inorganic compounds

Ag$_2$PdP$_2$O$_7$

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Disilver(I) palladium(II) diphosphate, Ag$_2$PdP$_2$O$_7$, is isotypic with Na$_2$PdP$_2$O$_7$. It consists of infinite diphosphato-palladate(II) [Pd(P$_2$O$_7$)$_{2/2}$]$^{2-}$ ribbons with the Pd^{II} ion in an almost square-planar coordination ($\bar{1}$ symmetry) and the P$_2$O$_7$ group exhibiting 2 symmetry. The [Pd(P$_2$O$_7$)$_{2/2}$]$^{2-}$ ribbons are linked by distorted [AgO$_6$] octahedra. ^{31}P-MAS NMR studies on Ag$_2$PdP$_2$O$_7$ are in accordance with one independent site for phosphorus; its isotropic chemical shift δ_{iso} = 21.5 p.p.m. is similar to that of Pd$_2$P$_2$O$_7$.

Related literature

For related literature on palladium oxo-compounds, see: Arndt & Wickleder (2007); Dahmen et al. (1994); Laligant et al. (1991); Palkina et al. (1978); Panagiotidis et al. (2005b); Waser et al. (1953). For related literature on polynary palladium phosphates, see: El Maadi et al. (2003); Laligant (1992a,b); Lii et al. (2004); For related literature on noble metal phosphates, see: Panagiotidis et al. (2005a, 2008). For background on chemical shift parameters, see: Moreno et al. (2002); Griffiths et al. (1986); Hayashi & Hayamizu (1989). For details of software used, see: Bak et al. (2000); Soose & Meyer (1980); Vosegaard et al. (2002).

Experimental

Crystal data

Ag$_2$PdP$_2$O$_7$
M_r = 496.10
Monoclinic, $C2/c$
a = 15.739 (2) Å
b = 5.7177 (7) Å
c = 8.187 (1) Å
β = 116.75 (1)°

V = 657.91 (15) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 9.08 mm^{-1}
T = 293 (2) K
0.08 × 0.05 × 0.05 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: ψ scan (North et al., 1968)
T_{min} = 0.551, T_{max} = 0.631
1890 measured reflections

947 independent reflections
591 reflections with $I > 2\sigma(I)$
R_{int} = 0.080
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.074
S = 0.97
947 reflections

58 parameters
$\Delta\rho_{max}$ = 1.30 e Å^{-3}
$\Delta\rho_{min}$ = −1.14 e Å^{-3}

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2008); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BR2086).

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supplementary materials

Ag$_2$PdP$_2$O$_7$

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Comment

With the synthesis and crystal structure refinement of the first gold phosphate Au^{III}PO$_4$ (Panagiotidis *et al.*, 2005*a*) and two modifications of Ir^{III}(PO$_3$)$_3$ (Panagiotidis *et al.*, 2008) we have widened the crystal chemical knowledge on anhydrous phosphates of the noble metals. Investigations in the ternary system Pd/P/O provided, apart from the already existing phosphates Pd(PO$_3$)$_2$ (Palkina *et al.*, 1978) and Pd$_2$P$_2$O$_7$ (Panagiotidis *et al.*, 2005*b*), no evidence for further thermodynamically stable palladium phosphates. Due to our interest in network structures built from square-planar units [MO$_4$] (M = Pd^{II}, Au^{III}) and phosphate tetrahedra we focused therefore our search on polynary palladium phosphates. Polynary phosphates of divalent palladium are rare in literature. Up to now, only the compositions M^{I}_2PdP$_2$O$_7$ (M = Li (Laligant, 1992*a*), Na (Laligant, 1992*b*), K (El Maadi *et al.*, 2003), K$_{3.5}$Pd$_{2.25}$(P$_2$O$_7$)$_2$ (El Maadi *et al.*, 2003) and Cs$_2$Pd$_3$(P$_2$O$_7$)$_2$ (Lii *et al.*, 2004) were reported. In Pd$_2$P$_2$O$_7$ itself, Li$_2$PdP$_2$O$_7$, and Na$_2$PdP$_2$O$_7$ infinite ribbons [Pd(P$_2$O$_7$)$_{2/2}$]$^{2-}$ are the characteristic structural motif. K$_2$PdP$_2$O$_7$ adopts a layer structure with the crystal chemical composition [Pd(P$_2$O$_7$)$_{4/4}$]$^{2-}$. The structures of K$_{3.5}$Pd$_{2.25}$(P$_2$O$_7$)$_2$ and Cs$_2$Pd$_3$(P$_2$O$_7$)$_2$ consist of [Pd^{II}O$_4$] and [P$_2$O$_7$] groups generating a three-dimensional framework.

