

Tetrakis[bis(difluorophosphino)methylamine]dichlorodimolybdenum. A New Type of Compound with a Metal–Metal Triple Bond

F. Albert Cotton,* William H. Ilsley, and Wolfgang Kaim

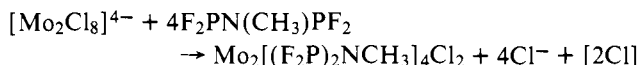
Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843. Received August 13, 1979

Abstract: Reaction of the $[\text{Mo}_2\text{Cl}_8]^{4-}$ ion with $\text{F}_2\text{PN}(\text{CH}_3)\text{PF}_2$ gives a yellow, crystalline compound, shown by mass spectrometry to have the composition $\text{Mo}_2[\text{F}_2\text{PN}(\text{CH}_3)\text{PF}_2]_4\text{Cl}_2$. The NMR spectrum is consistent with the presence of four equivalent $\text{F}_2\text{PN}(\text{CH}_3)\text{PF}_2$ ligands. X-ray crystallographic study has shown that the compound consists of discrete molecules in which the Mo–Mo distance is 2.457 (1) Å. The $\text{F}_2\text{PN}(\text{CH}_3)\text{PF}_2$ ligands are bridging and the Cl atoms are in axial positions with an Mo–Cl distance of 2.470 (1) Å. The rotational conformation of the Mo_2P_8 unit is twisted 21° from eclipsed. The virtual point symmetry of the molecule is D_4 , but the midpoint of the Mo–Mo axis lies on a crystallographic inversion center. This is possible because of a disordered packing in which the enantiomorphous forms of the twisted molecule occupy each site at random. The Mo, Cl, N, and CH_3 groups occupy the same positions for each enantiomorph, but the P atoms had to be refined as eight half-atoms. The fluorine atoms appear as a set of 16 half-atoms, but four pairs of these fall so close to each other that they could only be refined as four full atoms with unusually elongated vibrational ellipsoids. The crystals belong to space group $P2_1/n$ with $Z = 2$ and dimensions of $a = 10.076$ (2) Å, $b = 15.018$ (2) Å, $c = 9.622$ (1) Å, $\beta = 110.09$ (1)°, $V = 1367.5$ (4) Å³. Refinement with the disordered model just described converged to $R_1 = 0.043$, $R_2 = 0.064$, and a goodness of fit index of 1.386, using 3543 reflections with $F_o > 3\sigma(F_o)$ out of a total of 4565 measured in the range $0^\circ < 2\theta \leq 65^\circ$. This molecule is of a new, and so far unique, type with an M–M triple bond. It contains Mo(I) and has moderately strong bonds to axial (Cl^-) ligands, and the metal atoms have 18-electron configurations.

Introduction

There is now a considerable number of compounds known containing triple bonds between metal atoms.^{1,2} They are known with a number of elements, including vanadium, molybdenum, tungsten, and rhenium. Their electronic structures are surprisingly varied, ranging from the rather straightforward $\sigma^2\pi^4$ systems occurring in the M_2X_6 -type molecules formed by Mo and W to the more complicated $\sigma^2\pi^4\delta^2\delta^*2$ configurations in species such as $\text{Re}_2\text{Cl}_4(\text{PEt}_3)_4$ and the rather long bonds found in the $\text{Cp}_2\text{M}_2(\text{CO})_4$ compounds of Cr, Mo, and W. Despite this already great diversity, it is possible to find still other types of M–M triple bonds and we describe here an example in support of this assertion.

The reaction we have carried out can be represented by the equation



The fate of the two chlorine atoms has not been established positively but we presume that they have found their way into some form of P^{V} compound; that is, reduction of 2Mo^{VI} to 2Mo^{I} has been offset by oxidation of P^{III} to P^{V} . We have thoroughly characterized the above dimolybdenum(I) compound, despite the occurrence of an initially puzzling crystallographic disorder problem, and we report that characterization fully in this paper.

Experimental Section

The starting materials, $(\text{NH}_4)_5\text{Mo}_2\text{Cl}_9 \cdot \text{H}_2\text{O}$ and $(\text{F}_2\text{P})_2\text{NCH}_3$, were prepared according to literature procedures.^{3,4}

Preparation of $[\text{Mo}_2[(\text{F}_2\text{P})_2\text{NCH}_3]_4\text{Cl}_2]$. Pentaammonium octachlorodimolybdate chloride hydrate (0.93 g, 1.5 mmol) was suspended in 100 mL of dry acetonitrile. An excess of the phosphine $\text{F}_2\text{PN}(\text{CH}_3)\text{PF}_2$ (3 g, 18 mmol) was added and the mixture was left with continuous stirring at room temperature.

