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Two Bis(diphenylphosphinomethane) (DPPM) Complexes of Quadruply Bonded Dimolybdenum(II): Mo$_2$(DPPM)$_2$X$_4$, X = Cl, NCS

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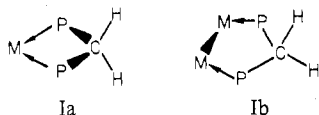
The preparation and structural characterization of the two compounds Mo$_2$(DPPM)$_2$X$_4$·2C$_3$H$_6$O, where DPPM = Ph$_2$PCH$_2$PPh$_2$ and X = Cl or NCS, are reported. Their structures, though similar, show small but significant differences. Each molecule has an MoX$_2$(μ-DPPM)$_2$MoX$_2$ type structure with the μ-DPPM units in a transoid relationship. For X = Cl, the molecule lies on a crystallographic inversion center and the rotational conformation is eclipsed. For X = NCS, no crystallographic symmetry is imposed and the rotational conformation deviates approximately 13.3° from being eclipsed. The fact that the thiocyanate ions are N bonded is notable. For the chloro compound, the main crystallographic data and some important molecular dimensions are space group C2/c, a = 18.762 (5) Å, b = 11.701 (4) Å, c = 25.741 (4) Å, β = 95.44 (2)°, V = 5626 Å^3, Z = 4, Mo–Mo = 2.138 (1) Å, and Mo–Cl = 2.39 (1) Å. For the isothiocyanato compound the important data and dimensions are space group P2$_1$/c, a = 13.761 (6) Å, b = 15.806 (6) Å, c = 31.14 (1) Å, β = 90.78 (3)°, V = 6773 Å^3, Z = 4, Mo–Mo = 2.167 (3) Å, and Mo–N = 2.06 (2) Å.

Introduction

Although well over 100 compounds containing the quadruply bonded Mo$_2$$^{4+}$ unit have been reported and upward of 20 of them have been structurally characterized by X-ray crystallography,[2] there are still some questions involving both preparative and structural aspects that merit consideration. Several such questions are addressed simultaneously in the work reported here.

The DPPM ligand is capable of serving either as a chelating ligand, Ia, forming an essentially planar, four-membered ring

Ia   Ib

or as a bridging ligand, Ib, forming a nonplanar, five-membered ring for which the typical conformation has the methylene carbon atom lying outside the common plane of the two metal and two phosphorus atoms. These structural studies show which role is played by DPPM in this type of molecule, namely, the bridging one.

A second question, of particular interest, has to do with the mode of attachment of the ambidentate ligand SCN$^-$ to the Mo$_2$$^{4+}$ unit. Very few thiocyanato compounds containing Mo$_2$$^{4+}$ and Re$_2$$^{6+}$ have been described previously,[3] and no X-ray study showing whether the ligand is thiocyanato (–SCN) or isothiocyanato (–NCS) in attachment has been made, though IR data have been interpreted[3-6] in favor of –NCS bonding.

Another interesting structural aspect of quadruply bonded M$_2$ systems that comes into play here is the extent to which the internal rotational conformation about the M–M bond deviates from the eclipsed one when the molecule is not constrained by any crystallographic symmetry element. Prior examples of the situation where the molecule as a whole is the asymmetric unit and is not constrained by any crystallographic plane, axis, or inversion center are remarkably few in number. The existence of the δ bond does not demand a *strictly* eclipsed conformation but only an approach thereto. Only when the surroundings of the molecule in the crystal do not impose an essentially eclipsed conformation is there a chance to see how much of a deviation can occur without loss of the δ component of the quadruple bond. A good example of such a situation is provided by the thiocyanate compound reported here.

As this work was nearing completion, the preparation of **2**, Mo$_2$(DPPM)$_2$Cl$_4$·2C$_3$H$_6$O, as a blue-green powder containing no solvent of crystallization, was reported by Walton.[8]

Experimental Section

Materials. Methylenebis(diphenylphosphine) (DPPM) was obtained from Strem Chemicals and used without further purification. Tetrakis(methanesulfonato)dimolybdenum(II) was prepared by the method of Hochberg and Abbott.[6] All procedures were carried out under dry nitrogen using commercial Schlenk-type glassware.

Preparation of Mo$_2$(NCS)$_4$(DPPM)$_2$. A solution was prepared from Mo$_2$(MeSO$_3$) (0.29 g), NH$_4$SCN (0.4 g), and 25 mL of methanol. A solution of 0.45 g of DPPM in 10 mL of dimethoxyethane was added dropwise. A deep green solution resulted. Dark green needles separated after ca. 12 h at 0 °C. The crystals were filtered and dried in a stream of nitrogen. They are soluble in chloroform, acetone, or benzene but insoluble in methanol, ethanol, or water. Anal. Calcd for C$_{54}$H$_{44}$N$_4$P$_4$S$_4$Mo$_2$: C, 54.36; H, 3.69; N, 4.69; P, 10.40; S, 10.74; Mo, 16.10. Found: C, 54.18; H, 3.67; N, 4.61; P, 10.51; Mo, 16.06.

The infrared spectrum of this compound shows ν(C≡N) at 2030 cm^{-1} and ν(C–S) at 864 cm^{-1}. Both values are in the range expected if NCS is N bonded to molybdenum,[9] as in previous cases.[3-6]

Table I. Crystallographic Data for Mo$_2$(DPPM)$_2$X$_4$·2C$_3$H$_6$O

parameter[a]	X = NCS	X = Cl
formula	Mo$_2$S$_4$P$_4$N$_4$C$_{54}$H$_{44}$· 2C$_3$H$_6$O	Mo$_2$Cl$_4$P$_4$C$_{50}$H$_{44}$· 2C$_3$H$_6$O
formula wt, g mol^{-1}	1309.17	1218.66
a, Å	13.761 (6)	18.762 (5)
b, Å	15.806 (6)	11.701 (4)
c, Å	31.14 (1)	25.741 (4)
β, deg.	90.78 (3)	95.44 (2)
V, Å^3	6773.2	5625.6
d_{calcd}, g cm^{-3}	1.284	1.439
Z	4	4
space group	$P2_1/c$	$C2/c$
μ, cm^{-1}	6.175	7.803
$I > 3\sigma(I)$	2439	2682
esd of obsrvn of unit wt	2.12	1.92
R_1	0.093	0.058
R_2	0.122	0.083

[a] Figures in parentheses following some numbers are esd's occurring in the least significant digit.

