

Strontium chromium(II) diphosphate,  
 $\text{SrCrP}_2\text{O}_7$ 

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The structure of the title compound,  $\text{SrCrP}_2\text{O}_7$ , belongs to the series of isotypic crystal structures  $\text{SrMP}_2\text{O}_7$  ( $M = \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$  or  $\text{Cd}$ ) and is closely related to  $\alpha\text{-Ca}_2\text{P}_2\text{O}_7$ . Chromium(II) shows a 4+1 square-pyramidal coordination by oxygen.  $[\text{CrO}_5]$  units and the  $[\text{P}_2\text{O}_7]$  groups build a three-dimensional framework with channels along the  $a$  axis, and Sr occupies these channels. In addition to the work on  $\text{SrCrP}_2\text{O}_7$ , lattice parameters for  $\text{SrMnP}_2\text{O}_7$  have been determined for the first time and unit-cell dimensions for  $\text{SrZnP}_2\text{O}_7$  have been redetermined.

## Comment

Despite recent progress (Glaum, 1999; Glaum & Schmidt, 1997), the crystal chemistry of  $\text{Cr}^{2+}$  in a plain O coordination is still not well established. Apart from preliminary investigations (Schmidt & Glaum, 1997, 1999; Belsky *et al.*, 1984), the spectroscopic and magnetic properties of  $\text{Cr}^{2+}$  in oxidic solids have not been studied. For this reason, we have started to synthesize new phosphates of  $\text{Cr}^{2+}$  in the systems  $A/\text{Cr}/\text{P}/\text{O}$  ( $A = \text{Mg}, \text{Ca}, \text{Sr}$  or  $\text{Ba}$ ). Our particular interest is focused on structures containing only one  $\text{Cr}^{2+}$  within the asymmetric unit, because these are particularly suitable for spectroscopic and magnetic measurements. The series of isotypic diphosphates  $\text{SrMP}_2\text{O}_7$  [ $M = \text{Mn}$  (Maaß *et al.*, 1999),  $\text{Fe}$  (Le Meins & Courbion, 1999),  $\text{Co}$  (Riou & Raveau, 1991),  $\text{Ni}$  (El-Bali, 1999),  $\text{Cu}$  (Moqine *et al.*, 1993),  $\text{Zn}$  (Maaß, 1999; Murashova *et al.*, 1991) or  $\text{Cd}$  (Alaoui El Belghiti *et al.*, 1991)] with square-pyramidal  $[\text{MO}_5]$  units meets this requirement. In this paper, we report on the synthesis of  $\text{SrCrP}_2\text{O}_7$  and its crystal structure refinement from X-ray single-crystal data. Lattice parameters for  $\text{SrMnP}_2\text{O}_7$  and  $\text{SrZnP}_2\text{O}_7$  have also been determined.

The X-ray single-crystal structure analysis of  $\text{SrCrP}_2\text{O}_7$  shows square-pyramidal coordination for  $\text{Cr}^{2+}$  [ $\text{Cr}-\text{O}$ : equatorial distances 1.995 (2)–2.109 (2) Å, and axial 2.362 (3) Å] similar to those observed for  $M^{2+}$  in the other members of this series. The  $\text{P}-\text{O}$  distances and  $\text{O}-\text{P}-\text{O}$  angles in  $\text{SrCrP}_2\text{O}_7$  are in the typical ranges found for diphosphate groups (Table 2). An almost eclipsed conformation (dihedral angle

15–20°) and a  $\text{P}-\text{O}-\text{P}$  bridging angle of 128.0 (2)° are observed for the  $[\text{P}_2\text{O}_7]$  units.

$\text{Cr}^{2+}$  is coordinated to the terminal O atoms of five  $[\text{P}_2\text{O}_7]$  groups. These  $[\text{CrO}_5]$  and  $[\text{P}_2\text{O}_7]$  groups are joined together to form a three-dimensional framework, with channels running along the crystallographic  $a$  and  $b$  axes (Fig. 1). The Sr atoms are located at the intersections of these channels. Calculations according to the concept of effective coordination numbers (ECoN; Hoppe, 1979) using the program MAPLE-4 (Hübenthal, 1993) yield  $\text{ECoN}(\text{Sr}^{2+}) = 7.88$ . Naïve counting of all O atoms closer to  $\text{Sr}^{2+}$  than the nearest cation leads to nine O neighbours. For  $\text{O}7^i$ , showing the longest distance to Sr, a contribution  $\delta(\text{ECoN}) = 0.098$  to  $\text{ECoN}(\text{Sr}^{2+})$  has been calculated, while for  $\text{O}5^i$ , with the shortest Sr–O distance,  $\delta(\text{ECoN}) = 1.227$  is obtained [symmetry code: (i)  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ ].

