METAL-ORGANIC COMPOUNDS

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A one-dimensionally extended chain aluminophosphate

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Abstract

A one-dimensionally extended chain aluminophosphate, ethylenediammonium bis(propane-1,3-diyldiammonium) dialuminium tetraphosphate, $[NH_3(CH_2)_2NH_3][NH_3(CH_2)_3NH_3]_2[Al_2P_4O_{16}]$, has been prepared by a solvothermal synthesis from an alcoholic system. The infinite $[AlP_2O_8]^{3-}$ chains composed of AlO_4 and $PO_2(=O)_2$ tetrahedra are held together *via* hydrogen bonds involving two kinds of protonated amines.

Comment

Much attention has been paid to a variety of microporous aluminophosphates because of their exploitable sorption and catalytic properties (Wilson *et al.*, 1982). These microporous aluminophosphates are classified into one-, two- and three-dimensional groups according to the way in which coordination polyhedra around Al and P are combined. In particular, the one-dimensional group is subdivided into three subgroups.

$[NH_3(CH_2)_2NH_3][H_3O][AlP_2O_8]$ (Wang *et al.*, 1990), $[CH_3(CH_2)_5NH_3][AlP_2O_6(OH)_2]$ (Jones *et al.*, 1990) and $[NH_3(CH_2)_2NH_3][NH_4][AlP_2O_8]$ (Gao *et al.*, 1996) are examples of subgroup 1 and their structures consist of chains of corner-shared four-membered rings. Structures of subgroup 2, *e.g.* $[NH_3(CH_2)_2NH_3][AlP_2O_7(OH)]$ (Williams *et al.*, 1997) and $(C_{10}N_2H_9)[AlP_2O_6(OH)_2]$ (Chippindale & Turner, 1997), show chains of edge-shared four-membered rings and the adjusting accessories of PO_4 tetrahedra with one or two hydroxyl ligands. Compounds of subgroups 1 and 2 indicate the same Al:P cation ratio of 1:2, while that for subgroup 3 is 3:5, and structures such as $(C_7H_{13}NH_3)_5[Al_3P_5O_{20}(OH)]$ and $(C_5H_9NH_3)_5[Al_3P_5O_{20}(OH)]$ (Oliver *et al.*, 1996*a*,*b*) are built up by rather complicated structural units. The solid-state reaction towards a two-dimensional structure was also reported for the compounds of subgroup 3.

The title compound, $[NH_3(CH_2)_2NH_3][NH_3(CH_2)_3NH_3]_2[Al_2P_4O_{16}]$, is recognized as a fourth example of subgroup 1 and the structure is shown in Fig. 1. The structure is constructed by AlO_4 and $PO_2(=O)_2$ tetrahedra so as to form infinite one-dimensional $[AlP_2O_8]^{3-}$ chains of corner-shared four-membered rings. These chains run parallel to the *a* axis and are further joined together along the *b* and *c* axes by the protonated amines.

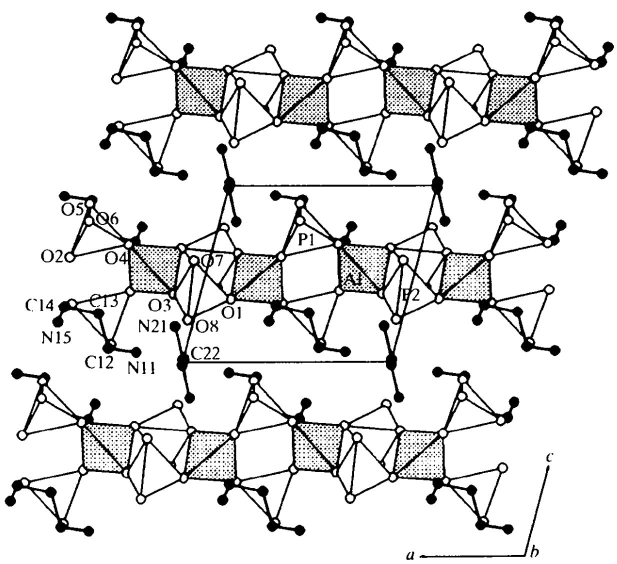

Fig. 1. The structure of the title compound. The PO_4 and AlO_4 tetrahedra are white and gray, respectively, and the open, solid and gray circles indicate O, N and C atoms, respectively. H atoms have been omitted.

