Contribution from the Department of Chemistry,
University of Arkansas, Fayetteville, Arkansas 72701

The Tetraphosphorus Trisulfide Cage Molecule as a Monodentate Group. Preparation and Crystal Structure of Pentacarbonyl(tetraphosphorus trisulfide)molybdenum, $Mo(CO)_5P_4S_3$

A. W. CORDES,* R. D. JOYNER, R. D. SHORES, and E. D. DILL

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The structure of pentacarbonyl(tetraphosphorus trisulfide)molybdenum, prepared by the reaction of molybdenum hexacarbonyl with tetraphosphorus trisulfide, has been determined by single-crystal analysis using film data and Cu Kα X-rays. Crystals of $Mo(CO)_5P_4S_3$ are monoclinic (space group $P2_1/c$) with $a = 6.764$ (4) Å, $b = 34.98$ (4) Å, $c = 12.59$ (2) Å, $\beta = 97.7$ (1)°, $d_o = 1.95$ (5) g/cm³, and $d_c(Z = 8) = 2.05$ g/cm³. Full-matrix isotropic refinement, based on 1476 reflections, converged to $R = 0.082$. The structure shows an intact P_4S_3 cage molecule attached to a $Mo(CO)_5$ moiety through the apical phosphorus atom. The Mo–P distance of 2.477 (6) Å, the P–S and Mo–C distances, and the infrared spectrum of the compound all suggest the P_4S_3 molecule has strong phosphine-like interactions with the $Mo(CO)_5$ system.

Introduction

The tetraphosphorus sulfides P_4S_3,[1] P_4S_5,[2] P_4S_7,[3] and P_4S_{10}[3] form a structurally unique series of cage-like molecules. As part of a general program of studying the chemistry of these molecules, we have been investigating their ability to function as ligands to transition metals. In this paper we report the preparation, infrared spectrum, and crystal structure of $Mo(CO)_5P_4S_3$.

Experimental Section

Preparation and Properties. P_4S_3 (Eastman) was subjected to boiling water for 1 hr to hydrolyze any higher sulfides present and then recrystallized from benzene. All solvents were flushed with nitrogen before use to remove dissolved oxygen. The best yields of $Mo(CO)_5P_4S_3$ were obtained by combining 2.5 g (10.5 mmol) of $Mo(CO)_6$ and 2.1 g (9.5 mmol) of P_4S_3 in 100 ml of cyclohexane containing 1 ml of diglyme and then heating the solution to reflux under a nitrogen atmosphere for 6 hr. After 3 hr of reflux the reaction solution is light orange, and after 6 hr it is dark orange; further heating results in decomposition. The yield is approximately 30%.

The air-stable crystals obtained from these solutions are pale orange and melt sharply at 135°. The majority of the crystals obtained are needlelike and were found to be twinned. A few untwinned platelike crystals were obtained, however; one such crystal was used for the data collection of this report. The infrared spectrum (Nujol mull) is 2075 (s), 1985 (w), 1965 (vs), 1940 (s), 603 (s), 573 (s), 475 (w), 435 (s), and 415 cm⁻¹ (s), where v = very, s = strong, and w = weak. The first four peaks are representative of carbonyl stretches of $Mo(CO)_5L$ compounds[4] (without the A_1–E accidental degeneracy of the PPh_3 analog), the 603- and 573-cm⁻¹ bands are near the region assigned to metal–C stretching vibrations for Cr carbonyls which suggests they are Mo–C vibrations, although these have not previously been observed for PPh_3 or $P(OPh)_3$ derivatives of Mo or W.[5] The last three bands are characteristics of P_4S_3.[6]

X-Ray Data. A 0.02 × 0.09 × 0.39 mm (all ±0.01 mm) crystal was used for all data collection. Unit cell parameters were determined by least-squares refinement of 91 2θ values measured on zero- and upper-layer Weissenberg films taken on both the *a* and *c* axes. The films were calibrated internally by superimposed Al ($a = 4.049$ Å) powder lines. The monoclinic cell showed systematic absences consistent with space group $P2_1/c$ (No. 14), with $a = 6.764$ (4) Å, $b = 34.98$ (4) Å, $c = 12.59$ (2) Å, and $\beta = 97.7$ (1)°. The density, as measured by suspension in a mixture of 1,2-dibromoethane and 1,2-dibromobutane, was 1.95 (5) g/cm³; this compares to the calculated density of 2.05 g/cm³ based on eight molecules per unit cell. Consequently there are two crystallographically independent molecules in the unit cell.

