metal-organic compounds

1,4-Dimethylpyridinium hexakis(dimethylformamide-κO)calcium(II) dodecamolybdophosphate

Xue-Jie Tan,[a,b] Si-Xiu Sun,[a,c]* Jian-Ping Ma,[d] Lian-Dong Liu,[d] Yu-Bin Dong,[d] Wen-Tao Yu[c] and Dian-Xiang Xing[b]

[a]Key Laboratory of Colloid and Interface Chemistry of the State Education Ministry, Shandong University, Jinan 250100, People's Republic of China, [b]Department of Chemical Industry, Shandong Institute of Light Industry, Jinan 250100, People's Republic of China, [c]State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, People's Republic of China, and [d]School of Chemistry, Shandong Normal University, Jinan 250100, People's Republic of China

Correspondence e-mail: ssx@sdu.edu.cn

In the title compound, $(C_7H_{10}N)[Ca(C_3H_7NO)_6][PMo_{12}O_{40}]$, two types of cations {*viz.* 1,4-dimethylpyridinium and a $[Ca(DMF)_6]^{2+}$ complex cation (DMF is dimethylformamide)} and dodecamolybdophosphate (tetracontaoxophosphidododecamolybdate) anions form an infinite three-dimensional assembly *via* electrostatic forces.

Comment

In crystal engineering and polyoxometalate chemistry, one of the major challenges is to establish reliable connections between new molecular and supramolecular structures on the basis of intermolecular interactions (Desiraju, 1995; Niu *et al.*, 2003). Ideally, we would like to identify substructural units in a
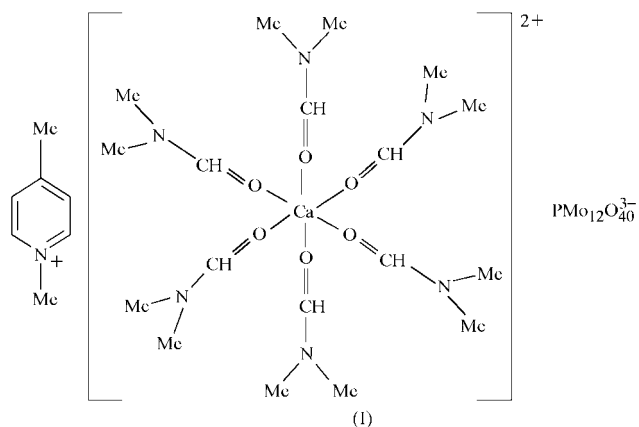
target supermolecule that can be assembled from logically chosen precursor molecules. We attempt here to use a simple method to realize such molecular assemblies. This paper deals with the preparation and crystal structure of a new supramolecular compound obtained from the reaction of 1,4-di-
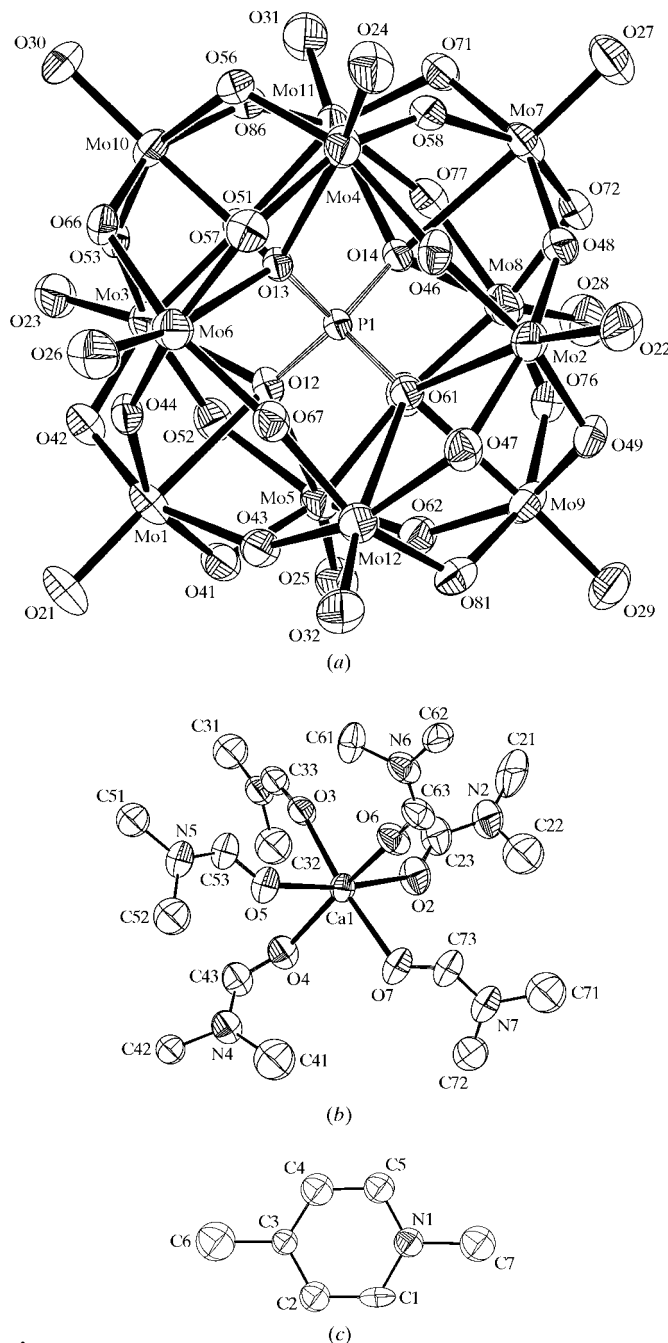