Preparation of Mo$_2$Cl$_4$(DPPM)$_2$. Approximately 45 mL of methanol was used to dissolve 0.4 g of Mo$_2$(MeSO$_3$) and 0.3 g of NMe$_4$Cl. The solution formed is deep pink. A solution of 0.45 g of DPPM in 25 mL of dimethoxyethane was added dropwise. Upon standing overnight at room temperature, green crystals formed. Anal. Calcd for C$_{50}$H$_{44}$Cl$_4$P$_4$Mo$_2$: C, 54.26; H, 3.98; Cl, 12.89; P, 11.58; Mo, 17.34. Found: C, 53.47; H, 4.57; Mo, 16.55. The crystals used in the X-ray study were obtained by recrystallization from acetone by slow cooling of a saturated solution.

X-ray Crystallography. Both compounds were recrystallized from acetone to obtain crystals suitable for structure determination. The crystals were cemented to the ends of glass fibers and examined on a Syntex $P\bar{1}$ four-circle, automated diffractometer. Both rotation photographs and ω scans were used to judge the quality of the crystals. Lattice parameters were obtained by a least-squares fit to the setting angles for 15 strong reflections.

Intensity data were collected using graphite-monochromated Mo Kα radiation and θ–2θ scan rates varying from 4 to 24°/min depending on the intensity of the reflection. The range of 2θ was 0–45° for each crystal. Background measurements were made at both limits of each scan. Three standard reflections were measured after every 97 data points. Only the reflections having intensities (I) greater than 3$\sigma(I)$ were retained as observed and, after correction for Lorentz and polarization effects, were used to solve and refine the structures. The function minimized during refinement was $\sum w(|F_o| - |F_c|)^2$ where $p = 0.07$ was used in the previously defined expression of weights.[10] The discrepancy indices used were

$$R_1 = \sum ||F_o| - |F_c||/\sum |F_o|$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$$

The calculations required for data reduction and refinement of the structures were carried out using the Enraf-Nonius Structure Determination package on a PDP 11/45 computer operated by Molecular Structure Corp., College Station, Texas.

The crystallographic data for the two compounds are summaried in Table I. Details of the solution and refinement of each structure are as follows.

Mo$_2$(DPPM)$_2$(NCS)$_4$·2C$_3$H$_6$O (1). This compound crystallizes in the space group $P2_1/c$ with one dinuclear unit per asymmetric unit. The structure was solved by conventional heavy-atom methods and refined to convergence using anisotropic thermal parameters for the Mo and P atoms and isotropic thermal parameters for the S, N, C, and O atoms. Two acetone molecules were found to make up the rest of the asymmetric unit. There is no chemical interaction between the acetone molecules and the dimolybdenum molecule. The acetone molecule composed of O(2), C(201), C(202), and C(203) shows evidence of being partially disordered. We were not able to find a satisfactory model for this disorder, and the structure was refined to convergence holding both the positional parameters and thermal parameters of this acetone molecule constant. A final difference map had no peaks with intensity greater than 0.6 e/Å^3.

Mo$_2$(DPPM)$_2$Cl$_4$·2C$_3$H$_6$O (2). This compound crystallizes in the space group $C2/c$ with $Z = 4$. Each dimolybdenum molecule resides

Figure 1. ORTEP drawing of compound 1, Mo$_2$(DPPM)$_2$(NCS)$_4$, in which each atom is represented by its ellipsoid of thermal vibration scaled to enclose 50% of the electron density.
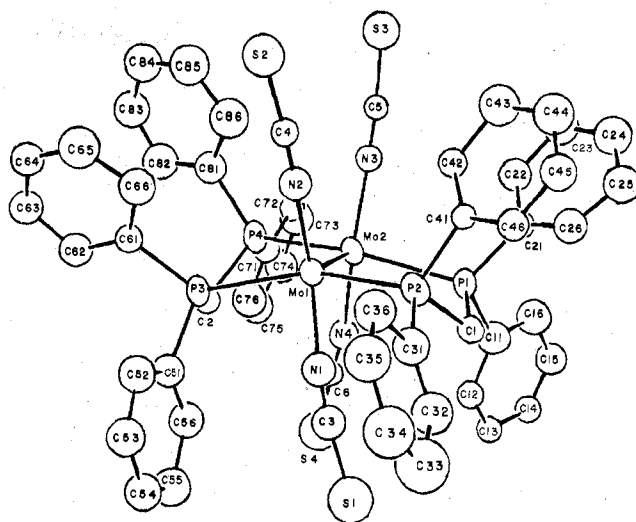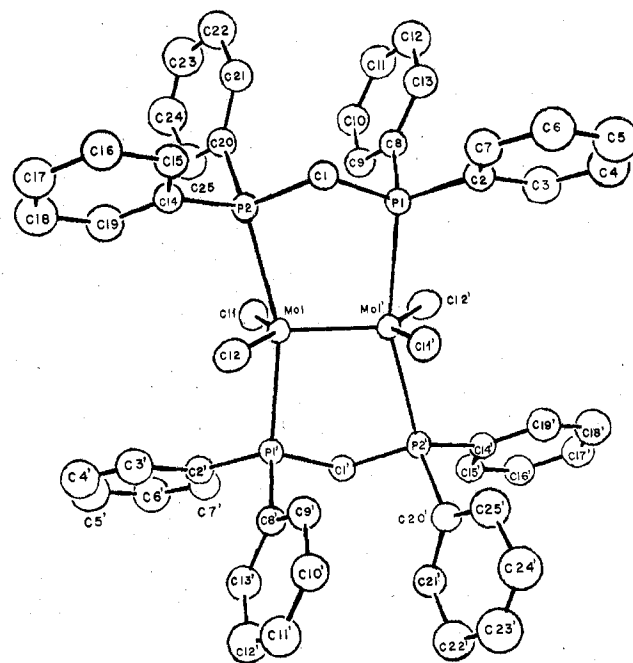