After 1 day a green color began to develop, and after 5 days the purple starting material had disappeared. After 10 days the mixture was filtered to yield a gray-white precipitate and a greenish solution. On slow evaporation of this solution under vacuum a small quantity (ca. 75 mg) of yellow, crystalline material separated on the glass wall. These crystals were dissolved in acetone and the solution left to

evaporate slowly in air. Well-shaped yellow crystals with dimensions up to 2 mm were formed by this procedure. The product is stable in humid air.

Spectral Measurements. The mass spectrum, measured on a high-resolution instrument (CEC21-110B), had a multiplet corresponding to the parent ion in which the pattern, mainly determined by the distribution of isotopes in Mo_2Cl_2 , fits the theoretical intensity distribution within experimental error, as shown in Figure 1. The computer program used to calculate isotope distribution patterns was kindly supplied by Dr. M. W. Extine. The high-resolution experiment, carried out at 240 °C probe temperature and 10^{-6} Torr, gave a value of 933.615 335 for one of the major peaks, while the calculated mass for the isotopic species $^{12}\text{C}_4^1\text{H}_1^{35}\text{Cl}_2^{19}\text{F}_{16}^{98}\text{Mo}_2^{14}\text{N}_4^{32}\text{P}_8$ is 933.620 298.

The NMR spectra were measured on solutions in acetone- d_6 . ¹H NMR (Varian T60): broad peak ($W_{1/2} = 12$ Hz) at δ 3.75 vs. Me_4Si , compared to δ 2.78 for the neat phosphine.⁵ ¹⁹F NMR spectra were recorded on a JEOL PFT 100/Nicolet 1080 instrument with a recording frequency of 93.660 MHz. The measurements were kindly performed by Dr. W. I. Bailey, Jr. The spectrum consists of a doublet ($^1J_{\text{PF}} = 1182$ Hz), with a chemical shift of 52.8 ppm upfield relative to CFCl_3 . This spectrum remains unchanged on lowering of the temperature to -100 °C. ³¹P decoupling (40.300 Hz) causes the doublet to collapse to a single line. The free phosphine ligand displays a complex spectrum, centered at 74.0 ppm upfield of CFCl_3 with $^1J_{\text{PF}} = 1264$ Hz.^{4,5}

Structure Determination. A crystal of approximate dimensions 0.30 × 0.40 × 0.40 mm was attached to the end of a thin glass fiber with epoxy cement and mounted on a Syntex PI automatic diffractometer.

Preliminary rotation and oscillation photographs indicated that the crystals were monoclinic and examination of selected reflections indicated that it was a single crystal of good quality. Several intense reflections had ω scans with widths at half-height of less than 0.3° . Careful centering on 15 reflections in the range $20^\circ < 2\theta < 31^\circ$ selected to give varied crystal orientations gave the unit cell parameters $a = 10.076$ (2) Å, $b = 15.018$ (2) Å, $c = 9.622$ (1) Å, and $\beta = 110.09$ (1)°. The volume, $V = 1367.5$ (4) Å³, is consistent with $Z = 2$. The procedures preliminary to data collection have been described previously.⁶

The intensity data were collected using Mo $K\alpha$ ($\lambda = 0.71073$ Å) radiation monochromatized in the incident beam with a graphite crystal. A total of 4565 independent reflections with $\theta < 2\theta \leq 65^\circ$ were collected at 22 ± 4 °C using the θ - 2θ scan technique. Variable scan rates, 4–24° min^{-1} , were used with a scan range of $K\alpha_1 - 1.0^\circ$ to $K\alpha_2$