Figure 1
30% probability displacement ellipsoid plots of (*a*) the dodecamolybdophosphate anion, (*b*) the $[Ca(DMF)_6]^{2+}$ cation and (*c*) the 1,4-dimethylpyridinium cation. For clarity, only one form of each of the disordered cations is shown and H atoms have been omitted.

methylpyridinium iodide (DMPI), $CaCl_2$ and Keggin-type $H_3PMo_{12}O_{40}$. The synthesis and structure of the title compound, (I), in which infinite stacking assemblies are achieved, may serve as useful models for the design of functional molecular assemblies.

The title compound is built from three subunits, *viz.* two cations {1,4-dimethylpyridinium (DMP) and a $[Ca(DMF)_6]^{2+}$ complex cation (DMF is dimethylformamide)} and dodecamolybdophosphate anions ($[PMo_{12}O_{40}]^{3-}$, denoted POM; Fig. 1). In the $[Ca(DMF)_6]^{2+}$ complex cation, the Ca atom is

DOI: 10.1107/S0108270104019705

coordinated in a distorted octahedral fashion by six O atoms of DMF ligands. The Ca—O bond lengths range from 2.275 (10) to 2.329 (9) Å (Table 1), with *para*-O—Ca—*para*-O angles ranging from 162.5 (4) to 171.1 (4)° and *ortho*-O—Ca—*ortho*-O angles ranging from 80.8 (4) to 104.7 (4)°. Because all of the DMF ligands are the same, the differences in bond lengths and angles (which cause the distortion of the octahedron) must be the result of internal pressure, induced by the crystal packing and intermolecular interactions. The Keggin structure $[PMo_{12}O_{40}]^{3-}$ consists of one PO_4 tetrahedron (atoms O*a*) surrounded by four corner-sharing Mo_3O_{13} units formed by three edge-sharing MoO_6 octahedra (corner-sharing O atoms between Mo_3O_{13} units are denoted O*b*, edge-sharing O atoms within Mo_3O_{13} units are denoted O*c* and unshared terminal O atoms are denoted O*t*). The P—O*a* bond

distances are 1.530 (6)–1.547 (7) Å, with angles of 109.1 (3)–110.0 (4)°, showing that the PO_4 tetrahedron is slightly distorted. In the MoO_6 octahedra, the Mo—O*t*, Mo—O*a* and Mo—O*b,c* bond distances fall in the ranges 1.659 (7)–1.690 (7), 2.413 (6)–2.435 (6) and 1.850 (7)–1.978 (8) Å, and the mean values are 1.676, 2.426 and 1.912 Å, respectively. These results show that the MoO_6 octahedra of the polyanions in (I) are severely distorted because of the influence of the outer cations (Pope, 1983; Niu *et al.*, 2002, 2003; Wang *et al.*, 2002). The three subunits of (I) form an infinite three-dimensional assembly *via* electrostatic forces (Fig. 2).

The packing structure is a multilayered system in which the different subunits form different types of layers. For example, three types of layers can be found along [100] (*a* axis) for every two of the subunits (Figs. 2 and 3). The POM and DMP ions form graphite-like layers; the POM and $[Ca(DMF)_6]^{2+}$ ions form interlaced layers, thus building the framework of the crystal.

