Dipotassium tristrontium dimanganese tris(diphosphate)

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The structure of the title mixed trimetallic diphosphate, $K_2Sr_3Mn_2(P_2O_7)_3$, is constructed of a three-dimensional matrix composed of SrO_{8-10}, MnO_5 and PO_4 polyhedra. The sharing of O atoms between these polyhedra creates tunnels of large dimensions parallel to (010), in which are found columns of K^+ ions. Thus, the presence of several cations differing in size in the solid matrix leads to the formation of large tunnels and potential conductivity.

Comment

There is extensive structural work reported in the literature concerning $A^{II}B^{II}P_2O_7$ and $A^I_2B^{II}P_2O_7$ complexes. For complexes of this type, which are of interest for their conductive properties, it is apparent that transition metal atoms plus larger alkali and alkaline earth elements form bonds having more covalent character with the O atoms of diphosphate groups and thus a relatively rigid matrix. Smaller and more electropositive elements (forming interactions with oxygen which is more ionic in nature) allow movement through the channels or tunnels in these matrices, giving rise to conductivity.

For example, the structure of $K_{3.5}Pd_{2.25}(P_2O_7)_2$ may be viewed as a matrix composed of $Pd_{2.25}(P_2O_7)_2$ groups. Corner-sharing PO_4 polyhedra and square-planar PdO_4 units are linked in a three-dimensional array, forming large parallel tunnels. These tunnels are of three types, *viz.* of dimensions 3.21×8.36, 3.84×8.14 and 3.55×10.65 Å, in which are found two, two and three columns, respectively, of K^+ ions. These columns are of sufficient diameter to allow movement of K^+ ions and thus conductivity of the solid ($\sigma_{673K} = 2.3 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$) (El Maadi *et al.*, 2002).

Similarly, the isostructural complexes $A^IB^{II}_6(P_2O_7)_2P_3O_{10}$, with $A = K$ and $B = Mn$, $A = Ag$ and $B = Mn$, and $A = Na$ and $B = Mn$ (Bennazha *et al.*, 2001, 2002), lead to the conclusion

that the $Mn_6(P_2O_7)_2P_3O_{10}$ matrix is rigid, providing a stable host solid into which the K^+, Ag^+ or Na^+ cations fit. One may conclude that the $Mn_6(P_2O_7)_2P_3O_{10}$ matrix is analogous to the zeolite-type matrices, which are rigid and solid, resisting conformational changes due to the presence of guest atoms or molecules in their cavities. In these three structures, the tunnels are of smaller dimensions (2.98×4.99 Å) and the Ag and Na atoms show valence-bond totals less than the ionic charge.

Another approach to creating a host matrix with tunnels and thus conducting properties may be to build the host matrix from P_2O_7 and two different cations, both of which tend to more covalent bonding character, but which differ in size. There is only one example in the literature of a trimetallic diphosphate, *viz.* $K_6Sr_2Ni_5(P_2O_7)_5$ (El Maadi *et al.*, 1995a). In this structure, the $Sr_2Ni_5(P_2O_7)_5$ matrix forms tunnels of large dimensions (3.64×9.28 Å) in which are found four individual columns of K^+ ions. The conductivity of this material has not been established.

The structure of $K_2Sr_3Mn_2(P_2O_7)_3$ described here (Figs. 1 and 2) does not resemble any of its known mono- or bimetallic parents, *e.g.* $Sr_2P_2O_7$ (Grenier & Masse, 1969), $Mn_2P_2O_7$ (Lukaszewicz & Smajkiewicz, 1961), $K_2SrP_2O_7$ (Trunov *et al.*, 1991) or $K_2MnP_2O_7$ (El Maadi *et al.*, 1994); $SrMnP_2O_7$ and $K_4P_2O_7$ are unknown. Thus, one cannot view the structure of $K_2Mn_2Sr_3(P_2O_7)_3$ as a simple substitution of potassium and manganese into an $Sr_2P_2O_7$ matrix, for example.