Figure 2. ORTEP drawing of compound **2**, Mo$_2$(DPPM)$_2$Cl$_4$, in which each atom is represented by its ellipsoid of thermal vibration scaled to enclose 50% of the electron density.

on an inversion center. This structure, too, was solved using conventional heavy-atom methods and refined to convergence using anisotropic thermal parameters for the Mo, Cl, and P atoms and isotropic thermal parameters for the C and O atoms. As for the SCN analogue, acetone molecules occupy sites between the dimolybdenum molecules but are not in any way bonded to them. A final difference map yielded six peaks in the electron density range 2.0–1.6 e/Å^3. Three of these are less than 1 Å away from acetone atoms, while the other three are less than 0.8 Å away from various benzene ring atoms. They may be indicative of slight disorder, but no further attention was paid to them.

The atomic positional and thermal parameters are given in Tables II and III for the NCS and Cl compounds, respectively. Tables of observed and calculated structure factors for both compounds are available as supplementary material.

Results

Figures 1 and 2 show the two Mo$_2$(DPPM)$_2$X$_4$ molecules and define the atomic numbering schemes used in the tables. Tables IV and V list interatomic distances and angles for both

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for Compound 1, $Mo_2(DPPM)_2(NCS)_4 \cdot 2C_3H_6O^a$

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo(1)	0.1728 (2)	0.2285 (2)	0.1545 (1)	2.5 (1)	2.9 (1)	3.6 (1)	0.1 (1)	0.1 (1)	0.2 (2)
Mo(2)	0.2866 (2)	0.3231 (2)	0.1583 (1)	2.5 (1)	2.9 (1)	3.9 (1)	0.0 (2)	0.0 (1)	0.6 (2)
P(1)	0.1765 (7)	0.4432 (6)	0.1840 (3)	2.9 (5)	3.3 (5)	4.9 (6)	0.3 (4)	0.3 (4)	-0.2 (5)
P(2)	0.0193 (6)	0.3259 (7)	0.1600 (3)	2.3 (4)	4.3 (5)	4.1 (5)	0.4 (5)	0.5 (4)	1.1 (5)
P(3)	0.2733 (7)	0.1033 (6)	0.1299 (3)	3.8 (5)	3.3 (5)	4.1 (5)	0.1 (4)	-0.2 (4)	-0.3 (5)
P(4)	0.4196 (6)	0.2370 (6)	0.1182 (3)	3.0 (4)	4.1 (5)	3.9 (5)	0.9 (5)	0.4 (4)	0.5 (5)

