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Cobalt Silicon Diphosphate, $Co_2Si(P_2O_7)_2$

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Abstract

The structure of dicobalt(II) silicon bis[diphosphate-(4−)], $Co_2Si(P_2O_7)_2$, consists of compressed CoO_6 octahedra, SiO_4 tetrahedra and P_2O_7 groups with a P—O—P angle of 132.3 (1)°. Co_2O_{10} units built from two edge-sharing CoO_6 octahedra are linked *via* four corners to other dimers, thus forming a two-dimensional network parallel to the *bc* plane. These planes are separated by bands formed from diphosphate groups and SiO_4 tetrahedra.

Comment

In the course of our investigations of the thermal behaviour and crystal chemistry of anhydrous phosphates of transition metals, we obtained cobalt silicon diphosphate as a product of chemical transport experiments intended to crystallize $Co_2P_4O_{12}$ (Thilo & Grunze, 1957). After the isotypic $Cd_2Si(P_2O_7)_2$ (Trojan, Brandová, Fábry, Hybler, Jurek & Petrícek, 1987), $Co_2Si(P_2O_7)_2$ is only the second mixed anhydrous phosphate of silicon with a late transition metal to be identified, whereas phosphates of silicon and the early transition metals, *e.g.* $(VO)Si(PO_4)_2$ (Middlemiss & Calvo, 1976), $V_3P_5SiO_{19}$ (Leclaire, Chaboun, Groult & Raveau, 1986) and $Mo_4P_6Si_2O_{25}$ (Leclaire, Lamire & Raveau, 1988), have been known for some time. An even wider variety of phosphate silicates is obtained by the introduction of alkali metals or alkaline earth metals in addition to the early transition metal (*e.g.* see Leclaire, Monier & Raveau, 1985).

The structure of $Co_2Si(P_2O_7)_2$ consists of compressed CoO_6 octahedra, almost ideal SiO_4 tetrahedra and P_2O_7 groups with an eclipsed conformation similar to that found in the triclinic modification of GeP_2O_7 (Kaiser & Glaum, 1994). The P—O—P bridging angle of 132.3 (1)° is rather small as a result of a chelate-type coordination to Co^{2+} (Fig. 1*a*). Two remarkably different P—O—Si bridging angles of 140.8 (1) and 168.9 (1)° are observed for $Co_2Si(P_2O_7)_2$, compared to 141.7 to 153.3° found in SiP_2O_7 (Tillmans, Gebert & Baur, 1973).

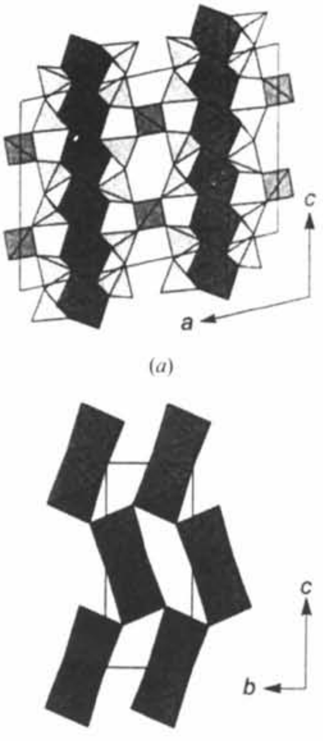

Fig. 1. (*a*) Projection of the title structure on the *ac* plane with schematic coordination polyhedra; P_2O_7 light grey, SiO_4 medium grey, CoO_6 dark grey. (*b*) Projection on the *bc* plane of sheets comprising dimeric Co_2O_{10} units. Both views were produced using *ATOMS* (Dowty, 1995).

The structure contains seven independent O-atom sites. Two show threefold coordination (by one P atom and two Co atoms) while the other five show twofold coordination either by two P atoms, a P and an Si atom (twice) or a P and a Co atom (twice). As expected, the bond lengths around an O atom depend on its coordination number and the valence of the counter cations. Within the diphosphate group, the P—O distance to the bridging O atom is about 0.04 Å longer than to the O atom bonded to Si. The P—O bonds to those O^{2-} ions further bonded to Co are rather short [1.483 (2)–1.513 (2) Å]. These differences in bond length within the PO_4 groups are in agreement with bond length–bond strength considerations. Similar relations were observed in other diphosphates, *e.g.* SiP_2O_7 (Tillmans, Gebert & Baur, 1973).

Co is octahedrally coordinated by O atoms with two short (*ca* 1.98 Å) and four long (*ca* 2.28 Å) bonds. Two CoO_6 octahedra are linked by edge-sharing, thus forming Co_2O_{10} units. These are connected by four corners with other dimers to form a two-dimensional network parallel to the *bc* plane (Fig. 1*b*). These planes are separated by bands formed from diphosphate groups and SiO_4 tetrahedra.

In contrast to red–violet $Co_2P_4O_{12}$, which contains only slightly distorted CoO_6 octahedra, the compressed octahedral geometry around Co^{2+} in the title compound leads to a pale blue–violet colour.