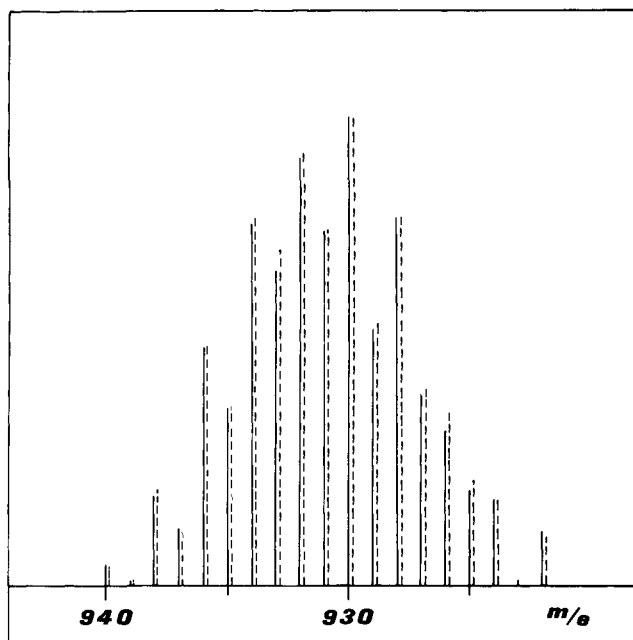


Figure 1. The parent ion, $[\text{Mo}_2\text{Cl}_2(\text{P}_2\text{F}_4\text{NCH}_3)_4]^+$, multiplet in the mass spectrum. Solid lines are observed relative intensities and dashed lines are those calculated from the natural abundance of the elements.

+ 1.0° and a scan to background time ratio of 2. The intensities of three standard reflections were measured after every 97 reflections; they remained essentially constant.

The usual Lorentz and polarization corrections were applied but absorption corrections were omitted in view of the low linear absorption coefficient (16.82 cm^{-1}) for Mo $K\alpha$ radiation.

Systematic absences in the data were indicative of the space group $P2_1/n$ and this was confirmed by satisfactory solution and refinement.⁷ The position of the single independent molybdenum atom was found by solution of the three-dimensional Patterson function. The remaining nonhydrogen atoms were found from successive Fourier and difference syntheses. Full-matrix anisotropic least-squares refinement of all heavy atom positional and temperature factors gave final discrepancy factors of

$$R_1 = (\sum ||F_o| - |F_c||) / \sum |F_o| = 0.043$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.064$$

and a goodness of fit parameter of 1.386. The function $\sum w(|F_o| - |F_c|)^2$ was minimized with the weighting factor, w , equal to $4F_o^2 / \sigma(F_o)^2$. All structure-factor calculations were executed using only those 3543 reflections for which $F_o^2 > 3\sigma(F_o)^2$. Atomic scattering factors were those of Cromer and Waber.⁸ Anomalous dispersion effects were included in the scattering factors of molybdenum.⁹

Results

Crystal Structure. Since there are two molecular units in space group $P2_1/n$, the conventional assumption would be that the molecule is centrosymmetric. The composition is not inconsistent with this, and the positions of the heavier atoms, Mo and Cl, were found to be so related. However, attempts to place all the remaining atoms in accord with the requirements of an inversion center at the midpoint of the Mo–Mo bond were unsuccessful and the possibility of disorder was then considered.

An ordered structure with a center of inversion would require the molecule to have virtual D_{4h} symmetry, but, since electronic considerations, discussed later, imply the presence of only a triple bond between the molybdenum atoms, twisting of this to a helical structure with only D_4 symmetry would not be opposed electronically. In order for twisted molecules of D_4 symmetry to meet the requirements of the crystallographic symmetry they would have to be disordered in such a way that

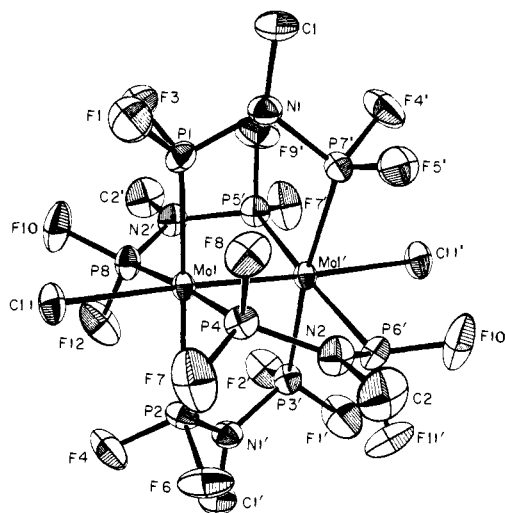


Figure 2. An ORTEP drawing of one of the two enantiomorphous $\text{Mo}_2[\text{F}_2\text{PN}(\text{CH}_3)\text{PF}_2]_4\text{Cl}_2$ molecules showing its numbering scheme.