Film data were collected using standard multiple-film equiinclination Weissenberg techniques with Ni-filtered Cu Kα (λ 1.5418 Å) radiation. The bulk of the data was gathered with the crystal oriented on the *a* axis (0*kl*–6*kl*); a data merge with the *c* axis data (*hk*0–*hk*8) put the data on a common scale. The 6*kl* data were not included in the refinement because of the poor quality of the reflections. Of the reflections accessible, 1476 could be measured with confidence, giving a final parameter:reflection ratio of 1:10.2. Intensities were estimated visually using a standard wedge made from the crystal. Uncertainties were assigned each observation[7] and these uncertainties were propagated to $\sigma(F)$ values.

The linear absorption coefficient for Cu Kα X-rays is 147.5 cm⁻¹; the absorption correction[8] factors (for F) vary from 0.82 to 0.68. No extinction correction was made.

Solution and Refinement of Structure. The molybdenum atom positions were determined from the Patterson map, and the Fourier map phased by the molybdenum atoms led to the complete structure, making use of P_4S_3 and $Mo(CO)_5$ rigid-group techniques early in the refinement process. In the final cycle of least-squares refinement all atoms were treated isotropically and real and imaginary anomalous dispersion corrections were made for Mo, P, and S.[9] The conventional residue $R = 0.082$, and a weighted R $(=(\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2)^{1/2}) = 0.091$. Only six reflections had $\Delta F/\sigma$ greater than 3 (the maximum was 4.1), and the standard deviation of an observation of unit weight was 1.03. The largest peak on a final difference map was 1.2 e/Å³, which is less than 20% of the value of a carbon atom on a regular Fourier map. The difference map clearly revealed anisotropic thermal motion for the two Mo atoms and some of the P and S atoms; however, an anisotropic refinement was not undertaken because it would strain the parameter:reflection ratio and also create computer demands such that less than all of the parameters could be refined simultaneously.

The final atomic positional and thermal parameters are listed in Table I, and the intramolecular distance and angles are given on Table II. A table of observed and calculated structure factors is available.[10] Figure 1 shows the atom-numbering scheme used in this report.

Results and Discussion

The structure determination shows the P_4S_3 cage molecule has indeed remained intact and functions as a monodentate ligand to a $Mo(CO)_5$ unit, bonding through the apical phosphorus atom. The crystal packing, depicted in Figure 2, does not involve any intermolecular approaches shorter than the corresponding van der Waals distances.

The Mo atom is bonded to the very apex of the P_4S_3 cage:

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(6) H. Gerding, J. W. Maarsen, and P. C. Nobel, *Recl. Trav. Chim. Pays-Bas*, 76, 757 (1957).

(7) The equation used is given by B. D. Sharma and J. F. McConnell, *Acta Crystallogr.*, 19, 797 (1965).

(8) Program BLAP, based on the methods of W. R. Busing and H. A. Levy, *Acta Crystallogr.*, 10, 180 (1957), using a 4 × 4 × 16 summation grid.

(9) D. T. Cromer, *Acta Crystallogr.*, 18, 18 (1965).

(10) See paragraph at end of paper regarding supplementary material.

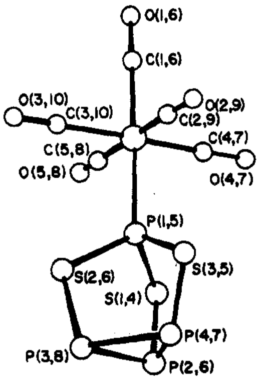

Figure 1. The atom numbering used for $Mo(CO)_5P_4S_3$.