atom	x	y	z	B, Å²	atom	x	y	z	B, Å²
S(1)	0.1433 (8)	0.1203 (8)	0.2980 (4)	7.0 (3)	C(42)	-0.131 (3)	0.235 (3)	0.1202 (13)	6.5 (11)
S(2)	0.1296 (10)	0.2089 (9)	0.0016 (5)	9.5 (4)	C(43)	-0.187 (3)	0.210 (3)	0.0815 (13)	7.0 (11)
S(3)	0.2097 (9)	0.4826 (8)	0.0297 (4)	8.0 (3)	C(44)	-0.168 (3)	0.254 (3)	0.0434 (13)	6.8 (11)
S(4)	0.3937 (8)	0.2437 (7)	0.3011 (4)	6.2 (3)	C(45)	-0.103 (3)	0.319 (3)	0.0368 (13)	7.2 (11)
O(1)	0.455 (2)	0.072 (2)	0.6618 (8)	5.7 (6)	C(46)	-0.048 (3)	0.345 (2)	0.0741 (12)	6.4 (11)
O(2)	0.081 (0)	0.437 (0)	0.9038 (0)	14.4 (0)	C(51)	0.343 (2)	0.043 (2)	0.1686 (10)	2.9 (7)
N(1)	0.163 (2)	0.177 (2)	0.2148 (9)	4.6 (7)	C(52)	0.377 (2)	-0.037 (2)	0.1584 (11)	4.0 (8)
N(2)	0.142 (2)	0.229 (2)	0.0904 (8)	4.3 (7)	C(53)	0.439 (3)	-0.080 (2)	0.1869 (11)	5.1 (9)
N(3)	0.262 (2)	0.384 (2)	0.1007 (9)	4.9 (7)	C(54)	0.439 (3)	0.034 (2)	0.2346 (11)	5.1 (10)
N(4)	0.344 (2)	0.299 (2)	0.2197 (8)	3.8 (7)	C(55)	0.473 (3)	-0.048 (2)	0.2247 (12)	5.7 (10)
C(1)	0.062 (2)	0.432 (2)	0.1523 (10)	3.1 (8)	C(56)	0.371 (2)	0.080 (2)	0.2059 (10)	3.0 (8)
C(2)	0.358 (2)	0.148 (2)	0.0918 (10)	3.1 (8)	C(61)	0.204 (2)	0.024 (2)	0.0999 (11)	4.6 (9)
C(3)	0.156 (2)	0.154 (2)	0.2503 (10)	3.0 (8)	C(62)	0.145 (3)	-0.027 (3)	0.1271 (13)	6.6 (11)
C(4)	0.133 (2)	0.220 (2)	0.0561 (11)	4.4 (9)	C(63)	0.096 (3)	-0.093 (3)	0.1061 (13)	7.0 (11)
C(5)	0.240 (2)	0.423 (2)	0.0722 (10)	3.5 (8)	C(64)	0.089 (3)	-0.102 (3)	0.0624 (14)	8.3 (13)
C(6)	0.367 (2)	0.276 (2)	0.2540 (9)	2.7 (7)	C(65)	0.138 (3)	-0.050 (3)	0.0371 (15)	8.9 (14)
C(11)	0.224 (2)	0.548 (2)	0.1688 (10)	3.2 (8)	C(66)	0.202 (3)	0.017 (2)	0.0581 (12)	5.9 (10)
C(12)	0.307 (2)	0.579 (2)	0.1937 (11)	4.4 (9)	C(71)	0.523 (2)	0.198 (2)	0.1481 (11)	4.1 (9)
C(13)	0.346 (3)	0.659 (3)	0.1840 (12)	6.4 (11)	C(72)	0.560 (2)	0.248 (2)	0.1816 (11)	4.5 (9)
C(14)	0.310 (3)	0.703 (2)	0.1511 (12)	6.2 (11)	C(73)	0.641 (3)	0.222 (3)	0.2075 (13)	6.5 (11)
C(15)	0.230 (3)	0.676 (3)	0.1264 (12)	6.3 (10)	C(74)	0.684 (3)	0.148 (3)	0.1944 (13)	7.0 (12)
C(16)	0.186 (3)	0.592 (2)	0.1350 (12)	5.2 (9)	C(75)	0.652 (3)	0.093 (3)	0.1634 (12)	6.3 (11)
C(21)	0.140 (2)	0.452 (2)	0.2376 (10)	3.6 (8)	C(76)	0.567 (2)	0.121 (2)	0.1386 (11)	4.2 (9)
C(22)	0.164 (3)	0.390 (3)	0.2684 (12)	6.3 (10)	C(81)	0.477 (2)	0.292 (2)	0.0711 (11)	4.1 (9)
C(23)	0.141 (3)	0.399 (3)	0.3115 (13)	7.0 (11)	C(82)	0.572 (2)	0.317 (2)	0.0780 (11)	4.8 (9)
C(24)	0.088 (3)	0.477 (3)	0.3235 (13)	6.8 (11)	C(83)	0.610 (2)	0.369 (2)	0.0414 (11)	4.3 (9)
C(25)	0.063 (3)	0.546 (3)	0.2966 (14)	7.5 (12)	C(84)	0.553 (3)	0.394 (2)	0.0068 (12)	5.6 (10)
C(26)	0.087 (3)	0.531 (2)	0.2526 (13)	6.0 (10)	C(85)	0.455 (3)	0.366 (2)	0.0034 (12)	5.6 (10)
C(31)	-0.060 (2)	0.335 (2)	0.2049 (10)	3.2 (8)	C(86)	0.419 (2)	0.314 (2)	0.0381 (10)	3.7 (8)
C(32)	-0.133 (2)	0.396 (2)	0.2061 (11)	4.3 (9)	C(101)	0.472 (3)	-0.031 (2)	0.6067 (12)	6.0 (10)
C(33)	-0.192 (2)	0.397 (2)	0.2417 (11)	4.8 (9)	C(102)	0.516 (3)	0.019 (3)	0.6419 (13)	7.3 (12)
C(34)	-0.183 (3)	0.344 (2)	0.2761 (12)	5.3 (10)	C(103)	0.618 (3)	0.014 (3)	0.6567 (13)	7.2 (12)
C(35)	-0.114 (3)	0.285 (3)	0.2764 (13)	7.0 (11)	C(201)	0.232 (0)	0.360 (0)	0.9139 (0)	9.6 (0)
C(36)	-0.049 (3)	0.276 (3)	0.2398 (13)	6.8 (11)	C(202)	0.124 (0)	0.376 (0)	0.9150 (0)	12.9 (0)
C(41)	-0.064 (3)	0.307 (2)	0.1167 (11)	5.1 (9)	C(203)	0.046 (0)	0.302 (0)	0.9022 (0)	11.7 (0)

^{a} The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table III. Positional and Thermal Parameters and Their Estimated Standard Deviations for Compound 2, $Mo_2(DPPM)_2Cl_4 \cdot C_3H_6O^a$

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo(1)	0.20476 (3)	0.19583 (5)	0.49043 (2)	1.85 (2)	2.60 (2)	2.24 (2)	-0.22 (2)	0.09 (2)	-0.05 (2)
Cl(1)	0.1164 (1)	0.3031 (2)	0.43831 (8)	2.69 (7)	5.4 (1)	3.32 (8)	0.84 (7)	0.10 (6)	0.91 (8)
Cl(2)	0.2376 (1)	0.0130 (2)	0.52755 (8)	3.33 (7)	2.79 (7)	4.04 (8)	0.08 (6)	0.28 (7)	0.32 (7)
P(1)	0.25193 (9)	0.3840 (2)	0.59284 (7)	2.32 (7)	2.96 (8)	2.49 (7)	-0.21 (6)	0.06 (6)	-0.22 (7)
P(2)	0.12115 (9)	0.2549 (2)	0.56223 (7)	2.16 (7)	2.74 (7)	2.76 (8)	-0.17 (6)	0.14 (6)	-0.08 (7)