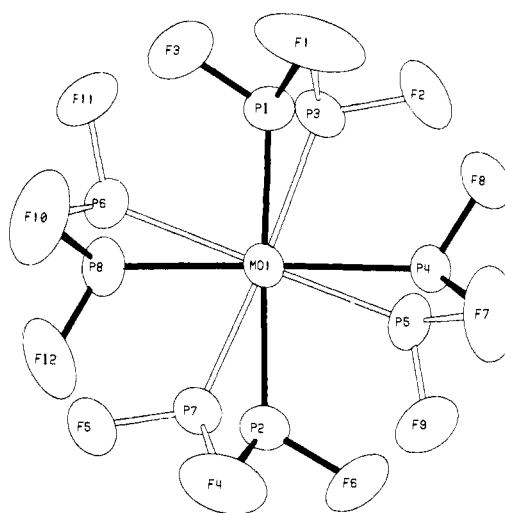


Figure 3. A superposition of portions of the Mo(1) halves of each of the enantiomorphous molecules showing how the set of eight half-phosphorus atoms arises.

half the sites would be occupied by one enantiomorph and half by the other in a random fashion.

Such an arrangement was found to be consistent with the data and allowed satisfactory refinement. Figure 2 shows one complete $\text{Mo}_2[\text{F}_2\text{PN}(\text{CH}_3)\text{PF}_2]_4\text{Cl}_2$ molecule, which is seen to have a partly staggered structure. The other enantiomorph differs in the rotational sense of the internal twist. Although each enantiomorph is at a different site, they appear to be superposed on the same site in the electron-density distribution, as shown in Figure 3, where one Mo atom and its apparent surroundings are depicted. One set of phosphorus atoms derives from each enantiomorph giving, in effect, a total of eight half-phosphorus atoms around the composite Mo atom. The operation of inversion generates the composite Mo' atom and its set of eight half-phosphorus atoms. If we designate the enantiomorphs as A and B, the relationships of phosphorus atoms to molybdenum atoms may be stated as follows:

- enantiomorph A: Mo: P(1), P(2), P(4), P(8)
 Mo': P(3)', P(5)', P(6)', P(7)'
- enantiomorph B: Mo: P(3), P(5), P(6), P(7)
 Mo': P(1)', P(2)', P(4)', P(8)'

The molecule shown in Figure 2 is enantiomorph A.