The AlO_4 tetrahedra share four O atoms with adjacent $PO_2(=O)_2$ tetrahedra, with Al—O distances ranging from 1.726 (2) to 1.745 (2) Å and the corresponding O—Al—O angles ranging between 107.9 (1) and 110.4 (1)°. Two crystallographically unique $PO_2(=O)_2$ tetrahedra each share two O atoms with adjacent AlO_4 tetrahedra, with P—O distances between 1.545 (2) and 1.563 (2) Å. The shorter P—O distances with respect to the terminal O atoms [P1—O5 1.509 (2), P1—O6 1.513 (2), P2—O7 1.506 (2) and P2—O8 1.519 (2) Å] suggest their double-bond character. The double-bond nature of these O atoms is also reflected in the large O5—P1—O6 and O7—P2—O8 angles of 112.8 (1) and 112.8 (1)°, respectively, as expected from the common valence-shell electron-pair repulsion (VSEPR) theory.

The two different protonated amine species, *i.e.* $[NH_3(CH_2)_3NH_3]^{2+}$ and $[NH_3(CH_2)_2NH_3]^{2+}$, which are feasible fragments of the parent homopiperazine molecules, play a co-templating role for the title compound. Each $-NH_3^+$ group supplies three H atoms, forming three single hydrogen bonds with the terminal O atoms (O5, O6, O7 and O8). Among these terminal O atoms, O5, O6 and O7 each accept two H atoms, whereas O8 accepts three H atoms, as summarized in Table 2.

Experimental

A gel mixture of $Al[OCH(CH_3)_2]_3$, H_3PO_4, $C_5N_2H_{12}$ (homopiperazine) and $H(OCH_2CH_2)_3OH$ (triethylene glycol) (1:1.8:5:25) was sealed in a Teflon-lined autoclave. The autoclave was heated to 453 K, kept at that temperature for 7 d and then water quenched. The crystals obtained were filtered off, washed with distilled water and dried at 323 K. The structure contains two kinds of protonated amine species, *i.e.* $[NH_3(CH_2)_3NH_3]^{2+}$ and $[NH_3(CH_2)_2NH_3]^{2+}$, so as to compensate the negative charge introduced by the infinite $[AlP_2O_8]^{3-}$ chains. It should be noted that the fragmentation of the organic amine has been observed frequently in the hydro- and solvothermal syntheses of aluminophosphates (Gao *et al.*, 1996; Pluth *et al.*, 1984).

Crystal data

$(C_2H_{10}N_2)(C_3H_{12}N_2)_2$-$[Al_2P_4O_{16}]$	Mo $K\alpha$ radiation
$M_r = 324.13$	$\lambda = 0.71069$ Å
Triclinic	Cell parameters from 25 reflections
$P\bar{1}$	$\theta = 15.15$–$16.65°$
$a = 8.9499 (12)$ Å	$\mu = 0.462$ mm^{-1}
$b = 9.2513 (9)$ Å	$T = 298 (2)$ K
$c = 8.6473 (11)$ Å	Irregular
$\alpha = 115.764 (8)°$	$0.20 \times 0.05 \times 0.05$ mm
$\beta = 99.704 (11)°$	Colorless
$\gamma = 98.247 (11)°$	
$V = 616.4 (1)$ Å^3	
$Z = 2$	
$D_x = 1.746$ Mg m^{-3}	
D_m not measured	

Data collection

Rigaku AFC-7*R* diffractometer	2695 reflections with $I > 2\sigma(I)$
ω–2θ scan	$R_{int} = 0.021$
Absorption correction: ψ scan (North *et al.*, 1968)	$\theta_{max} = 30°$
$T_{min} = 0.930$, $T_{max} = 0.980$	$h = -12 \rightarrow 0$
3761 measured reflections	$k = -12 \rightarrow 13$
3599 independent reflections	$l = -11 \rightarrow 12$
	3 standard reflections every 50 reflections intensity decay: none

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.002$
$R[F^2 > 2\sigma(F^2)] = 0.043$	$\Delta\rho_{max} = 0.597$ e Å^{-3}
$wR(F^2) = 0.103$	$\Delta\rho_{min} = -0.353$ e Å^{-3}
$S = 1.040$	Extinction correction: none
3761 reflections	Scattering factors from *International Tables for Crystallography* (Vol. C)
163 parameters	
Only H-atom *U*'s refined	
$w = 1/[\sigma^2(F_o^2) + (0.0412P)^2 + 0.2842P]$ where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. *Selected bond lengths (Å)*

P1—O5^i	1.509 (2)	Al1—O2^{iv}	1.731 (2)
P1—O6^i	1.513 (2)	Al1—O3^{iv}	1.734 (2)
P1—O4^i	1.545 (2)	Al1—O1	1.745 (2)
P1—O2^i	1.546 (2)	N11—C12	1.486 (3)
P2—O7^{ii}	1.506 (2)	C12—C13	1.512 (4)
P2—O8	1.519 (2)	C13—C14	1.520 (4)
P2—O3	1.554 (2)	C14—N15	1.481 (3)
P2—O1^{iii}	1.563 (2)	N21—C22	1.478 (3)
Al1—O4^i	1.726 (2)	C22—C22^v	1.516 (5)