The structure of  $\text{SrCrP}_2\text{O}_7$  is closely related to that of  $\alpha\text{-Ca}_2\text{P}_2\text{O}_7$  (Calvo, 1968).  $\text{Sr}^{2+}$  occupies the position Ca(1), while  $\text{Cr}^{2+}$  is located at the position Ca(2). In contrast to  $\text{Ca}^{2+}$  (coordination number = 8,  $[\text{Ca}_2\text{O}_{14}]$  'dimers'),  $\text{Cr}^{2+}$  shows coordination to only five O atoms. This leads to isolated  $[\text{CrO}_5]$  groups.

It is interesting to note that the  $[\text{CrO}_5]$  groups are aligned with their long axis almost parallel to the crystallographic  $a$  axis ( $\varphi = 8.42^\circ$ ). Fig. 2 gives a summary of the lattice parameters observed for the whole series  $\text{SrMP}_2\text{O}_7$  with  $M = \text{Cr}$ – $\text{Zn}$  and  $\text{Cd}$ . It is evident that the particular stereochemistry of  $\text{Cr}^{2+}$  and  $\text{Cu}^{2+}$ , which is due to the Jahn–Teller effect, leads to

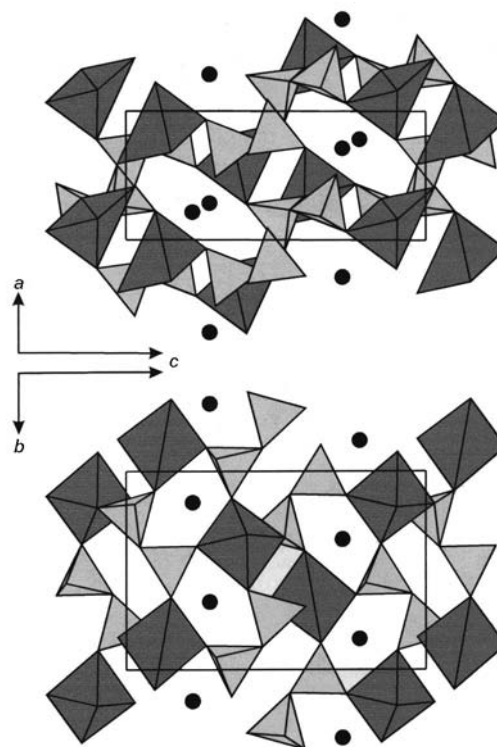
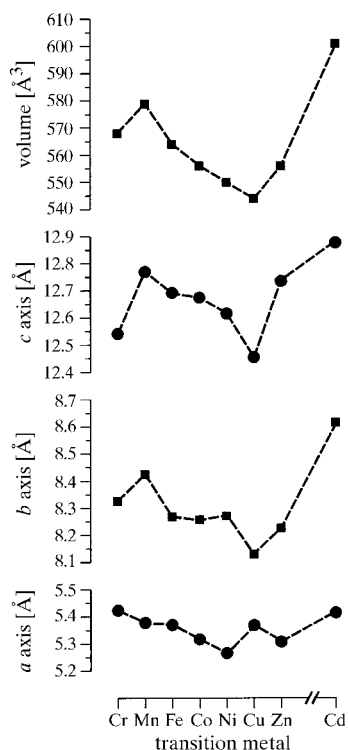


Figure 1

The crystal structure of  $\text{SrCrP}_2\text{O}_7$  projected along the  $a$  and  $b$  axes. Light-grey shading indicates  $[\text{PO}_4]$ , dark-grey shading  $[\text{CrO}_5]$  and black circles Sr.



**Figure 2**  
The unit-cell parameters of the series of diphosphates  $\text{SrMP}_2\text{O}_7$  ( $M = \text{Cr}$ – $\text{Zn}$  and  $\text{Cd}$ ).

an expansion of the crystallographic  $a$  axis compared with the other members of the series. At the same time, shrinking of the  $b$  and  $c$  axes is observed for  $\text{SrCrP}_2\text{O}_7$  and  $\text{SrCuP}_2\text{O}_7$ .  $\text{SrFeP}_2\text{O}_7$ , containing  $\text{Fe}^{2+}$  which is subject to a second-order Jahn–Teller distortion, shows similar behaviour although to a far smaller extent.