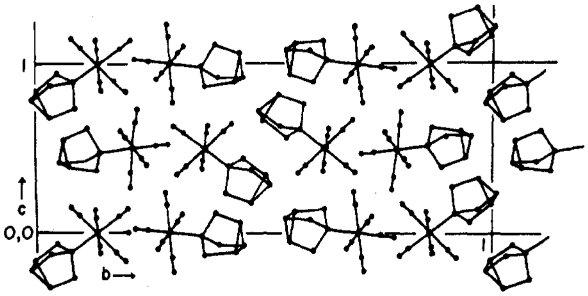

Figure 2. The crystal packing of $Mo(CO)_5P_4S_3$, as viewed parallel to the *a* axis.

Table I. Atomic Positional Parameters and Temperature Factors for $Mo(CO)_5P_4S_3$

	x	*y*	*z*	*B*, Å^2
Mo(1)	0.2630 (3)	0.13077 (7)	0.0080 (2)	2.72 (7)
C(1)	0.170 (5)	0.177 (1)	−0.089 (3)	6.4 (9)
O(1)	0.124 (4)	0.2005 (9)	−0.138 (2)	8.4 (8)
C(2)	0.427 (4)	0.1676 (9)	0.116 (2)	3.6 (7)
O(2)	0.504 (3)	0.1886 (6)	0.177 (2)	4.7 (5)
C(3)	0.498 (5)	0.126 (1)	−0.080 (3)	4.8 (8)
O(3)	0.620 (3)	0.1239 (7)	−0.134 (2)	6.3 (6)
C(4)	0.021 (4)	0.1362 (8)	0.087 (2)	2.9 (7)
O(4)	−0.118 (3)	0.1377 (6)	0.131 (2)	4.2 (5)
C(5)	0.100 (5)	0.094 (1)	−0.096 (3)	5.0 (8)
O(5)	−0.008 (3)	0.0746 (6)	−0.147 (2)	5.4 (5)
Mo(2)	0.8449 (3)	0.29522 (7)	0.0018 (2)	2.86 (7)
C(6)	0.739 (5)	0.241 (1)	−0.012 (3)	6.1 (9)
O(6)	0.700 (3)	0.2096 (8)	−0.027 (2)	7.1 (6)
C(7)	0.744 (5)	0.299 (1)	0.148 (3)	5.3 (9)
O(7)	0.689 (4)	0.2977 (8)	0.227 (2)	7.4 (7)
C(8)	0.573 (4)	0.3134 (9)	−0.064 (2)	2.8 (7)
O(8)	0.410 (3)	0.3223 (6)	−0.099 (2)	5.5 (5)
C(9)	1.120 (6)	0.276 (1)	0.066 (3)	6.2 (9)
O(9)	1.262 (4)	0.2627 (8)	0.105 (2)	7.1 (7)
C(10)	0.931 (4)	0.2909 (9)	−0.150 (3)	4.0 (7)
O(10)	0.983 (3)	0.2877 (6)	−0.232 (2)	5.6 (6)
P(1)	0.393 (1)	0.0762 (2)	0.1168 (6)	3.0 (1)
S(1)	0.192 (1)	0.0301 (2)	0.1323 (6)	3.8 (2)
P(2)	0.377 (1)	−0.0092 (3)	0.2255 (7)	3.9 (2)
S(2)	0.630 (1)	0.0468 (2)	0.0631 (6)	3.8 (2)
P(3)	0.680 (1)	0.0023 (3)	0.1764 (7)	4.1 (2)
S(3)	0.506 (1)	0.0842 (2)	0.2774 (6)	4.0 (2)
P(4)	0.591 (1)	0.0283 (3)	0.3260 (7)	4.0 (2)
P(5)	0.964 (1)	0.3608 (2)	0.0238 (6)	3.4 (2)
S(4)	0.771 (1)	0.4019 (3)	0.0806 (6)	4.2 (2)
P(6)	0.940 (1)	0.4519 (3)	0.0829 (7)	4.4 (2)
S(5)	1.224 (1)	0.3717 (3)	0.1284 (7)	4.5 (2)
P(7)	1.255 (1)	0.4310 (3)	0.1135 (7)	5.0 (2)
S(6)	1.033 (1)	0.3898 (3)	−0.1141 (7)	4.4 (2)
P(8)	1.119 (1)	0.4439 (3)	−0.0537 (7)	4.9 (2)