When the enantiomorphs are superimposed in their Mo and

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations^a

atom	x	y	z	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
Mo(1)	1.00091(3)	0.05551(2)	0.09406(2)	3.573(8)	2.735(8)	2.135(7)	0.046(8)	0.959(6)	-0.325(7)
Cl(1)	0.9916(1)	0.16687(7)	0.2794(1)	7.07(5)	4.69(4)	4.10(3)	0.17(4)	2.12(3)	-1.85(3)
P(1)	1.2478(2)	0.0428(1)	0.2163(2)	3.77(6)	4.34(8)	3.36(6)	-0.70(6)	0.68(5)	-0.70(6)
P(2)	0.7454(2)	0.0687(2)	-0.0154(2)	3.61(6)	5.35(9)	3.09(5)	0.76(6)	1.31(4)	0.26(6)
P(3)	1.2297(2)	0.0094(1)	0.2660(2)	4.45(7)	4.29(8)	2.55(5)	0.36(7)	0.35(5)	-0.21(6)
P(4)	0.9644(2)	-0.0593(1)	0.2605(2)	4.04(6)	4.28(7)	2.50(5)	-0.17(6)	1.33(4)	0.22(5)
P(5)	0.8844(2)	-0.0416(1)	0.2006(2)	5.54(7)	4.51(8)	4.03(5)	-0.26(6)	3.00(4)	0.14(6)
P(6)	1.1248(2)	0.1672(1)	-0.0079(2)	4.49(7)	3.40(6)	3.88(6)	-1.05(6)	1.24(5)	-0.21(6)
P(7)	0.7841(2)	0.1176(1)	-0.0644(2)	3.95(6)	3.55(7)	3.71(6)	0.53(6)	1.27(5)	-0.06(6)
P(8)	1.0261(2)	0.1740(1)	-0.0541(2)	6.09(8)	2.86(6)	4.48(6)	-0.30(6)	2.32(6)	0.15(6)
F(1)	1.3206(4)	0.0658(3)	0.3738(4)	7.5(2)	12.4(2)	6.5(1)	2.8(2)	-2.7(1)	-5.1(1)
F(2)	1.2355(7)	-0.0518(4)	0.4005(5)	8.4(3)	8.2(3)	3.3(2)	2.3(2)	1.9(2)	2.1(2)
F(3)	1.3497(6)	0.1122(4)	0.1867(7)	5.3(2)	6.0(3)	9.0(3)	-1.5(2)	2.7(2)	-0.7(3)
F(4)	0.6802(3)	0.1560(2)	0.0018(3)	6.8(1)	9.0(2)	6.3(1)	3.76(9)	1.85(9)	-1.7(1)
F(5)	0.7806(6)	0.2033(3)	-0.1562(7)	5.8(2)	4.3(2)	8.7(3)	0.6(2)	1.3(2)	2.8(2)
F(6)	0.6441(6)	0.0150(5)	0.0478(6)	5.0(2)	12.6(5)	7.7(2)	-1.3(2)	3.8(1)	1.3(3)
F(7)	0.8851(4)	-0.0358(2)	0.3580(3)	14.7(2)	7.2(2)	5.74(8)	0.9(1)	6.90(8)	0.5(1)
F(8)	1.0929(6)	-0.0903(4)	0.3947(5)	6.2(2)	6.0(2)	3.6(2)	-0.3(2)	0.4(2)	1.3(2)
F(9)	0.7210(6)	-0.0374(5)	0.1556(8)	5.5(2)	8.6(4)	11.5(3)	0.6(2)	4.8(2)	2.5(3)
F(10)	1.1041(4)	0.2604(2)	0.0095(4)	13.7(2)	4.2(1)	9.1(1)	-3.5(1)	6.0(1)	-2.0(1)
F(11)	1.2891(5)	0.1802(4)	0.0617(6)	5.2(2)	9.0(3)	6.7(3)	-3.7(2)	1.3(2)	0.2(3)
F(12)	0.8921(7)	0.2308(4)	-0.1434(7)	11.7(3)	6.2(2)	9.2(3)	4.4(2)	5.8(2)	4.2(2)
N(1)	1.3269(3)	-0.0498(2)	0.1943(4)	3.4(1)	4.9(1)	3.9(1)	0.3(1)	0.57(9)	0.1(1)
N(2)	0.8999(4)	-0.1533(2)	0.1840(3)	6.1(1)	4.0(1)	4.5(1)	-0.5(1)	2.71(8)	1.0(1)
C(1)	1.4745(5)	-0.0748(4)	0.2812(6)	3.4(2)	7.4(3)	5.9(2)	0.9(2)	-0.3(2)	0.5(2)
C(2)	0.8583(6)	-0.2226(4)	0.2735(5)	10.2(2)	6.2(2)	8.2(2)	-1.4(2)	5.2(1)	2.8(1)

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

Table II. Interatomic Distances (Å)

atoms	distance	atoms	distance
Mo(1)-Mo(1)'	2.457(1)	P(4)-P(5)	0.856(3)
Cl(1)	2.470(1)	F(7)	1.469(3)
P(1)	2.366(2)	F(8)	1.553(5)
P(2)	2.432(2)	N(2)	1.622(4)
Mo(1)'-P(3)'	2.431(2)	P(5)'-F(7)'	1.514(3)
Mo(1)-P(4)	2.466(2)	F(9)'	1.553(7)
Mo(1)'-P(5)'	2.320(2)	N(2)'	1.697(4)
P(6)'	2.485(2)	P(6)''-P(8)'	0.945(3)
P(7)'	2.383(2)	F(10)'	1.433(3)
Mo(1)-P(8)	2.347(2)	F(11)'	1.570(5)
P(1)-P(3)	0.757(2)	N(2)'	1.639(4)
F(1)	1.480(4)	P(7)''-F(4)'	1.515(3)
F(3)	1.557(6)	F(5)'	1.554(5)
N(1)	1.652(4)	N(1)'	1.700(3)
P(2)-P(7)	1.021(3)	P(8)-F(10)	1.532(3)
F(4)	1.502(3)	F(12)	1.579(7)
F(6)	1.577(6)	N(2)'	1.689(4)
N(1)'	1.648(4)	N(1)-C(1)	1.482(4)
P(3)''-F(1)'	1.406(3)	N(2)-C(2)	1.500(5)
F(2)'	1.572(5)		
N(1)'	1.640(4)		

Cl atoms so that the P atoms are arranged as just described, their N and C atoms are also superposed. Hence there is only one crystallographically distinguishable set of each, N(1) and N(2), and C(1) and C(2). With the fluorine atoms a more intricate situation arises. In principle, each of the enantiomorphs places its set of eight F atoms in different positions and there should be 16 half-fluorine atoms to be refined. Actually, the particular distances and angles involved are such that some of these F atom positions are so close that they cannot be resolved by the X-ray data. Hence, four full fluorine atoms, F(1), F(4), F(7), and F(10), were refined and eight half-fluorine atoms. The former have thermal vibration ellipsoids that are unusually elongated in directions perpendicular to the molecular axis because of the fact that the two half-fluorine atoms do not truly coincide.