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

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N11—H111···O8	0.89	1.94	2.815 (3)	169
N11—H113···O5	0.89	1.87	2.738 (3)	165
N15—H151···O6^i	0.89	1.85	2.726 (3)	170
N15—H152···O7^{ii}	0.89	1.93	2.812 (3)	172
N15—H153···O5^{iii}	0.89	1.96	2.812 (3)	160
N21—H211···O6^{iv}	0.89	1.95	2.737 (3)	146
N21—H212···O8^{iii}	0.89	1.88	2.714 (2)	154
N21—H213···O7^v	0.89	1.89	2.763 (3)	165

Symmetry codes: (i) $2-x, 1-y, 1-z$; (ii) $x, y-1, z$; (iii) $1-x, 1-y, 1-z$; (iv) $1-x, 2-y, 1-z$; (v) $-x, 2-y, 1-z$.

In order to compensate the negative charge of the infinite $[AlP_2O_8]^{3-}$ chains, the templating agents are suggested to be fully protonated. Aliphatic H atoms were placed geometrically and only an isotropic displacement parameter was refined for all H atoms.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ATOMS* (Dowty, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OH1114). Services for accessing these data are described at the back of the journal.

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Bis(cyclohexane-1,3-dionato)-C^2,O^1-(ethylenediamine-N,N')platinum(II) trihydrate and bis(cyclohexane-1,3-dionato)-C^2,O^1-(N,N-dimethylethylenediamine-N,N')-platinum(II)

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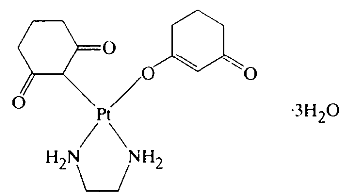
Abstract

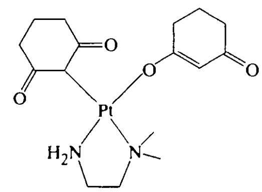
In each of the title organoplatinum(II) compounds, $[Pt(C_6H_7O_2)_2(C_2H_8N_2)]\cdot3H_2O$, (1), and $[Pt(C_6H_7O_2)_2(C_4H_{12}N_2)]$, (2), one 1,3-cyclohexanedionate monoanion is bound to the Pt atom at the Csp^3 atom and the other is bound at the enolate O atom. The Pt—C bond lengths in (1) and (2) are 2.123 (4) and 2.108 (5) Å, respectively. The shorter Pt—C distance in (2) may be due to a *trans* influence of the NMe_2 moiety of the *N*,*N*-dimethylethylenediamine ligand.

Comment

The reactions of bis(acetylacetonato)platinum(II) compounds with certain bases in organic solvents have been investigated previously. By means of vibrational and NMR spectroscopy, the acetylacetonate anions in the products were found to be an *O*,*O′*-bonded chelate or a central-*C*-bonded form (Ito *et al.*, 1976). We have recently reported the structure of [Pt(*trans*-1*R*,2*R*-dach)(acac-*O*,*O′*)](acac) (dach is diaminocyclohexane and Hacac is acetylacetone), crystallized from an aqueous solution containing a 1:2 ratio of $[Pt(trans\text{-}1R,2R\text{-dach})(OH)_2]$ and Hacac (Yuge & Miyamoto, 1997). By using 1,3-cyclohexanedione (Hchdo) in place of Hacac to be a potential monodentate ligand, the title compounds, (1) and (2), have been synthesized and their crystal structures are reported here.



(1)



(2)

In (1) and (2), two independent $chdo^-$ anions behave as monodentate ligands in different ways (Figs. 1 and 2); one coordinates to the Pt atom at the 2-C atom and the other is bound at the O atom as an enolate with a *Z* conformation. The donor C atoms of the former appear to be sp^3 hydridized because of their nearly tetrahedral environment. In the latter, the enolate O21—C21 bond lengths of 1.290 (4) Å in (1) and 1.290 (6) Å in (2) are apparently longer than the carbonyl O23=C23 of 1.256 (5) Å in (1) and 1.243 (7) Å in (2). The Pt—O21—C21=C22 torsion angles and the dihedral angles between the enolate ligands and the square planes about the Pt atoms are −10.2 (6) and 63.3 (2)° in (1), and −6.2 (8) and 88.2 (3)° in (2).

The coordination geometry about the Pt atom is similar to that of [Pt*L*(asc-C^2,O^5)]·$3H_2O$, (3) and (4) (*L* is *cis*- and *trans*-1*R*,2*R*-dach, and asc^{2-} is the L-ascorbate dianion; Hollis *et al.*, 1985; Yuge & Miyamoto, 1996), where the Pt atom is coordinated by a chelating diamine and by the asc^{2-} anion at the O and C atoms. The