The structure of $K_2Sr_3Mn_2(P_2O_7)_3$ is built up from $[Sr_3Mn_2P_4O_{16}]_\infty$ units in the form of SrO_{8-10}, MnO_5 and PO_4 coordination polyhedra, which create tunnels parallel to the [010] direction. Each tunnel is of dimensions 5.43×9.28 Å. In each of these tunnels are found two columns of K^+ ions. Tunnels, centered about $(\frac{1}{2}, y, \frac{1}{2})$ and $(\frac{1}{2}, y, 0)$, are delimited by four PO_4 tetrahedra, two MnO_5 square pyramids and two SrO_{8-10} polyhedra. Fig. 2, a projection on the (010) plane, shows these tunnels. Within the $[Sr_3Mn_2P_4O_{16}]_\infty$ units, $(Sr_3O_{21})_\infty$ repeat units, in the form of ribbons, extend in the [010] direction.

Atoms Sr1, Sr2 and Sr3 display nine-, eight- or ten-coordination, with average Sr—O distances of 2.717 (11), 2.601 (12) and 2.783 (12) Å, respectively (Table 1). Atoms K1 and K2 display nine- and seven-coordination, respectively. The average K—O distances of 2.983 (15) and 2.933 (15) Å are comparable to those in $K_2SrP_2O_7$ (Trunov *et al.*, 1991), $K_2CuP_2O_7$ (El Maadi *et al.*, 1995b) and $K_2CdP_2O_7$ (Faggiani & Calvo, 1976). Both Mn atoms have square-pyramidal geometry, with Mn—O distances of 2.112 (15) and 2.120 (14) Å.

The valence-bond sums (Brown, 1981) for the cations are: Sr1 1.927, Sr2 2.48, Sr3 1.819, Mn1 2.01, Mn2, 2.05, K1 0.98 and K2 0.87. These sums are normal for the Mn atoms and for Sr1 and Sr3. The high total for Sr2, which has the lowest coordination number of the three Sr atoms, is puzzling. We have often noted low totals (as seen for K2) for atoms which are mobile in their environment and thus involved in conductivity.

The space group is correctly chosen as $P2_1$. While the metal atoms and two of the diphosphate groups may be placed on
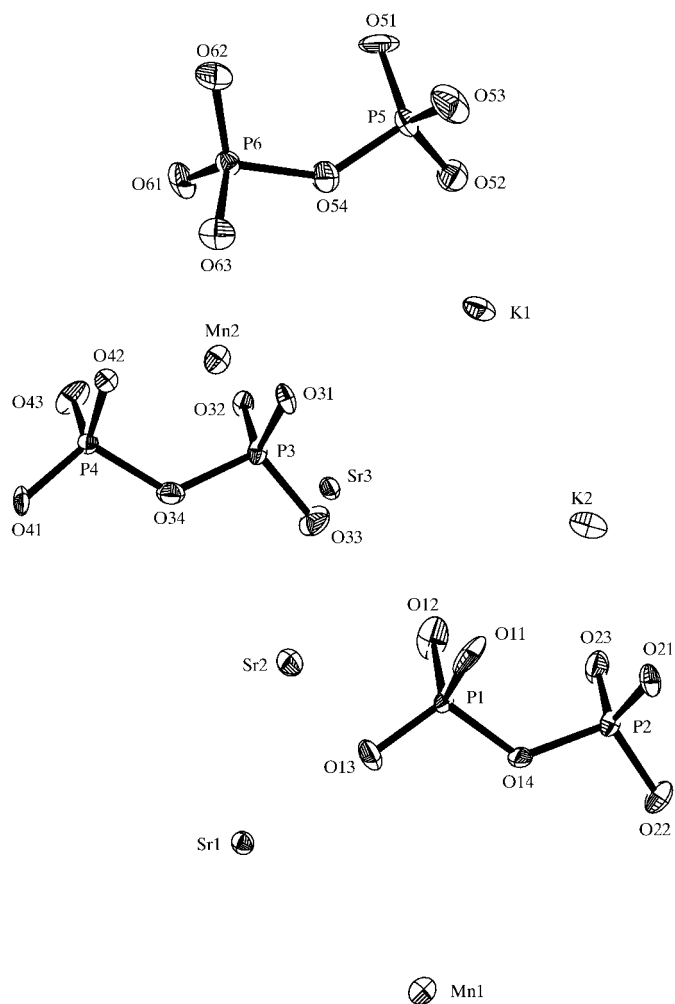
Figure 1
View of the asymmetric unit of $K_2Sr_3Mn_2(P_2O_7)_3$. Displacement ellipsoids are shown at the 50% probability level.