Table I gives the positional and thermal parameters for a set of atoms and half-atoms that satisfy the disordered arrangement just explained. Tables II and III give the nonredundant set of bond lengths and bond angles for one enantiomorph. Also given in these tables are some of the distances and angles between the half-atoms in different enantiomorphs; these, of course, have no physical significance, but are given to indicate the separation of the half-atoms in the model and the deviations from completely regular D_4 symmetry. The degree of staggering is most clearly indicated by the four torsional angles which are listed in Table IV.

Molecular Structure. As shown in Figure 2, the individual molecule has a chiral structure of idealized D_4 symmetry. The angle of twist away from an eclipsed structure, which would have D_{4h} symmetry, is indicated by the four torsional angles listed in Table IV, which have an average value of 21.3°. For perfect D_4 symmetry these would, of course, all have the same value, whereas there is a small variation, from 20.1° to 22.6°.

It is interesting to note that satisfactory internal packing of the fluorine atoms would be impossible in an eclipsed (D_{4h}) arrangement, because adjacent fluorine atoms, such as F(1) and F(8), would be too close. The twist around the Mo-Mo axis is really demanded by the steric requirements of the fluorine atoms and, since the Mo≡Mo triple bond (see below) has no inherent rotational barrier, the observed structure is easily attained.

The Mo-Mo bond is the longest one, 2.457 (1) Å, ever found for a triple bond between two metal atoms, exceeding even that in $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4$, 2.448 (1) Å,¹⁰ by a small amount. We shall discuss the metal-metal bonding in detail later.

The bond angles about each molybdenum atom are close to 90°, with the Mo-Mo-P angles tending to exceed this by a couple of degrees and the Cl-Mo-P and P-Mo-P angles running slightly less than 90° by corresponding amounts. The Mo-Cl distance, 2.470 (1) Å, is quite similar to those (2.45-2.47 Å) found in several compounds containing the $[\text{Mo}_2\text{Cl}_8]^{4-}$ ion³ and is only slightly greater than the 2.436 (2) Å Mo-Cl distance observed in $\text{Mo}_2\text{Cl}_2(\text{PET}_3)_2(\text{C}_7\text{H}_5\text{N}_2)_2$.¹⁴

Table III. Bond Angles (deg)

