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A Dihydrate Complex of Molybdosilicic Acid and Hexamethylphosphoramide, $\{[(\text{CH}_3)_2\text{N}]_3\text{PO}\}_5[\text{H}_4\text{SiMo}_{12}\text{O}_{40}]\cdot 2\text{H}_2\text{O}$

HOONG-KUN FUN,^a KANDASAMY CHINNAKALI,^{a†}
BOON-CHUAN YIP,^a JING-YANG NIU,^b JING-PING WANG^b
AND XIAO-ZENG YOU^b

^aX-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and
^bCoordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Centre for Advanced Studies in Science and Technology of Microstructures, Nanjing University, Nanjing 210093, People's Republic of China.
E-mail: hkfun@usm.my

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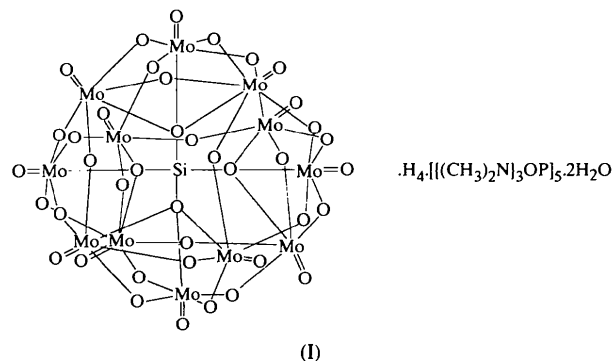
Abstract

The molybdosilicic acid residue, $\text{H}_4\text{SiMo}_{12}\text{O}_{40}$, has the Keggin structure, with $M\text{—O}$ distances varying between 1.796 (4) and 2.112 (3) Å. In the hexamethylphosphoramide groups, all N atoms except one show a planar coordination.

† On leave from: Department of Physics, Anna University, Chennai 600 025, India.

Comment

Complexes of polyoxometalates have attracted much attention because of their special properties of intermolecular charge transfer and photosensitivity (Niu *et al.*, 1996). Some of these compounds, such as $[\text{H}_2\text{quinolin-8-ol}]_3[\text{PW}_{12}\text{O}_{40}]\cdot\text{EtOH}\cdot 2\text{H}_2\text{O}$ (Attanasio *et al.*, 1990), $[(1,1,3,3\text{-tetramethylurea})_3\text{H}]_3[\alpha\text{-PW}_{12}\text{O}_{40}](1,1,3,3\text{-tetramethylurea})$ (Hill *et al.*, 1988) and $\alpha\text{-H}_3\text{PMo}_{12}\text{O}_{40}\cdot 6\text{DMA}\cdot\text{CH}_3\text{CN}\cdot 0.5\text{H}_2\text{O}$ (where DMA is *N,N*-dimethylacetamide; Williamson *et al.*, 1987), have been studied extensively. The X-ray structure analysis of the title compound, (I), was carried out to study the intermolecular charge-transfer behaviour in the complex, which possesses second and third-order non-linear optical properties.



The MoO_6 groups of molybdosilicic acid, $\text{H}_4\text{SiMo}_{12}\text{O}_{40}$, exhibit octahedral geometry; three such groups share edges to form an Mo_3O_{13} assembly and four such assemblies share corners to form an almost spherical $\text{Mo}_{12}\text{O}_{40}$ unit which has at its centre four O atoms arranged tetrahedrally, defining a cavity wherein the Si atom is located. The mean Si—O distance is 1.629 (3) Å and the O—Si—O angles indicate an ideal tetrahedral geometry for SiO_4 . The $M\text{=O}$ bonds project radially outwards with bond lengths varying from 1.668 (4) to 1.687 (4) Å. The Mo—O distances for the bridging O atoms are in the range 1.796 (4)–2.112 (3) Å and those involving O atoms of the central tetrahedron are longer, with an average value of 2.348 (3) Å. The P=O distances in the organic groups vary from 1.467 (4) to 1.524 (4) Å and show delocalized character (Allen *et al.*, 1987).

All N atoms in the hexamethylphosphoramide groups show planar coordination, except for the N3A atom, which is pyramidal. Except for a possible protonation of N3A, direct evidence for any other proton transfer from $\text{H}_4\text{SiMo}_{12}\text{O}_{40}$ and hence for the formation of the $[\text{SiMo}_{12}\text{O}_{40}]^{4-}$ anion has not been found. However, close non-bonding distances between $\text{O1C}\cdots\text{O1D}$ [2.373 (8) Å], $\text{O1B}\cdots\text{O1E}$ [2.409 (6) Å] and $\text{O1A}\cdots\text{O22}$ [2.662 (5) Å], along with longer P=O, Mo3—O22 and Mo6—O22 distances, suggest that protons may have

