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$CsMoO_2(HO_3P–CH_2–PO_3)$: a new metallodiphosphonate with a hybrid framework

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Crystals of caesium molybdenomethylenediphosphonate, $[CsMoO_2(CH_3O_6P_2)]$, were hydrothermally synthesized at 473 K. The monoclinic structure, as determined from single-crystal X-ray diffraction, is two-dimensional and consists of stacked mixed layers of corner-sharing tetrahedral diphosphonate groups and MoO_6 octahedra, between which Cs^+ cations are intercalated.

Comment

Phosphonic acids are well known for providing a wide range of hybrid organic–inorganic frameworks and they possess the ability to complex many metallic cations. The monophosphonic acids give rise to layered compounds which are promising for their exchange properties (Clearfield, 1996), while the diphosphonic acids are useful for the synthesis of hybrid three-dimensional frameworks exhibiting microporous properties (Bonavia *et al.*, 1996; Riou *et al.*, 2000).

Among the available diphosphonic acids, methylenediphosphonic acid is of particular interest, since it presents the geometrical characteristics of the P_2O_7 unit, but with the bridging O atom of the diphosphate unit being replaced by a CH_2 group. Like the diphosphate groups, its association with metallic cations yields a rich crystallochemistry. The present paper deals with the synthesis and the structure of $CsMoO_2(HO_3P–CH_2–PO_3)$, (I), a rare example of a metallodiphosphonate using Mo^{6+} as the metallic cation.

Compound (I) exhibits a two-dimensional structure built up from the stacking along [100] of $[MoO_2\{HO_3P–CH_2–PO_3\}]^-$ hybrid layers, whose global negative charge is neutralized by Cs^+ counter-cations (Fig. 1). The Cs^+ cations are 12-fold coordinated, with Cs—O distances in the range 3.001 (3)–3.669 (4) Å (Table 1), as usual (Shannon, 1976).

The hybrid layers are entirely composed of corner-sharing hexameric building blocks (Fig. 2). Each block contains two MoO_6 octahedra and two methylenediphosphonate groups, distributed in two subunits formulated as $Mo\{HO_3P–CH_2–PO_3\}$. These are built up from one central octahedron chelated by one ditetrahedral unit and are structurally similar to the MP_2O_{11} units commonly encountered in metallodiphosphates (see, for example, $RbMoP_2O_7$; Riou *et al.*, 1989).

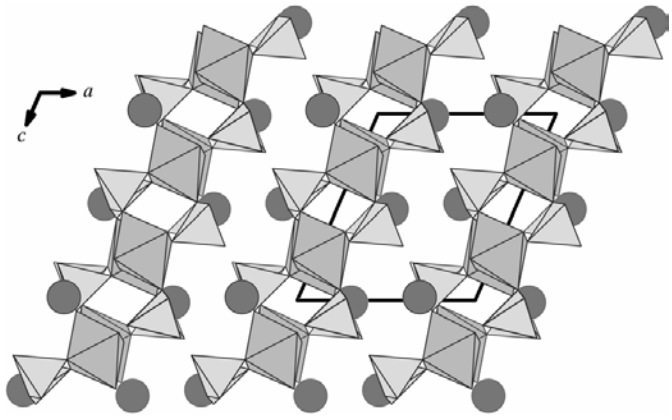

Figure 1
A projection of the structure of $CsMoO_2(HO_3P–CH_2–PO_3)$ along [010], showing the two-dimensional features. Grey circles denote Cs^+ cations and H atoms have been omitted.

The hexameric units are joined *via* their corners in such a way that each octahedron shares two O atoms with two PO_3C tetrahedra of the same diphosphonate group, another O atom with the second diphosphonate of the same hexamer and a fourth with a diphosphonate of another hexamer. The two remaining *cis*-located apices are terminal and give rise to two shorter Mo—O bond lengths (Table 1).

Valence-bond calculations (O'Keeffe & Brese, 1992) show unambiguously that the oxidation state of Mo in (I) is 6+. The diphosphonate units are in an eclipsed conformation (Fig. 1) and each tetrahedron presents a free apex. To ensure the electroneutrality of the structure, one of these two atoms (O1 or O4) has to be protonated to form a hydroxyl species.

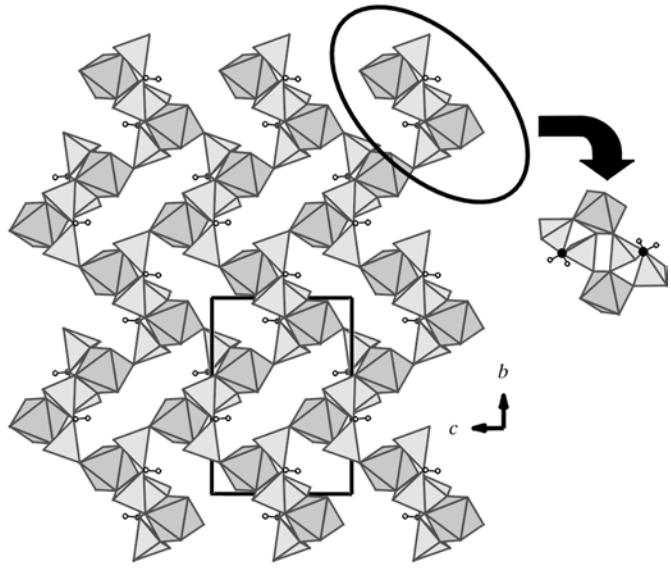

Figure 2
A projection of one hybrid layer in $CsMoO_2(HO_3P–CH_2–PO_3)$. The insert shows the detail of one hexameric building block.