In addition to the characterization of  $\text{SrCrP}_2\text{O}_7$ , two more mixed diphosphates,  $\text{SrZnP}_2\text{O}_7$  (Maaß, 1999; Murashova *et al.*, 1991) and  $\text{SrMnP}_2\text{O}_7$ , have been synthesized and their lattice parameters refined. The Mn compound has been obtained for the first time. The unit-cell dimensions fit well into the whole series obtained for  $\text{SrMP}_2\text{O}_7$  ( $M = \text{Cr}$ – $\text{Zn}$  and  $\text{Cd}$ ). The unit-cell volumes directly follow the development of the ionic radii of divalent  $3d$  metals as described in textbooks. The variation of the three axes, however, shows the anisotropy in bonding due to the particular number of antibonding  $d$  electrons.

## Experimental

Equimolar mixtures of the starting materials,  $\text{Cr}_2\text{P}_2\text{O}_7$  (Glaum *et al.*, 1991) and  $\text{Sr}_2\text{P}_2\text{O}_7$  [obtained from  $\text{SrCO}_3$  and  $(\text{NH}_4)_2\text{HPO}_4$  by slowly increasing the temperature to 1273 K], were sealed in evacuated silica ampoules ( $l \sim 10$  cm,  $d \sim 1.6$  cm) with iodine (100 mg) and CrP (5 mg) as mineralizers and heated at 1223 K for 10 d. The addition of CrP was intended to ensure reducing conditions. Furthermore, we have observed an improved recrystallization *via* the gas phase, and even chemical vapour transport reactions for many phosphates, using

iodine as a mineraliser/transport agent in combination with reducing agents such as metal, phosphorus or metal phosphide (Glaum *et al.*, 1991; Glaum, 1999). The reaction products were washed with dilute NaOH and water, and dried at 393 K. The experiments led to light-blue powders of  $\text{SrCrP}_2\text{O}_7$  which always contained small amounts of well recrystallized CrP and  $\text{Cr}_2\text{P}_2\text{O}_7$  as by-products. Occasionally, growth of prismatic crystals of  $\text{SrCrP}_2\text{O}_7$  with an edge-length of up to 1 mm was observed. Chemical vapour transport experiments in a temperature gradient (1323→1223 K), aimed at purification and crystallization of  $\text{SrCrP}_2\text{O}_7$ , led to decomposition of the mixed phosphate;  $\text{Cr}_2\text{P}_2\text{O}_7$  was deposited at the lower temperature region, while  $\text{Sr}_2\text{P}_2\text{O}_7$  remained at the higher temperature zone.  $\text{SrCrP}_2\text{O}_7$  is remarkably stable in air and against mild oxidizing agents. By heating  $\text{SrCO}_3$  with  $\text{MnCO}_3$  or  $\text{ZnO}$  and stoichiometric amounts of  $(\text{NH}_4)_2\text{HPO}_4$  in air slowly to 1073 K, single-phase powders of the isotopic diphosphates  $\text{SrMnP}_2\text{O}_7$  and  $\text{SrZnP}_2\text{O}_7$  have also been synthesized (Maaß *et al.*, 1999; Maaß, 1999).

### Crystal data

$\text{SrCrP}_2\text{O}_7$	$D_x = 3.679 \text{ Mg m}^{-3}$
$M_r = 313.56$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 36 reflections (Guinier photograph)
$a = 5.422$ (2) Å	$\theta = 6.34$ – $26.08^\circ$
$b = 8.3254$ (19) Å	$\mu = 11.890 \text{ mm}^{-1}$
$c = 12.542$ (4) Å	$T = 293$ (2) K
$\beta = 90.39$ (3)°	Prismatic, light blue
$V = 566.1$ (3) Å <sup>3</sup>	$0.34 \times 0.10 \times 0.09 \text{ mm}$
$Z = 4$	

### Data collection

Stoe IPDS diffractometer	1178 reflections with $I > 2\sigma(I)$
Integrated intensities from imaging plate scans	$R_{\text{int}} = 0.032$
Absorption correction: numerical (HABITUS; Herrendorf, 1993)	$\theta_{\text{max}} = 28.16^\circ$
$T_{\text{min}} = 0.259$ , $T_{\text{max}} = 0.366$	$h = -6 \rightarrow 6$
4907 measured reflections	$k = -11 \rightarrow 11$
1260 independent reflections	$l = -16 \rightarrow 16$
	Intensity decay: none

### Refinement

Refinement on $F^2$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.027$	$\Delta\rho_{\text{max}} = 0.784 \text{ e Å}^{-3}$
$wR(F^2) = 0.076$	$\Delta\rho_{\text{min}} = -0.741 \text{ e Å}^{-3}$
$S = 1.096$	Extinction correction: SHELXL97 (Sheldrick, 1997)
1260 reflections	Extinction coefficient: 0.093 (4)
101 parameters	
$w = 1/[\sigma^2(F_o^2) + (0.0555P)^2 + 0.2729P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

**Table 1**

Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>).