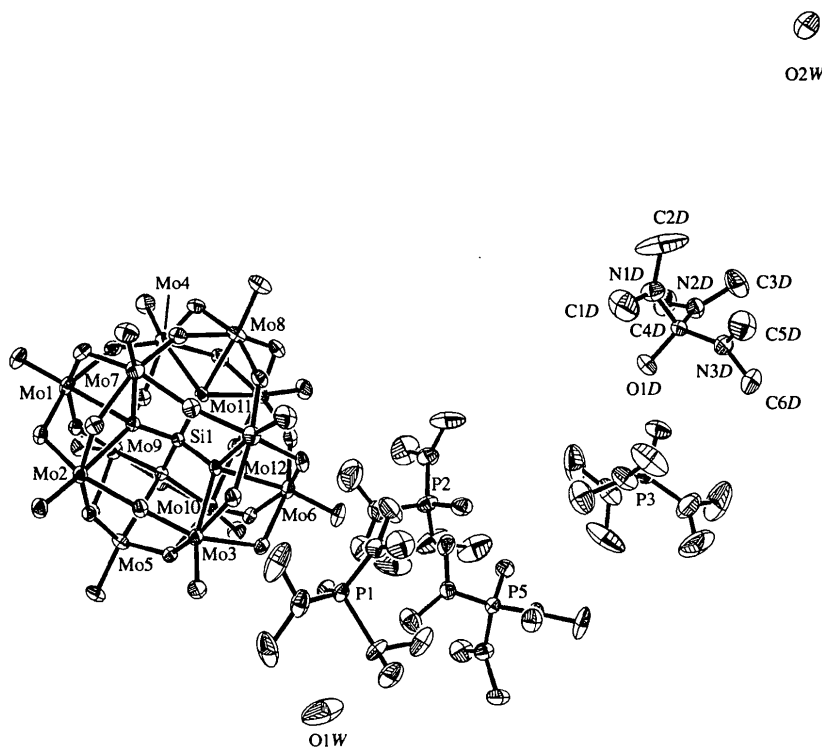


Fig. 1. The structure of title complex showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity.

transferred to these locations, with subsequent formation of hydrogen bonds. Since none of the acidic H atoms have been located, the existence of charge transfer in (I) has not been confirmed experimentally.

Experimental

The synthesis of (I) was carried out by reaction of 10 ml 0.1 M $H_4SiMo_{12}O_{40}$ and 0.2 ml $[(CH_3)_2N]_3PO$ in aqueous solution. Recrystallization was carried out from a mixture of acetonitrile and water. After standing the solution for several days at room temperature in the dark, yellow needles were obtained and one of suitable size was selected for X-ray diffraction analysis.

Crystal data

$(C_6H_{18}N_3OP)_5[H_4SiMo_{12}O_{40}]\cdot 2H_2O$

$M_r = 2755.41$

Triclinic

$P\bar{1}$

$a = 13.849(1) \text{ \AA}$

$b = 13.940(1) \text{ \AA}$

$c = 22.024(2) \text{ \AA}$

$\alpha = 95.77(1)^\circ$

$\beta = 99.45(1)^\circ$

$\gamma = 91.51(1)^\circ$

$V = 4168.9(6) \text{ \AA}^3$

$Z = 2$

$D_x = 2.192 \text{ Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 40 reflections

$\theta = 5.0\text{--}12.5^\circ$

$\mu = 1.947 \text{ mm}^{-1}$

$T = 293(2) \text{ K}$

Needle

$0.52 \times 0.26 \times 0.16 \text{ mm}$

Yellow in the dark and

turning green when

exposed to sunlight

Data collection

Siemens P4 diffractometer
 $\theta/2\theta$ scans

Absorption correction:

empirical ψ scans

(XSCANS; Siemens, 1994)

$T_{\min} = 0.535$, $T_{\max} = 0.732$

21 390 measured reflections

19 037 independent

reflections

13 504 reflections with
 $I > 2\sigma(I)$

$R_{\text{int}} = 0.021$

$\theta_{\max} = 27.52^\circ$

$h = -1 \rightarrow 17$

$k = -17 \rightarrow 17$

$l = -28 \rightarrow 28$

3 standard reflections

every 97 reflections

intensity decay: <3%

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.044$

$wR(F^2) = 0.125$

$S = 0.961$

19 037 reflections

1084 parameters

H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0757P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -0.002$

$\Delta\rho_{\max} = 1.38 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -1.36 \text{ e \AA}^{-3}$

Extinction correction:

SHELXL93

Extinction coefficient:

0.00099 (7)

Scattering factors from

International Tables for
Crystallography (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

Mo1—O13	1.875 (3)	Mo8—O26	1.837 (4)
Mo1—O6	1.929 (4)	Mo8—O9	1.884 (4)
Mo1—O15	1.935 (3)	Mo8—O4	1.973 (4)
Mo1—O20	1.935 (4)	Mo8—O29	2.016 (4)