According to our X-ray single-crystal study Ag$_2$PdP$_2$O$_7$ is isotypic to Na$_2$PdP$_2$O$_7$. The unit cell contains four formula units Ag$_2$PdP$_2$O$_7$ with one crystallographically independent site for silver, palladium and phosphorus (Fig. 1). As in the crystal structures of PdO (Waser *et al.*, 1953), *M*-Pd^{II}SO$_4$ (Dahmen *et al.*, 1994), Pd^{II}(NO$_3$)$_2$(H$_2$O)$_2$ (Laligant *et al.*, 1991), and Pd$_2$P$_2$O$_7$ the Pd^{2+} ions show a square-planar coordination by oxygen. In Ag$_2$PdP$_2$O$_7$ palladium is coordinated in a chelating way by two [P$_2$O$_7$] groups. This coordination mode, with a, for such diphosphates typically observed, bridging angle ⟨(P—O2—P) = 124.9°, leads to the formation of corrugated ribbons [Pd(P$_2$O$_7$)$_{2/2}$]$^{2-}$ (Fig. 2). These ribbons are linked by significantly distorted [Ag^{I}O$_6$] octahedra. Due to different crystal chemical environment of the four independent oxygen atoms, with O1 forming one bond to P and two to Ag, O2 forming two bonds to P and O3 and O4 forming one bond each to P, Pd and Ag, a radial distortion of the phosphate groups with one very short, two medium long and one elongated distance d(P—O) is observed. In accordance with the crystal structure of Ag$_2$PdP$_2$O$_7$ ^{31}P-MAS-NMR investigations (Varian Infinity Plus, 9.4 tesla-magnet, 2.5-mm MAS double resonance NMR probe, rotation frequency 3.0 kHz) show the presence of just one phosphorus site. Chemical shift parameters were determined by means of numerically calculated spectra (programme SIMPSON (Bak *et al.*, 2000), *MINUIT* routine in SIMPSON (Vosegaard *et al.*, 2002)) to δ$_{iso}$ = 21.5 p.p.m., δ$_{aniso}$ = 79.0 p.p.m. and η = 0.87. The chemical shifts are reported in parts per million (p.p.m.) from the external standard 85% H$_3$PO$_4$. As in Pd$_2$P$_2$O$_7$ (η = 0.86) and in contrast to other diphosphates (Moreno *et al.*, 2002; Griffiths *et al.*, 1986; Hayashi & Hayamizu, 1989) a remarkably high value for η is observed. The isotropical chemical shift of Ag$_2$PdP$_2$O$_7$ which is similar to the one observed for Pd$_2$P$_2$O$_7$ (δ$_{iso}$ = 28.3 p.p.m.) is exceptionally high in comparison to δ$_{iso}$ values of diphosphates of
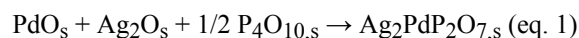
supplementary materials

the alkaline and alkaline earth metals (Moreno *et al.*, 2002; Griffiths *et al.*, 1986; Hayashi & Hayamizu, 1989). We attribute this observation to significant covalency in the Pd—O interaction.