Experimental

All organic solvents and common materials used in the synthesis were of reagent grade and were used without further purification. $H_3PMo_{12}O_{40}$ was prepared according to the method of Claude *et al.* (1983). 1,4-Dimethylpyridinium iodide was prepared according to the method described by Ren *et al.* (2000). Compound (I) was prepared by mixing $CaCl_2$/DMF, DMPI/DMF and $H_3PMo_{12}O_{40}$/DMF solutions (all 0.01 mol l^{-1}) in a 1:1:1 molar ratio. After 15 d of slow evaporation of water at room temperature, bright-green crystals of (I) were obtained from the solution; the crystals were transparent without further purification. Analysis calculated: C 12.46, H 2.18, N 4.07%; found: C 12.26, H 2.18, N 3.94%. IR (KBr, cm^{-1}): 1061, 957, 878, 797 ($[PMo_{12}O_{40}]^{3-}$), 1654 (C=O), 1600, 1497, 1437 (pyridine ring), 1382 (–CH$_3$).
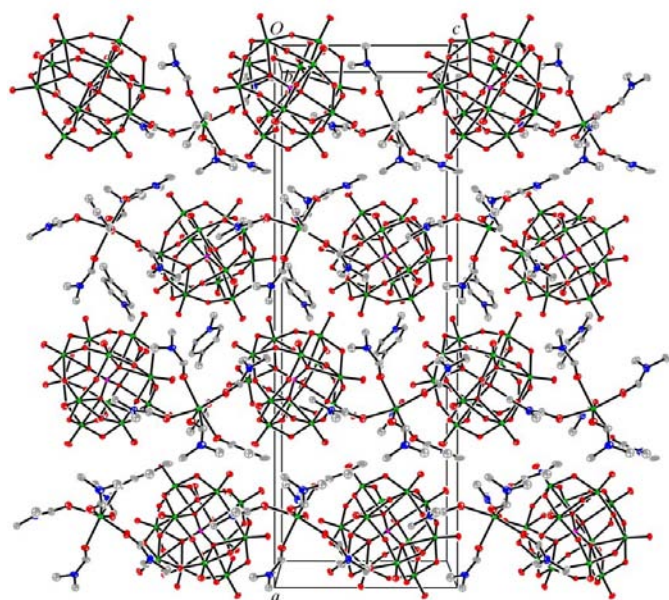

Figure 2
A packing diagram of (I), viewed along the *b* axis, depicted at the 10% probability level. All H atoms and minor components of disordered groups have been omitted for clarity.
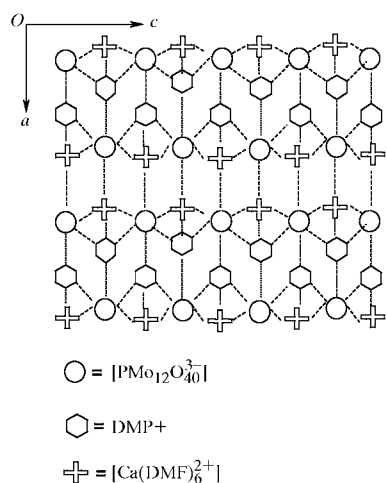

$\bigcirc$ = $[PMo_{12}O_{40}^{3-}]$

$\hexagon$ = DMP+

$\plus$ = $[Ca(DMF)_6^{2+}]$

Figure 3
A schematic representation of the multilayered crystal structure of (I).

Crystal data

$(C_7H_{10}N)[Ca(C_3H_7NO)_6]$-$[PMo_{12}O_{40}]$	Mo $K\alpha$ radiation
$M_r = 2409.07$	Cell parameters from 380 reflections
Orthorhombic, $Pca2_1$	$\theta = 7.5$–27.0°
$a = 38.293$ (6) Å	$\mu = 2.43$ mm^{-1}
$b = 13.246$ (2) Å	$T = 293$ (2) K
$c = 12.888$ (2) Å	Block, green
$V = 6537.6$ (17) Å^3	$0.49 \times 0.11 \times 0.08$ mm
$Z = 4$	
$D_x = 2.442$ Mg m^{-3}	

Data collection

Bruker SMART CCD area-detector diffractometer	14 090 independent reflections
φ and ω scans	12 008 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)	$R_{int} = 0.038$
	$\theta_{max} = 27.1$°
$T_{min} = 0.733$, $T_{max} = 0.824$	$h = -48 \rightarrow 49$
39 117 measured reflections	$k = -14 \rightarrow 16$
	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0518P)^2 + 11.3547P]$
$R[F^2 > 2\sigma(F^2)] = 0.060$	
$wR(F^2) = 0.127$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{max} = 0.002$
14 090 reflections	$\Delta\rho_{max} = 1.08$ e Å^{-3}
746 parameters	$\Delta\rho_{min} = -0.63$ e Å^{-3}
H-atom parameters constrained	Absolute structure: Flack (1983), 6579 Friedel pairs
	Flack parameter = -0.01 (5)

metal-organic compounds

Table 1
Selected interatomic distances (Å).