atoms	angle	atoms	angle
Mo(1)'-Mo(1)-Cl(1)	177.55(3)	Mo(1)-P(8)-F(10)	123.2(2)
P(1)	92.98(5)	F(12)	119.3(3)
P(2)	89.84(5)	F(1)-P(1)-F(3)	84.6(3)
Mo(1)'-Mo(1)'-P(3)'	94.21(5)	N(1)	103.6(2)
Mo(1)'-Mo(1)'-P(4)	92.23(4)	F(3)-P(1)-N(1)	99.3(3)
Mo(1)-Mo(1)'-P(5)'	91.26(5)	F(4)-P(2)-F(6)	92.2(3)
P(6)'	92.57(4)	N(1)	102.2(3)
P(7)'	91.19(4)	F(6)-P(2)-N(1)	101.7(3)
Mo(1)'-Mo(1)-P(8)	92.40(5)	F(1)'-P(3)''-F(2)''	85.1(3)
Cl(1)-Mo(1)-P(1)	89.42(5)	N(1)'	107.8(2)
P(2)	87.74(5)	F(2)''-P(3)''-N(1)'	99.8(3)
Cl(1)'-Mo(1)'-P(3)'	87.93(5)	F(7)-P(4)-F(8)	91.3(3)
Cl(1)-Mo(1)-P(4)	87.33(5)	N(2)	106.2(2)
Cl(1)'-Mo(1)'-P(5)'	87.49(6)	F(8)-P(4)-N(2)	101.9(3)
P(6)'	88.68(5)	F(7)''-P(5)''-F(9)''	85.2(3)
P(7)'	86.76(5)	N(2)'	100.5(2)
Cl(1)-Mo(1)-P(8)	87.95(6)	F(9)''-P(5)''-N(2)'	97.8(3)
P(1)-Mo(1)-P(2)	176.16(7)	F(10)''-P(6)''-F(11)''	90.2(3)
P(3)	18.08(6)	N(2)''	105.6(3)
P(4)	89.22(8)	F(11)''-P(6)''-N(2)''	102.7(3)
P(3)''-Mo(1)''-P(5)''	91.46(9)	F(4)''-P(7)''-F(5)''	92.3(3)
P(7)''	173.45(7)	N(1)''	99.3(3)
P(4)-Mo(1)-P(5)	20.31(7)	F(5)''-P(7)''-N(1)''	101.4(3)
P(8)	174.58(6)	F(10)-P(8)-F(12)	89.2(4)
P(2)-Mo(1)-P(7)	24.45(8)	N(2)	98.9(3)
P(8)-Mo(1)-P(6)	22.32(7)	F(12)-P(8)-N(2)	102.0(3)
P(1)	92.79(9)	P(1)-N(1)-P(2)'	102.6(2)
P(6)''-Mo(1)''-P(7)''	87.57(7)	P(7)''	111.9(2)
P(2)-Mo(1)-P(8)	89.71(8)	C(1)	125.1(3)
Mo(1)-P(1)-F(1)	123.9(2)	P(3)''-N(1)''-P(2)	114.8(2)
F(3)	120.1(3)	P(7)	107.3(3)
Mo(1)-P(2)-F(4)	117.5(2)	C(1)''	121.9(3)
F(6)	121.4(3)	P(2)-N(1)''-C(1)''	122.9(3)
Mo(1)'-P(3)''-F(1)''	123.7(2)	P(7)''-N(1)-C(1)	122.9(3)
F(2)''	119.0(3)	P(4)-N(2)-P(6)''	118.4(2)
Mo(1)-P(4)-F(7)	118.8(2)	P(8)''	106.6(2)
F(8)	118.8(2)	C(2)	119.4(3)
Mo(1)'-P(5)''-F(7)''	125.2(2)	P(5)''-N(2)''-P(6)	103.7(2)
F(9)''	120.0(3)	P(8)	109.2(2)
Mo(1)'-P(6)''-F(10)''	120.0(2)	C(2)''	125.4(3)
F(11)''	121.0(2)	P(6)''-N(2)-C(2)	122.2(3)
Mo(1)'-P(7)''-F(4)''	119.6(1)	P(8)-N(2)''-C(2)''	125.4(3)
F(5)''	121.6(2)		

The distance is, however, significantly longer than the 2.39 (1) (av) and 2.348 (3) Å (av) Mo-Cl distances observed for Mo₂(DPPM)₂Cl₄¹² (DPPM = Ph₂PCH₂PPh₂) and Mo₂Cl₂(NMe₂)₄.¹³

The Mo-P distances vary over a considerable range, namely, from 2.320 (2) to 2.485 (2) Å, with an average of 2.40 ± 0.050 Å. This rather large spread in what should be equivalent bond lengths may be partly a genuine effect of intermolecular forces, but we believe that at least some of it, and probably most, is an artifact of the refinement of the disordered model. The average value is in good agreement with the 2.433 (3) and 2.454 (4) Å Mo-P distances reported for the two isomers of (guaiazulene)Mo₂(CO)₅PtEt₃.¹⁴ The distances are, however, somewhat shorter than the 2.58 (3) (av) and 2.58 (4) Å Mo-P distances observed in Mo₂(DPPM)₂(NCS)₄ and Mo₂(DPPM)₂Cl₄, respectively.¹²

The entire set of P-F distances covers a considerable range, 1.406-1.597 Å, but these 16 distances should be subdivided into two sets, one consisting of bonds to the four fluorine atoms, F(1), F(4), F(7), and F(10), that are really poorly defined, unresolvable superpositions of two half-atoms from different enantiomorphs. It is mainly because of these that the overall range of P-F distances is so large. They vary from 1.406 to 1.532 Å, with an average of 1.481 ± 0.034 Å. Doubtless this considerable spread, as well as the rather low average value, is due to inaccuracies arising from the disorder. The low av-