Experimental

Microcrystalline $Ag_2PdP_2O_7$ was synthesized *via* a solid state reaction by heating an amorphous precursor for 24 h at T = 773 K in air. The precursor was obtained by drying a mixture of 100.0 mg (0.94 mmol) palladium powder (99.99%, UMICORE AG, Hanau–Wolfgang) with an excess of conc. nitric acid and stoichiometric amounts of 319.2 mg $AgNO_3$ (1.88 mmol) (p.A., Merck) and 18.8 ml H_3PO_4 (0.1 *M*) at 423 K as a brownish powder.

Isothermal heating of 100.0 mg (0.82 mmol) PdO, 189.3 mg (0.82 mmol) Ag_2O (p.A. Merck) and 116.0 mg (0.41 mmol) P_4O_{10} (99%, Riedel de Häen) (addition of 8.0 mg $PdCl_2$ as mineralizer) carried out in sealed and evacuated silica tubes at 773 K for seven days gave besides microcrystalline, single-phase $Ag_2PdP_2O_7$ (eq. 1) also small amounts of yellow plate-like single crystals which were distributed over the whole ampoule.
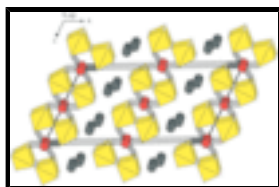
$$PdO_s + Ag_2O_s + 1/2\ P_4O_{10,s} \rightarrow Ag_2PdP_2O_{7,s}\ \text{(eq. 1)}$$

Figures

Fig. 1. Projection of the crystal structure of $Ag_2PdP_2O_7$ along [010] with tetrahedral [PO_4] units (yellow), Pd^{2+} (red) and Ag^+ grey (*DIAMOND* v3.1f).
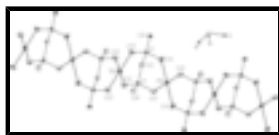

Fig. 2. Diphosphato-palladate(II) ribbon [$Pd(P_2O_7)_{2/2}$]$^{2-}$ along [001]. Thermal elipsoids with 50% probability (*DIAMOND*, v3.1f).

Disilver(I) palladium(II) diphosphate

Crystal data

$Ag_2PdP_2O_7$	The lattice parameters given were refined with the program SOS (Soose & Meyer, 1980), using 40 reflections from a Guinier IP photograph.
$M_r = 496.10$	$D_x = 5.008$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -C 2yc	Cell parameters from 40 reflections
$a = 15.739\ (2)$ Å	$\theta = 6.3–34.3°$
$b = 5.7177\ (7)$ Å	$\mu = 9.08$ mm^{-1}
$c = 8.187\ (1)$ Å	$T = 293\ (2)$ K
$\beta = 116.75\ (1)°$	Cell measurement pressure: 101.3 kPa
$V = 657.91\ (15)$ Å^3	Prism, yellow
$Z = 4$	$0.08 \times 0.05 \times 0.05$ mm

$F_{000} = 904$

Data collection

Enraf–Nonius CAD-4 diffractometer	591 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.080$
Monochromator: graphite	$\theta_{max} = 29.9°$
$T = 293(2)$ K	$\theta_{min} = 2.9°$
$P = 101.3$ kPa	$h = -22 \rightarrow 22$
Nonprofiled ω scans	$k = -8 \rightarrow 0$
Absorption correction: ψ scan (North *et al.*, 1968)	$l = -11 \rightarrow 11$
$T_{min} = 0.551$, $T_{max} = 0.631$	3 standard reflections
1890 measured reflections	every 60 min
947 independent reflections	intensity decay: none

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0245P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.035$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.074$	$\Delta\rho_{max} = 1.30$ e Å^{-3}
$S = 0.97$	$\Delta\rho_{min} = -1.14$ e Å^{-3}
947 reflections	Extinction correction: SHELXL97 (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
58 parameters	Extinction coefficient: 0.00104 (17)
Primary atom site location: structure-invariant direct methods	

Special details

Geometry. All e.s.d.'s 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 and angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry.