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However, the P—O distances are not significantly different [1.530 (4) and 1.516 (4) Å, respectively] to distinguish the OH unit precisely. Furthermore, the calculated valences of atoms O1 and O4 are both slightly larger than 1.4; this value is not sufficient for an oxide anion, but is slightly larger than the valence of the O atom of a hydroxyl group. Consequently, it is assumed that each diphosphonate is monoprotonated and that the H atoms are randomly distributed on the O1 and O4 apices.

Experimental

Compound (I) was prepared from a mixture of molybdenum trioxide, caesium chloride, methylenediphosphonic acid and deionized water in the molar ratio 1:2:1:500. This mixture was sealed in a Teflon-lined autoclave (Parr) and heated for 48 h at 443 K under autogeneous pressure. The pH remained 1 throughout the synthesis. After cooling at room temperature, the solid was separated from the liquid phase by filtration, washed with water and dried in air. Pure (I) was obtained in a yield close to 80% (based on MoO_3 as reference). A single crystal was selected optically for the present diffraction study and glued to a glass fibre.

Crystal data

$[CsMoO_2(CH_3O_6P_2)]$
M_r = 434
Monoclinic, $P2_1/c$
a = 8.0859 (5) Å
b = 11.8567 (7) Å
c = 9.2347 (5) Å
β = 113.5120 (10)°
V = 811.84 (8) Å^3
Z = 4
D_x = 3.552 Mg m^{-3}
D_m = 3.423 (8) Mg m^{-3}
D_m measured by pycnometry
Mo $K\alpha$ radiation
Cell parameters from 5728 reflections
θ = 2.8–29.9°
μ = 6.44 mm^{-1}
T = 296 (2) K
Parallelepiped, blue
0.20 × 0.12 × 0.08 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: semi-empirical (*SADABS*; Blessing, 1995)
T_{min} = 0.390, T_{max} = 0.597
5609 measured reflections
2142 independent reflections
1646 reflections with $I > 2\sigma(I)$
R_{int} = 0.028
θ_{max} = 29.9°
$h = -10 \rightarrow 6$
$k = -15 \rightarrow 16$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.081
S = 1.11
2142 reflections
119 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0487P)^2 + 0.4123P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.62 e Å^{-3}
$\Delta\rho_{min}$ = −1.58 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0013 (3)

The H atoms of the diphosphonate groups were specified by applying geometrical constraints. The present determination of the structure cannot resolve the location of the H atoms of the hydroxyl groups; their attribution to particular O atoms was made from both electroneutrality considerations and bond-valence calculations (O'Keeffe & Brese, 1992).

Table 1
Selected geometric parameters (Å, °).

Cs—O7^{i}	3.001 (3)	Mo—O7	1.697 (3)
Cs—O8	3.081 (3)	Mo—O3^{vi}	2.014 (3)
Cs—O4^{ii}	3.106 (3)	Mo—O2^{v}	2.037 (3)
Cs—O1^{iii}	3.143 (3)	Mo—O5^{iv}	2.115 (3)
Cs—O7	3.159 (3)	Mo—O6^{vii}	2.172 (3)
Cs—O5	3.257 (3)	P1—O6	1.513 (3)
Cs—O3^{iii}	3.339 (3)	P1—O1	1.530 (4)
Cs—O8^{iv}	3.394 (4)	P1—O2	1.543 (3)
Cs—O2^{ii}	3.443 (3)	P1—C	1.790 (4)
Cs—O6^{v}	3.461 (3)	P2—O5	1.514 (3)
Cs—O1	3.552 (3)	P2—O4	1.516 (4)
Cs—O4	3.669 (4)	P2—O3	1.540 (3)
Mo—O8	1.692 (3)	P2—C^{viii}	1.795 (4)
O8—Mo—O7	102.2 (2)	O5^{iv}—Mo—O6^{vii}	81.17 (12)
O8—Mo—O3^{vi}	96.16 (14)	O6—P1—O1	113.6 (2)
O7—Mo—O3^{vi}	92.57 (14)	O6—P1—O2	112.1 (2)
O8—Mo—O2^{v}	93.46 (15)	O1—P1—O2	107.7 (2)
O7—Mo—O2^{v}	94.47 (14)	O6—P1—C	109.4 (2)
O3^{vi}—Mo—O2^{v}	166.62 (13)	O1—P1—C	106.7 (2)
O8—Mo—O5^{iv}	88.39 (14)	O2—P1—C	106.9 (2)
O7—Mo—O5^{iv}	169.40 (13)	O5—P2—O4	111.2 (2)
O3^{vi}—Mo—O5^{iv}	85.51 (13)	O5—P2—O3	111.3 (2)
O2^{v}—Mo—O5^{iv}	85.49 (13)	O4—P2—O3	108.7 (2)
O8—Mo—O6^{vii}	169.53 (14)	O5—P2—C^{viii}	109.1 (2)
O7—Mo—O6^{vii}	88.27 (14)	O4—P2—C^{viii}	108.3 (2)
O3^{vi}—Mo—O6^{vii}	83.91 (12)	O3—P2—C^{viii}	108.1 (2)
O2^{v}—Mo—O6^{vii}	84.95 (13)		

Symmetry codes: (i) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (ii) $1-x, -y, 2-z$; (iii) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (iv) $2-x, -y, 2-z$; (v) $1+x, y, z$; (vi) $x, y, z-1$; (vii) $1+x, \frac{1}{2}-y, z-\frac{1}{2}$; (viii) $1-x, y-\frac{1}{2}, \frac{5}{2}-z$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SHELXTL* (Siemens, 1994); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ1019). Services for accessing these data are described at the back of the journal.

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