Table II. Bond Distances and Bond Angles within $Mo(CO)_5P_4S_3$

Bond Distances, Å			
Mo(1)–C(1)	2.10 (4)	Mo(2)–C(6)	2.05 (4)
Mo(1)–C(2)	2.10 (3)	Mo(2)–C(7)	2.04 (3)
Mo(1)–C(3)	2.06 (3)	Mo(2)–C(8)	2.03 (3)
Mo(1)–C(4)	2.03 (3)	Mo(2)–C(9)	2.05 (4)
Mo(1)–C(5)	2.06 (3)	Mo(2)–C(10)	2.06 (3)
C(1)–O(1)	1.05 (5)	C(6)–O(6)	1.18 (5)
C(2)–O(2)	1.14 (4)	C(7)–O(7)	1.10 (4)
C(3)–O(3)	1.13 (4)	C(8)–O(8)	1.17 (4)
C(4)–O(4)	1.16 (3)	C(9)–O(9)	1.12 (5)
C(5)–O(5)	1.14 (4)	C(10)–O(10)	1.14 (4)
Mo(1)–P(1)	2.471 (9)	Mo(2)–P(5)	2.483 (9)
P(1)–S(1)	2.16 (1)	P(5)–S(4)	2.14 (1)
P(1)–S(2)	2.11 (1)	P(5)–S(5)	2.08 (1)
P(1)–S(3)	2.07 (1)	P(5)–S(6)	2.12 (1)
S(1)–P(2)	2.13 (1)	S(4)–P(6)	2.13 (1)
S(2)–P(3)	2.12 (1)	S(5)–P(7)	2.14 (1)
S(3)–P(4)	2.14 (1)	S(6)–P(8)	2.13 (1)
P(2)–P(3)	2.25 (1)	P(6)–P(7)	2.25 (1)
P(3)–P(4)	2.24 (1)	P(7)–P(8)	2.22 (1)
P(2)–P(4)	2.23 (1)	P(6)–P(8)	2.24 (1)
Mo–C(av)[a]	2.06 (2)	P–S (av)	2.12 (3)
C–O (av)	1.14 (4)	P–P (av)	2.24 (1)
Mo–P (av)	2.477 (6)		
Bond Angles, Deg			
C(1)–Mo(1)–C(2)	88 (1)	C(6)–Mo(2)–C(7)	89 (1)
C(1)–Mo(1)–C(3)	87 (1)	C(6)–Mo(2)–C(8)	89 (1)
C(1)–Mo(1)–C(4)	90 (1)	C(6)–Mo(2)–C(9)	91 (1)
C(1)–Mo(1)–C(5)	92 (1)	C(6)–Mo(2)–C(10)	90 (1)
C(2)–Mo(1)–C(3)	91 (1)	C(7)–Mo(2)–C(8)	87 (1)
C(2)–Mo(1)–C(4)	91 (1)	C(7)–Mo(2)–C(9)	94 (1)
C(2)–Mo(1)–C(5)	179 (1)	C(7)–Mo(2)–C(10)	177 (1)
C(3)–Mo(1)–C(4)	177 (1)	C(8)–Mo(2)–C(9)	179 (1)
C(3)–Mo(1)–C(5)	90 (1)	C(8)–Mo(2)–C(10)	90 (1)
C(4)–Mo(1)–C(5)	88 (1)	C(9)–Mo(2)–C(10)	89 (1)