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	$U_{iso}*/U_{eq}$
Pd1	0	0	0	0.0145 (2)
Ag1	0.23426 (5)	0.85894 (13)	0.79398 (9)	0.0217 (2)
P1	0.10116 (14)	0.3445 (4)	0.8422 (3)	0.0137 (4)

O1	0.8200 (4)	0.5226 (10)	0.5959 (7)	0.0177 (13)
O2	0	0.4744 (14)	0.75	0.0139 (16)
O3	0.8949 (4)	0.1859 (11)	0.8057 (7)	0.0220 (14)
O4	0.6031 (4)	0.2953 (11)	0.5045 (8)	0.0213 (14)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pd1	0.0103 (4)	0.0178 (5)	0.0135 (4)	−0.0012 (4)	0.0036 (3)	0.0055 (4)
Ag1	0.0197 (4)	0.0247 (4)	0.0171 (3)	−0.0044 (3)	0.0050 (3)	−0.0017 (3)
P1	0.0111 (9)	0.0152 (11)	0.0146 (9)	−0.0028 (9)	0.0055 (8)	0.0003 (10)
O1	0.016 (3)	0.016 (3)	0.019 (3)	0.011 (3)	0.006 (2)	0.005 (3)
O2	0.014 (4)	0.011 (4)	0.015 (4)	0	0.006 (3)	0
O3	0.018 (3)	0.027 (4)	0.019 (3)	−0.003 (3)	0.007 (3)	0.010 (3)
O4	0.011 (3)	0.026 (4)	0.023 (3)	0.004 (3)	0.004 (2)	−0.012 (3)

Geometric parameters (Å, °)

Pd1—O4^i	1.987 (5)	P1—O4^x	1.539 (6)
Pd1—O4^{ii}	1.987 (5)	P1—O2	1.605 (4)
Pd1—O3^{iii}	2.007 (6)	O1—P1^{vii}	1.505 (6)
Pd1—O3^{iv}	2.007 (6)	O1—Ag1^{xi}	2.321 (5)
Ag1—O1^v	2.321 (5)	O1—Ag1^{vii}	2.436 (6)
Ag1—O4^{vi}	2.368 (6)	O2—P1^{xii}	1.605 (4)
Ag1—O1^{vii}	2.436 (6)	O3—P1^{vii}	1.537 (6)
Ag1—Ag1^{viii}	3.0427 (6)	O3—Pd1^{xiii}	2.007 (6)
Ag1—Ag1^{ix}	3.0427 (6)	O4—P1^{xiv}	1.539 (6)
P1—O1^{vii}	1.505 (6)	O4—Pd1^{xv}	1.987 (5)
P1—O3^{vii}	1.537 (6)	O4—Ag1^{xvi}	2.368 (5)
O4^i—Pd1—O4^{ii}	180.0 (4)	Ag1^{viii}—Ag1—Ag1^{ix}	139.96 (5)
O4^i—Pd1—O3^{iii}	94.5 (2)	O1^{vii}—P1—O3^{vii}	110.2 (3)
O4^{ii}—Pd1—O3^{iii}	85.5 (2)	O1^{vii}—P1—O4^x	111.6 (3)
O4^i—Pd1—O3^{iv}	85.5 (2)	O3^{vii}—P1—O4^x	112.4 (4)
O4^{ii}—Pd1—O3^{iv}	94.5 (2)	O1^{vii}—P1—O2	109.8 (4)
O3^{iii}—Pd1—O3^{iv}	180.0 (6)	O3^{vii}—P1—O2	106.6 (3)
O1^v—Ag1—O4^{vi}	159.7 (2)	O4^x—P1—O2	106.0 (3)
O1^v—Ag1—O1^{vii}	88.23 (19)	P1^{vii}—O1—Ag1^{xi}	123.5 (3)
O4^{vi}—Ag1—O1^{vii}	87.5 (2)	P1^{vii}—O1—Ag1^{vii}	141.5 (3)
O1^v—Ag1—Ag1^{viii}	116.60 (15)	Ag1^{xi}—O1—Ag1^{vii}	91.77 (19)
O4^{vi}—Ag1—Ag1^{viii}	77.30 (15)	P1^{xii}—O2—P1	124.9 (5)
O1^{vii}—Ag1—Ag1^{viii}	57.82 (14)	P1^{vii}—O3—Pd1^{xiii}	128.7 (3)
O1^v—Ag1—Ag1^{ix}	84.21 (15)	P1^{xiv}—O4—Pd1^{xv}	126.2 (3)
O4^{vi}—Ag1—Ag1^{ix}	93.96 (16)	P1^{xiv}—O4—Ag1^{xvi}	127.8 (3)