In addition to $Co_2Si(P_2O_7)_2$, three isotypic diphosphates $M_2Si(P_2O_7)_2$ (M = Fe, Ni, Cu) have been synthesized. Their lattice parameters at ambient temperature were determined from Guinier photographs [$Fe_2Si(P_2O_7)_2$: a = 16.909 (6), b = 4.991 (1), c = 12.381 (5) Å, β = 103.32 (3)°; $Ni_2Si(P_2O_7)_2$: a = 16.892 (5), b = 4.900 (1), c = 12.215 (4) Å, β = 103.73 (3)°; $Cu_2Si(P_2O_7)_2$: a = 17.38 (1), b = 4.70 (1), c = 12.28 (1) Å, β = 105.6 (1)°; Glaum, Hofmann & Schmidt (1996)].

Experimental

Single crystals of $Co_2Si(P_2O_7)_2$ suitable for X-ray single-crystal investigations were grown by isothermal heating of $Co_2P_4O_{12}$ (Thilo & Grunze, 1957) in silica ampoules at 1173 K under 3 atm (1 atm = 101 325 Pa) of chlorine as mineralizer. Migration in a temperature gradient from 1223 to 1123 K was not observed. Microcrystalline $Co_2Si(P_2O_7)_2$ was obtained as a single phase by heating pellets of stoichiometric mixtures of $Co_2P_4O_{12}$ and amorphous SiO_2 in silica ampoules at 1173 K using 10 mg NH_4Cl as mineralizer.

Crystal data

$Co_2Si(P_2O_7)_2$
M_r = 493.83
Monoclinic
$C2/c$
a = 16.897 (2) Å
b = 4.9442 (5) Å
c = 12.2950 (10) Å
β = 103.418 (9)°
V = 999.1 (2) $Å^3$
Z = 4
D_x = 3.283 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 68 reflections (19 independent)
θ = 16.5–24.9°
μ = 4.174 mm^{-1}
T = 293 (2) K
Plate
0.10 × 0.08 × 0.02 mm
Pale violet

Data collection

AED-2 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
T_{min} = 0.587, T_{max} = 0.725
5468 measured reflections
1446 independent reflections

1123 observed reflections [$I > 2\sigma(I)$]
R_{int} = 0.0381
θ_{max} = 29.95°
$h = -23 \rightarrow 23$
$k = -6 \rightarrow 6$
$l = -17 \rightarrow 17$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0200
$wR(F^2)$ = 0.0505
S = 1.047
1446 reflections

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0018 (2)

97 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0247P)^2 + 0.5839P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.408 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.404 e $Å^{-3}$

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Co	0.24670 (2)	0.14994 (6)	0.62975 (2)	0.00773 (9)
Si	0	0.8439 (2)	3/4	0.00535 (15)
P1	0.12470 (3)	0.63442 (12)	0.63418 (4)	0.00626 (11)
P2	0.13536 (3)	0.83091 (11)	0.41479 (4)	0.00596 (11)
O1	0.04428 (9)	0.6531 (3)	0.67674 (12)	0.0090 (3)
O2	0.14261 (9)	0.3447 (3)	0.61930 (12)	0.0111 (3)
O3	0.30755 (9)	0.3038 (3)	0.79627 (12)	0.0099 (3)
O4	0.09356 (10)	0.7791 (3)	0.51626 (12)	0.0101 (3)
O5	0.34594 (9)	−0.0690 (3)	0.63241 (12)	0.0108 (3)
O6	0.20389 (9)	1.0275 (3)	0.45361 (12)	0.0099 (3)
O7	0.06365 (10)	0.9656 (3)	0.33043 (13)	0.0126 (3)

Table 2. *Selected geometric parameters (Å, °)*

Co—O2	1.983 (2)	Si—$O1^{vi}$	1.604 (2)
Co—O5	1.990 (2)	P1—O2	1.484 (2)
Co—$O6^{i}$	2.165 (2)	P1—$O3^{vii}$	1.513 (2)
Co—O3	2.2024 (15)	P1—O1	1.568 (2)
Co—$O6^{ii}$	2.2028 (15)	P1—O4	1.593 (2)
Co—$O3^{iii}$	2.232 (2)	P2—$O5^{viii}$	1.483 (2)
Si—$O7^{iv}$	1.590 (2)	P2—O6	1.502 (2)
Si—$O7^{v}$	1.590 (2)	P2—O7	1.551 (2)
Si—O1	1.604 (2)	P2—O4	1.591 (2)
P1—O1—Si	140.81 (11)	$P2^{viii}$—O5—Co	136.39 (10)
P1—O2—Co	131.60 (10)	P2—O6—Co^{i}	132.82 (9)
$P1^{iii}$—O3—Co	117.59 (8)	P2—O6—Co^{ix}	122.90 (9)
$P1^{iii}$—O3—Co^{vii}	121.50 (8)	Co^{i}—O6—Co^{ix}	100.85 (6)
Co—O3—Co^{vii}	119.76 (7)	P2—O7—Si^{v}	168.89 (13)
P2—O4—P1	132.33 (11)		

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

Data collection: *Stadi*-4 *Software* using the peak/background method (Stoe & Cie, 1995). Cell refinement: *Stadi*-4 *Software*. Data reduction: *Stadi*-4 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ATOMS* (Dowty, 1995). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: JZ1108). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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