	$x$	$y$	$z$	$U_{\text{eq}}$
Sr1	0.28539 (6)	0.34270 (3)	0.27851 (2)	0.0090 (2)
Cr1	0.79177 (11)	0.14493 (6)	0.11053 (4)	0.0080 (2)
P1	0.7538 (2)	0.53916 (9)	0.16150 (6)	0.0069 (2)
P2	0.3140 (2)	0.19796 (9)	0.98505 (6)	0.0069 (2)
O1	0.6791 (5)	0.3652 (3)	0.1493 (2)	0.0113 (5)
O2	0.6620 (5)	0.4009 (3)	0.4052 (2)	0.0110 (5)
O3	0.9351 (5)	0.1222 (3)	0.2666 (2)	0.0100 (5)
O4	0.7676 (5)	0.1166 (3)	0.4543 (2)	0.0109 (5)
O5	0.4865 (5)	0.0633 (3)	0.2980 (2)	0.0132 (5)
O6	0.0897 (5)	0.3351 (3)	0.4716 (2)	0.0103 (5)
O7	0.2224 (5)	0.1818 (3)	0.0979 (2)	0.0113 (5)

**Table 2**

Selected geometric parameters (Å, °).

Sr1—O5 <sup>i</sup>	2.539 (3)	Cr1—O2 <sup>iv</sup>	2.057 (2)
Sr1—O5	2.580 (3)	Cr1—O6 <sup>v</sup>	2.058 (3)
Sr1—O2	2.624 (2)	Cr1—O3	2.109 (2)
Sr1—O3 <sup>iii</sup>	2.645 (2)	Cr1—O7 <sup>vi</sup>	2.361 (3)
Sr1—O6	2.651 (3)	Cr1—Sr1 <sup>iv</sup>	3.6715 (10)
Sr1—O7	2.652 (2)	Cr1—Sr1 <sup>vi</sup>	3.7731 (13)
Sr1—O1	2.695 (3)	P1—O5 <sup>iii</sup>	1.507 (3)
Sr1—O3 <sup>iii</sup>	2.836 (3)	P1—O3 <sup>iii</sup>	1.534 (3)
Sr1—O7 <sup>i</sup>	3.221 (2)	P1—O4 <sup>iii</sup>	1.593 (2)
Sr1—P1	3.3660 (13)	P2—O7 <sup>vii</sup>	1.509 (2)
Sr1—P1 <sup>ii</sup>	3.6164 (14)	P2—O6 <sup>viii</sup>	1.530 (3)
Sr1—P1 <sup>iv</sup>	3.6289 (12)	P2—O2 <sup>ix</sup>	1.533 (2)
Cr1—O1	1.994 (2)	P2—O4 <sup>ix</sup>	1.611 (3)
P1 <sup>iv</sup> —O4—P2 <sup>v</sup>	128.1 (2)		

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

The Guinier photograph of SrCrP<sub>2</sub>O<sub>7</sub> was indexed on the basis of the pattern of SrCoP<sub>2</sub>O<sub>7</sub> (Riou & Raveau, 1991). The structure refinement of SrCrP<sub>2</sub>O<sub>7</sub> from X-ray single-crystal data, using *SHELXL97* (Sheldrick, 1997) and the coordinates of SrCoP<sub>2</sub>O<sub>7</sub> (Riou & Raveau, 1991) as starting parameters, proceeded in a straightforward manner. The crystal shape was optimized by minimizing the internal *R* value of the whole data set using the program *HABITUS* (Herrendorf, 1993). The habitus so derived was used for the numerical absorption correction. The lattice parameters of SrMnP<sub>2</sub>O<sub>7</sub> and SrZnP<sub>2</sub>O<sub>7</sub> were also determined from Guinier photographs [Cu *K*α, α-SiO<sub>2</sub> as internal standard, SrMnP<sub>2</sub>O<sub>7</sub>: *a* = 5.378 (2), *b* = 8.424 (2) and *c* = 12.770 (3) Å, and β = 90.24 (3)°; SrZnP<sub>2</sub>O<sub>7</sub>: *a* = 5.309 (2), *b* = 8.225 (2) and *c* = 12.749 (6) Å, and β = 90.22 (3)°]. The lattice parameters obtained for SrZnP<sub>2</sub>O<sub>7</sub> have lower s.u.'s and deviate somewhat from the values reported earlier by Murashova *et al.* (1991).

Data collection: *IPDS Software* (Stoe & Cie, 1997); cell refinement: *IPDS Software*; data reduction: *IPDS Software*; program(s) used to refine structure: *SHELXL97*; molecular graphics: *ATOMS for Windows* (Dowty, 1998); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1092). Services for accessing these data are described at the back of the journal.

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