O1^{vii}—Ag1—Ag1^{ix}	161.97 (14)	Pd1^{xv}—O4—Ag1^{xvi}	105.4 (2)

Symmetry codes: (i) $x-1/2$, $-y+1/2$, $z-1/2$; (ii) $-x+1/2$, $y-1/2$, $-z+1/2$; (iii) $x-1$, y, $z-1$; (iv) $-x+1$, $-y$, $-z+1$; (v) $x-1/2$, $-y+3/2$, $z+1/2$; (vi) $x-1/2$, $y+1/2$, z; (vii) $-x+1$, y, $-z+3/2$; (viii) $-x+1/2$, $y-1/2$, $-z+3/2$; (ix) $-x+1/2$, $y+1/2$, $-z+3/2$; (x) $x-1/2$, $-y+1/2$, $z+1/2$; (xi) $x+1/2$, $-y+3/2$, $z-1/2$; (xii) $-x$, y, $-z+3/2$; (xiii) $x+1$, y, $z+1$; (xiv) $x+1/2$, $-y+1/2$, $z-1/2$; (xv) $-x+1/2$, $y+1/2$, $-z+1/2$; (xvi) $x+1/2$, $y-1/2$, z.
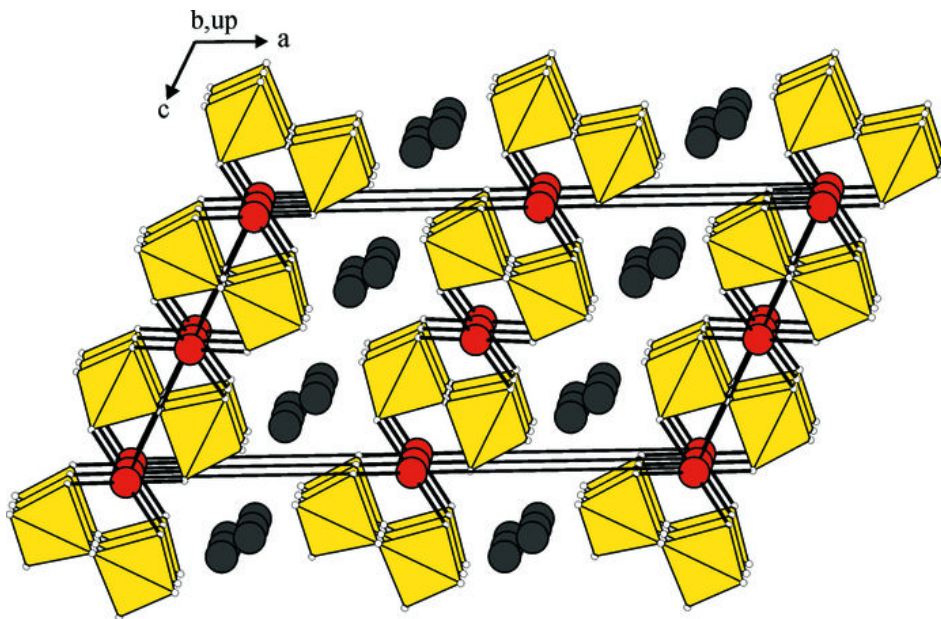
Fig. 1

Fig. 2