Mo2—O14	1.871 (4)	Mo9—O35	1.825 (4)
Mo2—O15	1.876 (3)	Mo9—O36	1.890 (4)
Mo2—O7	1.960 (3)	Mo9—O13	1.969 (3)
Mo2—O5	1.984 (3)	Mo9—O31	2.020 (3)
Mo3—O5	1.814 (3)	Mo10—O18	1.887 (3)
Mo3—O12	1.832 (4)	Mo10—O23	1.896 (3)
Mo3—O21	2.016 (4)	Mo10—O36	1.950 (4)
Mo3—O22	2.074 (4)	Mo10—O10	1.956 (4)
Mo4—O29	1.836 (4)	Mo11—O19	1.837 (4)
Mo4—O6	1.865 (4)	Mo11—O10	1.857 (4)
Mo4—O19	1.985 (4)	Mo11—O9	1.964 (4)
Mo4—O35	2.001 (4)	Mo11—O11	2.037 (4)
Mo5—O31	1.845 (3)	Mo12—O21	1.841 (4)
Mo5—O7	1.861 (3)	Mo12—O16	1.863 (4)
Mo5—O18	1.979 (4)	Mo12—O17	1.955 (4)
Mo5—O12	2.037 (3)	Mo12—O26	2.017 (4)
Mo6—O11	1.796 (4)	P1—O1A	1.467 (4)
Mo6—O17	1.879 (4)	P1—N1A	1.595 (5)
Mo6—O23	1.947 (3)	P1—N2A	1.610 (5)
Mo6—O22	2.112 (3)	P1—N3A	1.806 (5)
Mo7—O4	1.881 (4)	P2—O1B	1.495 (5)
Mo7—O20	1.910 (4)	P3—O1C	1.497 (5)
Mo7—O16	1.949 (4)	P4—O1D	1.501 (5)
Mo7—O14	1.995 (4)	P5—O1E	1.524 (4)
C6A—N3A—C5A	108.7 (5)	C5A—N3A—P1	118.7 (4)
C6A—N3A—P1	109.5 (4)		

The Mo atoms were first located by direct methods and successive full-matrix least-squares refinements revealed the complete structure. 23 H atoms were located from successive difference Fourier maps and were refined isotropically. A further 69 H atoms were positioned geometrically and were then allowed to ride on their parent C atoms. One of the water molecules (O2W) is disordered and its H atoms were not located, and neither were the four attached to the molybdosilicate residue. The two highest peaks in the difference Fourier map lie close to Mo5 (0.731 Å) and Mo9 (0.738 Å).

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXTL/PC (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL/PC. Geometrical calculations: PARST (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1354). Services for accessing these data are described at the back of the journal.

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1,1,1,2,2,2,3,3,3-Nonacarbonyl-1,2- $[\mu$ -bis(diphenylphosphino)methane- P' , P'']-3-(trimethylphosphite- P)-triangulotruthenium(0)†

OMAR BIN SHAWKATALY,^a KUPPUKANNU RAMALINGAM,^{a,†} DEWIYANA MOHMAD ASHARI,^a HOONG-KUN FUN^b AND IBRAHIM ABDUL RAZAK^b

^aChemical Sciences Programme, Centre for Distance Education, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and ^bX-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia. E-mail: omarsa@usm.my

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Abstract

In $[\text{Ru}_3(\text{C}_3\text{H}_9\text{O}_3\text{P})(\text{C}_{25}\text{H}_{22}\text{P}_2)(\text{CO})_9]$, one Ru—Ru bond is slightly longer than the other two and axial Ru—CO bonds are longer than corresponding equatorial bonds. The bridging bis(diphenylphosphino)methane (dppm) forms longer P—Ru distances than the equatorial trimethylphosphite ligand.

Comment

Extensive synthetic studies have been performed on mixed-ligand triruthenium cluster carbonyls (Bruce, Liddel, Hughes *et al.*, 1988; Bruce, Kehoe *et al.*, 1982; Bruce, Nicholson *et al.*, 1983; Bruce, Matison *et al.*, 1982; Bruce, Liddel, Shawkataly *et al.*, 1988). In particular, mixed-ligand cluster carbonyls with group 15

† Alternative name: μ -bis(diphenylphosphino)methane- $1\kappa^P:2\kappa^P$ -nonacarbonyl- $1\kappa^3C,2\kappa^3C,3\kappa^3C$ -trimethylphosphite- $3\kappa^P$ -triangulo-truthenium(0)(3 Ru—Ru).

‡ On leave from: Department of Chemistry, Annamalai University, Annamalaiagar 608 002, Tamilnadu, India.