atom	x	y	z	B, Å²	atom	x	y	z	B, Å²
O(1)	0.4192 (6)	0.968 (1)	0.3201 (5)	10.4 (3)	C(15)	-0.0084 (4)	0.3772 (7)	0.5447 (3)	3.4 (1)
C(1)	0.1544 (4)	0.3964 (6)	0.5824 (3)	2.8 (1)	C(16)	-0.0831 (5)	0.3836 (8)	0.5280 (3)	4.3 (2)
C(2)	0.2850 (4)	0.5260 (6)	0.6086 (3)	3.1 (1)	C(17)	-0.1185 (5)	0.2896 (8)	0.5072 (4)	4.7 (2)
C(3)	0.3595 (5)	0.5379 (9)	0.6230 (4)	4.9 (2)	C(18)	-0.0839 (6)	0.1908 (9)	0.5002 (4)	5.5 (2)
C(4)	0.3859 (6)	0.6512 (10)	0.6339 (4)	5.9 (2)	C(19)	-0.0081 (5)	0.1810 (8)	0.5174 (4)	4.5 (2)
C(5)	0.3439 (6)	0.7399 (12)	0.6311 (5)	6.6 (3)	C(20)	0.1099 (4)	0.1749 (7)	0.6220 (3)	3.1 (1)
C(6)	0.2700 (6)	0.7319 (10)	0.6163 (4)	5.8 (2)	C(21)	0.0968 (4)	0.2262 (8)	0.6678 (3)	3.9 (2)
C(7)	0.2421 (4)	0.6218 (8)	0.6059 (4)	4.2 (2)	C(22)	0.0861 (5)	0.1638 (9)	0.7132 (4)	5.5 (2)
C(8)	0.2675 (4)	0.3094 (6)	0.6550 (3)	2.9 (1)	C(23)	0.0897 (6)	0.0418 (10)	0.7074 (5)	6.5 (2)
C(9)	0.2763 (4)	0.1921 (7)	0.6557 (3)	3.5 (2)	C(24)	0.0988 (6)	-0.0101 (10)	0.6645 (5)	6.2 (2)
C(10)	0.2833 (5)	0.1324 (8)	0.7032 (4)	4.3 (2)	C(25)	0.1112 (5)	0.0603 (9)	0.6194 (4)	5.1 (2)
C(11)	0.2819 (5)	0.1931 (8)	0.7483 (4)	5.0 (2)	C(26)	0.5417 (7)	0.9885 (13)	0.3243 (6)	8.2 (3)
C(12)	0.2732 (5)	0.3090 (9)	0.7492 (4)	5.5 (2)	C(27)	0.4755 (6)	0.9219 (11)	0.3248 (5)	7.0 (3)
C(13)	0.2671 (5)	0.3682 (8)	0.7013 (3)	4.2 (2)	C(28)	0.5038 (16)	0.7946 (30)	0.3095 (15)	17.7 (9)
C(14)	0.0271 (4)	0.2740 (6)	0.5386 (3)	2.8 (1)					

^{a} The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table IV. Selected Bond Distances (Å) in the Mo₂(DPPM)₂X₄ Molecules[a,b]

X = NCS		X = Cl	
Mo(1)-Mo(2)	2.167 (3)	Mo(1)-Mo(1)'	2.138 (1)
Mo(1)-P(2)	2.622 (7)	Mo(1)-P(1)'	2.541 (1)
-P(3)	2.538 (7)	Mo(1)-P(2)	2.628 (1)
Mo(2)-P(1)	2.564 (7)		
-P(4)	2.611 (7)		
av Mo-P	2.58 (3)	av Mo-P	2.58 (4)
Mo(1)-N(1)	2.05 (2)	Mo(1)-Cl(1)	2.388 (1)
-N(2)	2.03 (2)	Mo(1)-Cl(2)	2.400 (1)
Mo(2)-N(3)	2.06 (2)		
-N(4)	2.09 (2)		
av Mo-N	2.06 (2)	av-Mo-Cl	2.39 (1)
C(1)-P(1)	1.86 (2)	C(1)-P(1)	1.830 (5)
-P(2)	1.79 (2)	-P(2)	1.828 (6)
C(2)-P(3)	1.82 (3)		
-P(4)	1.83 (3)		
av P-CH₂	1.83 (2)	av P-CH₂	1.829 (1)
P(1)-C(11)	1.85 (3)	P(1)-C(2)	1.806 (6)
-C(21)	1.75 (3)	-C(8)	1.822 (6)
P(2)-C(31)	1.79 (3)	P(2)-C(14)	1.826 (5)
-C(41)	1.78 (3)	-C(20)	1.830 (6)
P(3)-C(51)	1.81 (3)		
-C(61)	1.82 (3)		
P(4)-C(71)	1.80 (3)		
-C(81)	1.89 (3)		
av P-C	1.81 (3)	av P-C	1.82 (1)
N(1)-C(3)	1.17 (3)		
N(2)-C(4)	1.08 (2)		
N(3)-C(5)	1.12 (3)		
N(4)-C(6)	1.16 (3)		
C(3)-S(1)	1.59 (3)		
C(4)-S(2)	1.71 (2)		
C(5)-S(3)	1.67 (3)		
C(6)-S(4)	1.59 (3)		

[a] Figures in parentheses following individual distances are esd's occurring in the least significant digit, while for each average value this figure is the mean deviation of the individual values from the average. [b] All C–C distances in the phenyl rings are available as supplementary material; see final paragraph of the text.

Table V. Selected Bond Angles (deg) in the Mo₂(DPPM)₂X₄ Molecules[a,b]