Figure 2
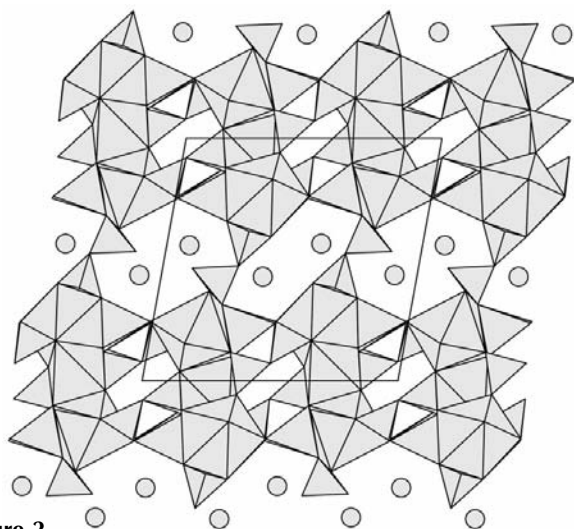Projection of $K_2Sr_3Mn_2(P_2O_7)_3$ on the (010) plane. The Sr–O polyhedra, MnO_5 pentagonal pyramids and PO_4 tetrahedra are shown as solid forms surrounding the tunnels, in each of which are seen two columns of K^+ ions. The c axis is horizontal, with the a axis subtending an angle of 100.19°.

positions of mirror symmetry in the centrosymmetric space group $P2_1/m$ (mandating an eclipsed conformation of the P_2O_7 groups), the third diphosphate group is disordered when forced to have the bonded O—P—O—P—O atoms on a mirror plane. This disorder is completely resolved in the non-centrosymmetric space group $P2_1$. This third diphosphate group is seen in a pseudo-eclipsed conformation (the average O—P—P—O angle is 69.8°).

Thus, the transition from host matrices built up of one cation with 'covalent tendencies' and diphosphate groups to matrices built of two such cations of different sizes and diphosphate groups appears to lead to matrices with tunnels of larger size. Evidence suggests that the presence of strontium or palladium in the solid matrix is of particular importance in the construction of large tunnels.

Experimental

Crystals of $K_2Sr_3Mn_2(P_2O_7)_3$ were prepared by fusing a stoichiometric mixture of K_2CO_3, $SrCO_3$, $MnCO_3$ and $(NH_4)_2HPO_4$ according to the equation

$$K_2CO_3 + 2MnCO_3 + 3SrCO_3 + 6(NH_4)_2HPO_4 \rightarrow$$
$$K_2Mn_2Sr_3(P_2O_7)_3 + 6CO_2 + 12NH_3 + 9H_2O.$$
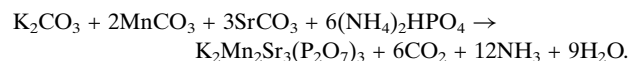
The reaction mixture was ground together and heated slowly, with intermittent grinding, to the temperature of fusion, 1073 K, in a porcelain crucible. The molten material obtained was held at this temperature for 24 h and then subjected to controlled cooling (6 K h^{-1}) to 473 K, after which the furnace was turned off. Violet crystals were obtained.