P(1)–Mo(1)–C(1)	176 (1)	P(5)–Mo(2)–C(6)	178 (1)
P(1)–Mo(1)–C(2)	91.1 (9)	P(5)–Mo(2)–C(7)	89 (1)
P(1)–Mo(1)–C(3)	89 (1)	P(5)–Mo(2)–C(8)	90.4 (9)
P(1)–Mo(1)–C(4)	93.5 (8)	P(5)–Mo(2)–C(9)	90 (1)
P(1)–Mo(1)–C(5)	88.2 (9)	P(5)–Mo(2)–C(10)	92.6 (9)
Mo(1)–C(1)–O(1)	179 (3)	Mo(2)–C(6)–O(6)	170 (3)
Mo(1)–C(2)–O(2)	175 (3)	Mo(2)–C(7)–O(7)	174 (3)
Mo(1)–C(3)–O(3)	176 (3)	Mo(2)–C(8)–O(8)	176 (3)
Mo(1)–C(4)–O(4)	177 (2)	Mo(2)–C(9)–O(9)	173 (3)
Mo(1)–C(5)–O(5)	172 (3)	Mo(2)–C(10)–O(10)	178 (3)
Mo(1)–P(1)–S(1)	117.9 (4)	Mo(2)–P(5)–S(4)	118.3 (4)
Mo(1)–P(1)–S(2)	116.8 (4)	Mo(2)–P(5)–S(5)	118.7 (4)
Mo(1)–P(1)–S(3)	119.0 (4)	Mo(2)–P(5)–S(6)	118.4 (4)
S(1)–P(1)–S(2)	99.4 (4)	S(4)–P(5)–S(5)	99.6 (5)
S(2)–P(1)–S(3)	100.1 (4)	S(5)–P(5)–S(6)	99.2 (5)
S(3)–P(1)–S(1)	100.0 (4)	S(6)–P(5)–S(4)	98.6 (5)
P(1)–S(1)–P(2)	102.8 (5)	P(5)–S(4)–P(6)	103.3 (5)
P(1)–S(2)–P(3)	102.8 (5)	P(5)–S(5)–P(7)	102.4 (5)
P(1)–S(3)–P(4)	101.4 (5)	P(5)–S(6)–P(8)	103.6 (5)
S(1)–P(2)–P(3)	102.8 (5)	S(4)–P(6)–P(7)	102.5 (5)
S(1)–P(2)–P(4)	101.6 (5)	S(4)–P(6)–P(8)	103.0 (5)
S(2)–P(3)–P(2)	104.4 (5)	S(5)–P(7)–P(6)	104.0 (5)
S(2)–P(3)–P(4)	102.1 (5)	S(5)–P(7)–P(8)	104.7 (5)
S(3)–P(4)–P(2)	105.8 (5)	S(6)–P(8)–P(6)	103.7 (5)
S(3)–P(4)–P(3)	103.9 (5)	S(6)–P(8)–P(7)	101.9 (5)
P(2)–P(3)–P(4)	59.6 (4)	P(6)–P(7)–P(8)	60.3 (4)
P(3)–P(4)–P(2)	60.5 (4)	P(7)–P(8)–P(6)	60.5 (4)
P(4)–P(2)–P(3)	60.0 (4)	P(8)–P(6)–P(7)	59.2 (4)
Mo–P–S (av)	118.2 (8)	S–P–P (av)	103 (1)
S–P–S (av)	99.5 (6)	P–P–P (av)	60.0 (5)
P–S–P (av)	102.7 (8)		