X = NCS		X = Cl	
Mo(2)-Mo(1)-P(2)	100.0 (2)	Mo(1)'-Mo(1)-P(1)'	95.86 (4)
-P(3)	99.1 (2)	-P(2)	101.29 (4)
-N(1)	106.1 (6)	-Cl(1)	108.15 (5)
-N(2)	101.2 (5)	-Cl(2)	105.57 (4)
P(2)-Mo(1)-P(3)	157.0 (2)	P(1)'-Mo(1)-P(2)	161.79 (4)
-N(1)	96.3 (6)	-Cl(1)	88.85 (5)
-N(2)	84.5 (5)	-Cl(2)	88.27 (5)
P(3)-Mo(1)-N(1)	90.6 (6)	P(2)-Mo(1)-Cl(1)	80.08 (5)
-N(2)	79.3 (5)	-Cl(2)	95.87 (5)
N(1)-Mo(1)-N(2)	152.1 (8)	Cl(1)-Mo(1)-Cl(2)	146.18 (5)
Mo(1)-Mo(2)-P(1)	95.6 (2)		
-P(4)	97.2 (2)		
-N(3)	99.7 (6)		
-N(4)	100.7 (6)		
P(1)-Mo(2)-P(4)	163.0 (2)		
-N(3)	80.5 (6)		
-N(4)	93.7 (6)		
P(4)-Mo(2)-N(3)	86.3 (6)		
-N(4)	94.9 (6)		
N(3)-Mo(2)-N(4)	159.2 (9)		
Mo(2)-P(1)-C(1)	105.3 (7)	Mo(1)'-P(1)-C(1)	107.5 (2)
-C(11)	111.8 (9)	-C(2)	113.4 (2)
-C(21)	122 (1)	-C(8)	121.8 (2)
C(1)-P(1)-C(11)	105 (1)	C(1)-P(1)-C(2)	106.1 (2)
-C(21)	105 (1)	-C(8)	104.0 (2)
C(11)-P(1)-C(21)	106 (1)	C(2)-P(1)-C(8)	102.8 (2)
Mo(1)-P(2)-C(1)	106.0 (7)	Mo(1)-P(2)-C(1)	103.1 (2)
-C(31)	126.8 (9)	-C(14)	114.9 (2)
-C(41)	111 (1)	-C(20)	125.5 (2)
C(1)-P(2)-C(31)	103 (1)	C(1)-P(2)-C(14)	106.1 (2)
-C(41)	105 (1)	-C(20)	106.8 (2)
C(31)-P(2)-C(41)	102 (1)	C(14)-P(2)-C(20)	99.1 (2)
Mo(1)-P(3)-C(2)	104.6 (9)		
-C(51)	119.9 (9)		
-C(61)	114 (1)		
C(2)-P(3)-C(51)	108 (1)		
-C(61)	105 (1)		
C(51)-P(3)-C(61)	104 (1)		
Mo(2)-P(4)-C(2)	107.0 (8)		
-C(71)	119.1 (1)		
-C(81)	115.8 (8)		
C(2)-P(4)-C(71)	109 (1)		
-C(81)	102 (1)		
C(71)-P(4)-C(81)	103 (1)		
Mo(1)-N(1)-C(3)	175 (2)		
Mo(1)-N(2)-C(4)	170 (2)		
Mo(2)-N(3)-C(5)	171 (2)		
Mo(2)-N(4)-C(6)	171 (2)		
N(1)-C(3)-S(1)	178 (3)		
N(2)-C(4)-S(2)	175 (2)		
N(3)-C(5)-S(3)	179 (2)		
N(4)-C(6)-S(4)	177 (3)		
P(1)-C(1)-P(2)	107 (1)	P(1)-C(1)-P(2)	106.2 (3)
P(3)-C(2)-P(4)	107 (1)		

[a] Figures in parentheses following individual distances are esd's occurring in the least significant digit. [b] All angles in the phenyl rings are available as supplementary material; see final paragraph of the text.

compounds. Some additional distances and angles, involving the phenyl groups and acetone molecules, are omitted from these tables but may be found in the supplementary material.

The chloro compound, **2**, has a structure that presents no remarkable features. The DPPM ligands are present in the bridging mode, Ib, and are opposite (transoid) to each other. The steric demands of the phenyl groups would appear to require this transoid relationship quite apart from the influence of any electronic factors. The molecular unit has a crystallographic inversion center at its midpoint. This means that the rotational conformation is strictly eclipsed, although, because of other distortions, the torsional angles about the Mo–Mo axis are not exactly zero.

The central Mo₂P₄Cl₄ group has idealized D_{2h} symmetry, but there are appreciable distortions from this, which we believe are caused by internal crowding. Thus, the DPPM ligand is tilted away from the ideal, symmetrical relationship to the Mo₂Cl₄ unit, so that, instead of being equal, the Mo–Mo–P angles are 96 and 101° and the Mo–P distances differ by about 0.07 Å. Both the Mo₂Cl and Mo₂P₄ sets of atoms show deviations of ca. 0.05 Å from rigorous coplanarity. The mean Mo–Cl distance, 2.39 (1) Å, is a little shorter than those (2.45–2.47 Å) found in the several compounds containing the Mo₂Cl₈⁴⁻ ion.[11] This shortening may be of either electrostatic or steric origin or of both. The presence of only four Cl⁻ ions could lead to their being drawn in more closely than when there are eight. Also, the Mo–P distances, 2.58 (4) Å, are much greater, thus allowing closer approach by the Cl atoms. The Mo–Mo distance, 2.138 (1) Å, is very similar to the distances found in the Mo₂Cl₈⁴⁻ ion,[11] viz., 2.139 (4), 2.134 (1), and 2.150 (5) Å, in three different compounds.

The thiocyanate compound possesses a number of more interesting structural features, of which the most obvious is the greater length of the Mo–Mo bond, 2.167 (3) Å. Another is that no crystallographic symmetry is imposed on the Mo₂(DPPM)₂(NCS)₄ molecule, and thus internal rotation away from a strictly eclipsed rotational conformation is permitted. In fact, such a rotation, of significant magnitude, is observed. In a system such as this, where no symmetry restrictions exist, there is no unique or rigorous way to define the rotational conformation. We have adopted the following practical approach. We calculate each of the four independent torsional angles about the Mo–Mo bond; these are listed in Table VI. In a situation where local C_{2v} (mm) symmetry existed in each MoP₂N₂ end of the molecule, a simple internal

Table VI. Torsional Angles (deg) in $Mo_2(DPPM)_2(NCS)_4$

planes defining the angle		
atoms in plane 1	atoms in plane 2	angle
N(1), Mo(1), Mo(2)	Mo(1), Mo(2), N(4)	8.9
N(2), Mo(1), Mo(2)	Mo(1), Mo(2), N(3)	18.6
P(2), Mo(1), Mo(2)	Mo(1), Mo(2) P(1)	13.6
P(3), Mo(1), Mo(2)	Mo(1), Mo(2), P(4)	12.0
	mean angle	13.3
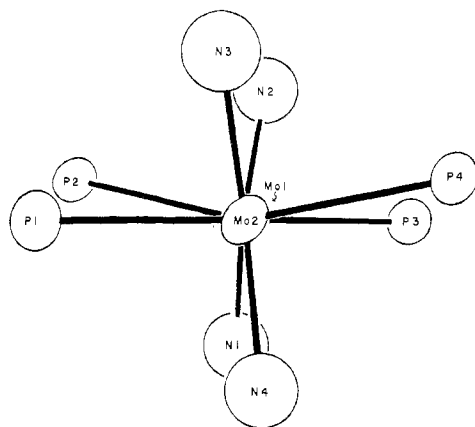
Figure 3. ORTEP drawing showing the $Mo_2P_4N_4$ moiety of **1** looking down the 4° Mo–Mo bond.

rotation away from a perfectly eclipsed conformation (in which there would be full D_{2h} symmetry in the entire $Mo_2P_4N_4$ unit) would result in all four torsional angles being equal. As Table VI clearly shows, this is far from being true in the actual case. We take the point of view that these angles differ because each of them results from the combined effects of a true internal rotation and other steric distortions. We further assume that these other steric distortions will tend to be random, so that by averaging the four individual tortional angles we arrive at a meaningful estimate of the angle of internal rotation away from the eclipsed conformation. We thus conclude that there is a deviation of ca. 13° from the eclipsed conformation in $Mo_2(DPPM)_2(NCS)_4$.