Crystal data

$K_2Sr_3Mn_2(P_2O_7)_3$	$D_x = 3.331$ Mg m^{-3}
$M_r = 972.76$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 47
$a = 13.285$ (6) Å	reflections
$b = 5.394$ (2) Å	$\theta = 3.5–9.6°$
$c = 13.750$ (6) Å	$\mu = 10.49$ mm^{-1}
$\beta = 100.19$ (3)°	$T = 293$ (2) K
$V = 969.8$ (7) Å^3	Chunk, violet
$Z = 2$	$0.1 \times 0.1 \times 0.1$ mm

Data collection

Syntex $P4$ four-circle diffractometer	$R_{int} = 0.082$
$\theta/2\theta$ scans	$\theta_{max} = 30.0°$
Absorption correction: ψ scan	$h = -18 \rightarrow 1$
($XEMP$; Siemens, 1991)	$k = -1 \rightarrow 7$
$T_{min} = 0.87$, $T_{max} = 0.91$	$l = -19 \rightarrow 19$
4061 measured reflections	3 standard reflections
3650 independent reflections	every 97 reflections
2492 reflections with $I > 2\sigma(I)$	intensity decay: none

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.015$
$R(F) = 0.066$	$\Delta\rho_{max} = 0.07$ e Å^{-3}
$wR(F^2) = 0.174$	$\Delta\rho_{min} = -0.05$ e Å^{-3}
$S = 1.01$	Extinction correction: $SHELXL97$
3650 reflections	Extinction coefficient: 0.0018 (5)
307 parameters	Absolute structure: Flack (1983)
$w = 1/[\sigma^2(F_o^2) + (0.0843P)^2$	Flack parameter = 0.22 (3)
$+ 3.6291P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1
Selected interatomic distances (Å).

Sr1—O61^i	2.449 (13)	Mn1—O51^{xi}	2.042 (12)
Sr1—O13^{ii}	2.547 (10)	Mn1—O23^v	2.101 (16)
Sr1—O21^{iii}	2.655 (14)	Mn1—O12^v	2.151 (17)
Sr1—O63^{iv}	2.667 (12)	Mn1—O21^{iii}	2.169 (15)
Sr1—O42^i	2.753 (17)	Mn1—O11^{iii}	2.190 (17)
Sr1—O23^v	2.771 (16)	Mn2—O63	2.082 (11)
Sr1—O43^i	2.847 (16)	Mn2—O32^x	2.092 (14)
Sr1—O22^v	2.86 (2)	Mn2—O31	2.133 (14)
Sr1—O22^{iii}	2.91 (2)	Mn2—O43^x	2.139 (16)
Sr2—O33	2.410 (10)	Mn2—O42	2.158 (15)
Sr2—O22^{vi}	2.437 (10)	K1—O53^{iv}	2.824 (16)
Sr2—O43^{vii}	2.457 (18)	K1—O32^i	2.834 (15)
Sr2—O11^{viii}	2.483 (19)	K1—O52	2.839 (13)
Sr2—O42^{ix}	2.536 (17)	K1—O52^i	2.882 (14)
Sr2—O12	2.557 (19)	K1—O31^i	2.908 (14)
Sr2—O13	2.92 (2)	K1—O54^i	2.951 (18)
Sr2—O41^{ix}	3.015 (19)	K1—O54^{iv}	3.149 (19)
Sr3—O53^{iv}	2.509 (15)	K1—O61^i	3.206 (14)
Sr3—O41^{vii}	2.579 (9)	K1—O63^{iv}	3.258 (14)
Sr3—O52^i	2.650 (13)	K2—O62^{iv}	2.693 (16)
Sr3—O32^x	2.705 (13)	K2—O61^i	2.851 (12)
Sr3—O31	2.771 (14)	K2—O21	2.864 (14)
Sr3—O33^x	2.85 (2)	K2—O62^{xi}	2.888 (12)
Sr3—O11	2.882 (16)	K2—O51^i	2.985 (16)
Sr3—O12	2.955 (18)	K2—O23	2.991 (17)
Sr3—O51^i	2.967 (15)	K2—O62^i	3.264 (17)
Sr3—O33	2.97 (2)		

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

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

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