.8 (2)
O13^{iii}—Cu1—O13^{iv}	180.0	O12—P1—O13	111.6 (3)
O12^{v}—Ag1—O12^{vi}	88.36 (14)	O11—P1—O13	111.1 (3)
O12^{v}—Ag1—O11^{vii}	89.54 (16)	O12—P1—O14	108.1 (2)
O12^{vi}—Ag1—O11^{vii}	159.70 (18)	O11—P1—O14	106.1 (2)
O12^{v}—Ag1—O13^{viii}	112.94 (18)	O13—P1—O14	106.8 (2)
O12^{vi}—Ag1—O13^{viii}	95.64 (14)	P1—O14—P1^{x}	120.1 (3)
O11^{vii}—Ag1—O13^{viii}	66.72 (14)		

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+1, -y, -z$; (iii) $x-1, -y, z-1/2$; (iv) $-x+1, y, -z+1/2$; (v) $x, -y+1, z+1/2$; (vi) $-x+3/2, y-1/2, -z+1/2$; (vii) $x, y, z+1$; (viii) $x, -y, z+1/2$; (ix) $-x+3/2, -y+1/2, -z+1$; (x) $-x+2, y, -z+1/2$.