In order to visualize the situation and see the reality of the internal rotation despite the occurrence of other distortions from ideal symmetry, it is helpful to examine Figure 3 where the view is directly along the Mo(2)–Mo(1) line and it can be immediately recognized that all four torsional angles are, indeed, in the same sense and thus have the "concerted" effect of an internal rotation.

The third important structural feature of **1** is the presence of the NCS ligands as isothiocyanato (i.e., –NCS) groups. As shown in Table V, the Mo–N–C–S chains are very nearly linear in each case and the small bends observed are largely, if not entirely, of steric origin.

Discussion

The presence of SCN ligands bonded through nitrogen, long suspected in other cases as well as here on the basis of infrared spectra, is now confirmed. This result has some potential synthetic implications. If the Mo_2^{4+} unit has an inherent preference for bonding to a first-row rather than a second-row ligand atom (a hypothesis also supported by the generally greater ease of preparation and stability of $(RCO_2)_4Mo_2$ as compared to $(RCS_2)_4Mo_2$ compounds), then we are encouraged to believe that stable fluoro complexes of Mo_2^{4+} should be obtainable. None have yet been reported, but this may only reflect the lack of convenient ways to prepare them as well as a lack of efforts to do so.

The ca. 13° rotation from the eclipsed configuration is of special interest. As noted in the Introduction, in crystals

quadruply bonded, Mo_2^{4+} and Re_2^{6+} complexes have nearly always been found on a crystallographic symmetry element, meaning, in effect, that packing interactions with their surroundings would oppose internal rotation. In nearly all of the rare instances where this was not the case the ligands were of such a rigid nature (e.g., RCO_2, o-oxopyridine) as to effectively oppose rotation. Thus, the related questions of (1) what degree of rotation would exist in a molecule not subject to severe restraints either internally or externally and (2) what angle of rotation could be tolerated without loss of the σ bond have remained entirely unilluminated. Only in one case,[12] namely, $Re_2(PhNCPhNPh)_2Cl_4(THF)$, has a small but significant twist, ca. 6°, been observed, but even here there are two fairly rigid restraining ligands in the form of the *N,N'*-diphenylbenzamidine ligands.

We have here, in $Mo_2(DPPM)_2(NCS)_4$, an excellent illustration of the fact that while, on one hand, maximum strength of a δ bond will be attained in a precisely eclipsed conformation, on the other hand, repulsive forces between nonbonded atoms decrease as internal rotation away from this conformation occurs. The energy of the system as a whole may thus be minimized at some degree of rotation sufficient to relieve part of the strain without causing too much weakening of the δ bond. For the molecule $Mo_2(DPPM)_2$-$(NCS)_4$ the requisite angle appears to be about 13°. We say "appears to be" rather than "is" because we must recognize that the observed angle of rotation may still be partly influenced by intermolecular packing forces.

A rotation of only 13° should cause only a slight decrease in the strength of the Mo–Mo bond. The δ and π components are insensitive to such a rotation when fourfold axial symmetry prevails, as in $Mo_2Cl_8^{4-}$, for example. In the lower symmetry prevailing here, the σ bond will probably still be insignificantly affected. It is, however, possible that with an alternating set of ligands on each metal atom, viz., *trans*-MoX_2Y_2, the effectiveness of Mo–Mo π bonding could vary if the ligands X and Y differ appreciably in their ability to interact with the metal dπ orbitals. The Mo–Mo δ interaction is, of course, angle sensitive even under fourfold symmetry, but it should be noted that the δ overlap will decrease only as cos 2θ, where θ is the angle of rotation from the eclipsed (θ = 0°) conformation. Thus, for θ = 13° the δ contribution to the Mo–Mo bond may decrease to only about 0.89 of its maximal value (i.e., much less than the linear value of (45 − 13)/45 = 0.71). Thus, if the π bonding is essentially insensitive to the rotation, the entire Mo–Mo bond strength will be but slightly affected since the δ component is a weak contributor. However, even if the Mo–Mo bond is significantly weakened through a variation in the strength of the π bond as a function of θ, the δ bond will still retain much of its strength and there will be no resultant unpairing of the δ electrons, for a value of θ as small as 13°.

Three possible causes of the unusual Mo–Mo bond length come to mind: (1) intramolecular repulsive forces; (2) weakening of the π and/or δ bonding by interaction of the metal d orbitals with π* orbitals of the isothiocyanate ligands; (3) weakening of the δ and/or π bonds as a result of the approximately 13° rotation away from the eclipsed configuration. There is certainly no way to come to any conclusion about the relative importance of these three factors. Of course, the fact that the Mo–Mo distance is increased, *whatever the cause*, means that the strength of the δ bond is lessened. However, it retains sufficient strength to keep the compound diamagnetic.

Supplementary Material Available: C–C distances (Table A) and bond angles (Table B) in phenyl groups and acetone molecules and tables of observed and calculated structure factors for Mo$_2$-(DPPM)$_2$NCS and Mo$_2$(DPPM)$_2$Cl$_4$ (29 pages). Ordering information is given on any current masthead page.