O2—Ca1	2.289 (10)	O22—Mo2	1.690 (7)
O3—Ca1	2.278 (9)	O23—Mo3	1.659 (7)
O4—Ca1	2.289 (11)	O24—Mo4	1.681 (8)
O5—Ca1	2.329 (9)	O25—Mo5	1.669 (8)
O6—Ca1	2.275 (10)	O26—Mo6	1.686 (8)
O7—Ca1	2.324 (10)	O27—Mo7	1.677 (8)
O11—P1	1.535 (6)	O28—Mo8	1.668 (8)
O12—P1	1.547 (7)	O29—Mo9	1.674 (7)
O13—P1	1.534 (6)	O30—Mo10	1.689 (7)
O14—P1	1.530 (6)	O31—Mo11	1.668 (8)
O21—Mo1	1.678 (6)	O32—Mo12	1.671 (7)

For other DMP salts (Khan *et al.*, 1998; Fun *et al.*, 1996; Houghton & Wallwork, 1999; Mckinney *et al.*, 1997), disordered *para*-C and *para*-N atoms could be treated as each having occupancies of 50%; however, our attempts to refine the title compound in the same way were unsuccessful. In fact, the DMP cation is rocking, and the populations of the two possible orientations, C1/C2/C3/C5/N1/C6/C7 and C1'/C2'/C3'/C5'/N1'/C6'/C7', are 72.5 (10) and 27.5 (10)%, respectively. In the $[Ca(DMF)_6]^{2+}$ cation, the torsional motion of the NMe_2 groups of the DMF ligands leads to substantial disorder. Each NMe_2 moiety has two possible positions, with site-occupancy factors of 72.5 (10) and 27.5 (10)%. This disorder in the cations contributes to the high s.u. values of the bond lengths and angles (0.006–0.02 Å and 0.2–1.9°). A number of atoms have apparently high displacement parameters and some cannot be treated as anisotropic for the same reason. None of the H atoms bonded to C atoms was clearly revealed in the difference map plots. Because of the disorder, *SHELXL*97 (Sheldrick, 1997) restraints and constraints (DFIX, SADI, FLAT, EXYZ and EADP) were used in the refinement to control the geometry and displacement parameters of the atoms in the DMP and DMF molecules. All H atoms were then placed at calculated positions using *SHELXL*97 HFIX commands and allowed to ride on their parent atoms, with C—H distances in the range 0.93–0.96 Å, and with $U_{iso}(H)$ values of $1.5U_{eq}(C)$ for methyl H atoms and $1.2U_{eq}(C)$ for the other H atoms.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXTL/NT* (Bruker, 2000); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL/NT*; software used to prepare material for publication: *SHELXL*97.

References

Bruker (2000). *SMART*, *SAINT*, *SADABS* and *SHELXTL/NT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Claude, R. D., Michel, F., Raymonde, F. & Rene, T. (1983). *Inorg. Chem.* **22**, 207–216.
Desiraju, G. R. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 2311–2327.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Fun, H.-K., Sivakumar, K., Zuo, J.-L., You, F. & You, X.-Z. (1996). *Acta Cryst.* C**52**, 2153–2155.
Houghton, T. J. & Wallwork, S. C. (1999). *J. Chem. Res.* (*S*), pp. 196–197; *J. Chem. Res.* (*M*), pp. 1065–1081.
Khan, A., Low, J. N., Wardell, J. L. & Ferguson, G. (1998). *Acta Cryst.* C**54**, 1399–1401.
Mckinney, J. D., Mcquillan, F. S., Chen, H., Hamor, T. A., Jones, C. J., Slaski, M., Cross, G. H. & Harding, C. J. (1997). *J. Organomet. Chem.* **547**, 253–262.
Niu, J. Y., Wei, M. L., Wang, J. P. & Dang, D. B. (2003). *J. Mol. Struct.* **655**, 171–178.
Niu, J. Y., Wu, Q. & Wang, J. P. (2002). *J. Chem. Soc. Dalton Trans.* pp. 2512–2516.
Pope, M. T. (1983). In *Heteropoly and Isopoly Oxometalates*. Berlin/New York: Springer-Verlag.
Ren, Y., Fang, Q., Yu, W. T., Liu, Z., Liu, Z. Q., Lei, H. & Jiang, M. H. (2000). *Acta Chim. Sin.* **58**, 1457–1462.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Wang, J. P., Wu, Q. & Niu, J. Y. (2002). *Sci. China Ser. B*, **6**, 647–654.