[a] Averages are weighted averages with rms deviations.

the two Mo–P bonds make angles of 177.7 (4) and 178.6 (8)° with the threefold axis of the cage. The two P_4S_3 units are in nearly identical orientations with respect to the carbonyl octahedron. Figure 3, which illustrates the dihedral angles between the P–S–P vertical planes and the carbonyl octahedron, shows one P–S–P plane nearly bisects a C–Mo–C angle in both of the crystallographically independent molecules.

The bonding around the Mo atom can be described as a relatively undistorted octahedral arrangement, with both of

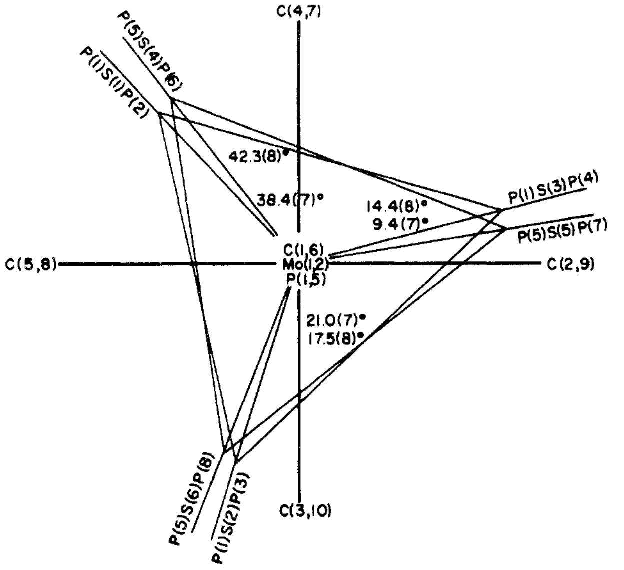

Figure 3. Dihedral angles between the trigonal planes of P_4S_3 and the planes of the $Mo(CO)_5P$ octahedron of $Mo(CO)_5P_4S_3$.

the independent Mo atoms displaced from the $(CO)_4$ plane by 0.021 (3) Å toward the phosphorus side of the octahedron. The two Mo-P bonds are 2.471 (9) and 2.483 (9) Å, Mo-C bonds average 2.06 (2) Å, the C-O bonds average 1.14 (4) Å, and the average bend in the Mo-C-O linkages is 175 (3)°. These Mo-P distances are shorter than majority of the molybdenum-phosphine bond distances which have been reported, such as 2.37,[11] 2.421,[12] 2.425-2.527,[13] 2.473,[14] 2.505,[15] 2.516,[16] 2.517,[17] and 2.518-2.537 Å.[18] The Mo-C average of 2.06 (2) Å is somewhat longer than the 1.93-2.01-Å distances usually found in substituted carbonyls[19] but is equal to the average value for $Mo(CO)_6$[20] and $Mo(CO)_5PF_3$.[11] There are no interpretable differences between the cis and the trans Mo-C and C-O distances of the structures being reported.

The comparison of the structural features of the coordinated P_4S_3 molecule with those of the free P_4S_3[1] was one of the main goals of this work. This comparison shows that the P-P distances and the SPS, PSP, SPP, and PPP bond angles of P_4S_3 have not changed upon coordination. The P-S bonds, however, are longer when P_4S_3 is a ligand. In the free P_4S_3 molecule the P(apical)-S bonds average 2.086 (11) Å and the S-P(basal) bonds average 2.094 (4) Å. Corresponding values found in $Mo(CO)_5P_4S_3$ are 2.12 (4) and 2.13 (1) Å. The refinement of both free P_4S_3 and this present structure gave larger variations in the apical P-S bonds than in the S-P basal bonds. In the Mo complexes the one short P-S bond present in both molecules (P1-S3 and P5-S5) cannot be related to the orientation of the cage with respect to the $Mo(CO)_5$ octahedron (see Figure 3).

The similarity of the carbonyl portion of the ir spectrum of $Mo(CO)_5P_4S_3$ to those of $Mo(CO)_5P(OEt)_3$ and $Mo(CO)_5$-PPh_3,[21] the relatively long Mo-C bonds and P-S bonds, and the relatively short Mo-P bonds all appear to be consistent with the conclusion that the P_4S_3 molecule has as strong, or a stronger, interaction with the $Mo(CO)_5$ moiety as the more common phosphine ligands. The lengthening of all of the P-S bonds, whether due primarily to σ[21] or π[4] interactions with the metal, carries interesting implications on the molecular orbital domains of P_4S_3.

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Registry No. $Mo(CO)_5P_4S_3$, 28667-92-7; $Mo(CO)_6$, 13939-06-5.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-132.

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