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A New Class of Trinuclear Tungsten(IV) Cluster Compounds with W–W Single Bonds

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The reaction of tungsten hexacarbonyl with carboxylic acids, followed by suitable workup procedures, allows the isolation of compounds whose common feature is the presence of a $[W_3O_2(O_2CR)_6]^{2+}$ unit, to which three additional donors are coordinated. This consists of an equilateral triangle of tungsten atoms with oxygen atoms on the threefold axis above and below the triangle so that the W$_3$O$_2$ set of atoms defines a trigonal bipyramid. Each W–W edge is bridged by two bidentate carboxylato ions. Each tungsten atom is coordinated by an additional ligand, such as H$_2$O or an anion, and is therefore nine-coordinate, counting its neighboring tungsten atoms. The W–W distances, which are all about 2.75 Å, are consistent with the existence of W–W single bonds. Additional anions or cations are present as necessary for electroneutrality. Four compounds, all of which have been structurally characterized by X-ray crystallography, are reported here: **1**, {[W$_3$-O$_2$(O$_2$CCH$_3$)$_6$](H$_2$O)$_3$}(CF$_3$SO$_3$)$_2$; **2**, {[W$_3$O$_2$(O$_2$CC$_2$H$_5$)$_6$](H$_2$O)$_3$}(BF$_4$)$_2$·5.5H$_2$O; **3**, {[W$_3$O$_2$(O$_2$CC(CH$_3$)$_3$)$_6$](O$_2$CC(C-H$_3$)$_3$)$_2$(H$_2$O)}(CH$_3$)$_3$CCO$_2$H; **4**, Cs{[W$_3$O$_2$(O$_2$CCH$_3$)$_6$](CH$_3$CO$_2$)$_3$}·3H$_2$O. All four are yellow solids and are stable in air. The principal crystallographic data for each of the compounds are as follows: (**1**) monoclinic $C2/c$, a = 19.798 (5) Å, b = 11.424 (5) Å, c = 15.079 (5) Å, β = 115.94 (5)°, V = 3067 Å^3, Z = 4; (**2**) triclinic $P\bar{1}$, a = 13.285 (6) Å, b = 12.614 (5) Å, c = 12.453 (5) Å, α = 93.84 (5)°, β = 92.17 (5)°, γ = 102.37 (5)°, V = 2031 Å^3, Z = 2; (**3**) orthorhombic $Pnnm$, a = 16.159 (3) Å, b = 26.053 (6) Å, c = 16.941 (3) Å, V = 7132 Å^3, Z = 4; (**4**) monoclinic $C2/c$, a = 20.702 (5) Å, b = 12.987 (2) Å, c = 25.535 (5) Å, β 92.61 (6)°, V = 6858 Å^3, Z = 8.

Introduction

Ever since the discovery that Mo(CO)$_6$ reacts with carboxylic acids to give yellow compounds[2] subsequently shown to be the dinuclear,[3] quadruply bonded[4] molecules Mo$_2$-(O$_2$CR)$_4$, Figure 1A, efforts have been made[5,6] to prepare analogous tungsten compounds, but without any conclusive success. With several carboxylic acids, materials thought to be the W$_2$(O$_2$CR)$_4$ compounds were obtained[5] but none was obtained in crystalline form, so that X-ray crystallographic confirmation of such suggested structures is lacking.

In the case of acetic acid the only product previously isolated[5,6] was recognized to be an oxo compound and was probably trinuclear. Formulas such as W$_3$O(O$_2$CCH$_3$)$_9$,[5] W$_3$O(O$_2$CCH$_3$)$_8$(OH)(H$_2$O),[6] and W$_3$O(O$_2$CCH$_3$)$_8$(O-H)(CH$_3$OH)[6] were suggested. However, there has been no evidence for the details of these proposals and they were suggested by analogy with the well-known oxotrimetal hexacarboxylate structure, Figure 1B, exhibited by many transition-metal compounds.[7] An important characteristic of this structure is that the oxygen atom resides at the center of the equilateral triangle of metal atoms and thus prevents the metal atoms from approaching one another closely enough to form direct metal–metal bonds. Compounds with this structure are therefore *not* metal atom cluster compounds in the true sense of that term.[8]

The present work was undertaken with the purpose of understanding more fully what happens when an excess of acetic acid, or a mixture of the acid and its anhydride, reacts with W(CO)$_6$. The product isolated and discussed in the earlier investigations, which precipitates from the reaction mixture, contains only a small fraction of the total tungsten introduced and one obvious task was to determine the fate of the rest of the tungsten, which remained in solution. In this paper we report that essentially all of that remaining tungsten appears to be present in one form, namely, as a true trinuclear cluster, and that various compounds can be isolated depending on the workup procedure. We also report that with acids other than acetic, specifically propionic and pivalic, crystalline products containing the same type of trinuclear cluster can be isolated.

Experimental Section

Materials. W(CO)$_6$ was used as obtained from Pressure Chemical Co. All solvents and chemicals were reagent grade and were used without further purification.

Preparation of {[W$_3$O$_2$(O$_2$CCH$_3$)$_6$](H$_2$O)$_3$}(CF$_3$SO$_3$)$_2$ (1). W(CO)$_6$ (1 g, 2.8 mmol) was refluxed overnight with 100 mL of a 1:1 mixture of acetic acid and acetic anhydride. The yellow precipitate that formed upon cooling was filtered off. This substance is still under investigation. The resulting clear solution was diluted with 100 mL of H$_2$O and absorbed on a cation exchange column (Dowex 50W-X2) and eluted with 0.5 M CF$_3$SO$_3$H. Slow evaporation of the eluate gave beautiful yellow crystalline material whose elemental analysis suggested the formula [W$_3$(O$_2$CCH$_3$)$_6$O$_2$(H$_2$O)$_3$](CF$_3$SO$_3$)$_2$. Anal. Calcd for W$_3$C$_{14}$O$_{23}$H$_{24}$F$_6$S$_2$: C, 13.02; F, 8.83; H, 1.86; S, 4.96. Found: C, 13.01; F, 8.73; H, 2.20; S, 5.22.

Preparation of {[W$_3$O$_2$(O$_2$CCH$_2$CH$_3$)$_6$](H$_2$O)$_3$}(BF$_4$)$_2$·5.5H$_2$O (2). This compound was prepared in a way analogous to the acetate