Table IV. Torsional Angles (deg)

atoms	atoms	angle
Mo'-Mo-P(1)	Mo-Mo'-P(7)'	21.8
Mo'-Mo-P(2)	Mo-Mo'-P(3)'	20.7
Mo'-Mo-P(4)	Mo-Mo'-P(6)'	20.1
Mo'-Mo-P(8)	Mo-Mo'-P(5)'	22.6
	mean	21.3

erage value may arise because the pertinent distances should be to the farther ends of the long vibrational ellipsoids, whereas those given by the standard bond distance computation are to the centroids of these ellipsoids. For the other eight P-F distances, the range is only from 1.553 to 1.579 Å, with an average of 1.564 ± 0.010 Å. This is very similar to the P-F distance in the free ligand,¹⁵ 1.583 (2) Å.

There are related anomalies in the F-P-F angles, which range from 84.6 to 92.3°, whereas in the free ligand this angle has a value of 95.1 (3)°. These, too, can be traced mainly to the four ill-behaved fluorine atoms just mentioned. The F-P-N angles involving these atoms show a large variation, from 98.9 to 107.8°, with an average of 103.0°. This is 3.6° larger than the value (99.6°) in the free ligand. The other F-P-N angles fall in a much narrower range (97.8-102.7°) and have an average value (100.8°) that is closer to the value in the free ligand. While there may be some genuine decrease in the F-P-F angle, at least part of the apparent decrease appears to be due to the errors caused by the disordering of the ligands.

The remaining distances and angles in the ligands, which involve the ordered N and C atoms, are all rather close to their values in the free ligand. Thus, the eight P-N distances range from 1.622 to 1.700 Å, and the mean value, 1.661 ± 0.026 Å, is close to that (1.680 Å) in the free ligand. The C-N distances here average 1.491 ± 0.009 Å while in the free ligand this distance is 1.479 ± 0.017 Å.

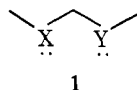
NMR Spectra. The ¹H NMR spectrum consists of a single resonance which is abnormally broad, presumably because of superimposed but unresolved splittings by ³¹P and ¹⁹F nuclei. The position of the resonance, 3.75 ppm downfield from Me₄Si, indicates that there is a significant effect from the expected diamagnetic anisotropy of the Mo-Mo triple bond. In the free ligand, F₂PN(CH₃)PF₂, the proton signal is at δ 2.78 and in a number of complexes such as M[(F₂P)₂NCH₃]₃ with M = Cr, Mo, W, and [CH₃N(P₂F)₂]₂FeCO the resonance is found at essentially the same position,⁵ i.e., in the range δ 2.62-2.73. This shows that the mere inclusion of the ligand in bidentate fashion in a complex does not in itself cause any significant shift. We believe, therefore, that the downfield shift of about 1.0 ppm is due primarily to the diamagnetic anisotropy of the Mo-Mo triple bond.

Although the methyl protons are at a considerable distance (>4.8 Å) from the Mo-Mo bond, they are located practically in the equatorial plane where the effect should be greatest. The first attempt to detect the chemical-shift effects of diamagnetic anisotropy was made by San Filippo,¹⁶ who examined several Re₂Cl₆L₂ and Mo₂Cl₄L₄ molecules. He found evidence for small shifts, but the protons available as probes in these molecules are not well placed, either angularly (they are near the cone of zero effect) or in terms of proximity, and there are also direct chemical shift effects to be concerned about. In the M₂(NR₂)₆ molecules,² the shifts are very large (ca. 2.5 ppm) and clear-cut between the proximal and distal R groups. The former are close to, though not right in, the equator; the latter are located where they may have some unfield shift. Moreover, both are closer to the M-M bond than are the CH₃ protons in the present case. Thus, it is not unreasonable that the chemical shift due to diamagnetic anisotropy should be smaller in the present case than the observed proximal/distal shift differences in the M₂(NR₂)₆ molecules.

The other aspect of the NMR results that is highly significant is the apparent equivalence, even at $-100\text{ }^{\circ}\text{C}$, of all fluorine atoms. The ^{31}P - ^{19}F coupling is essentially the same as in the free ligand and in other complexes.⁵ The indistinguishability of the two structural types of fluorine atom is presumably due to the occurrence of rapid interconversion of the two enantiomorphs. Without knowledge of the chemical-shift difference for the two types of fluorine atom it is impossible to estimate the activation energy for this process, but it is unlikely to exceed 15 kcal mol^{-1} unless the chemical shift difference is extremely small. From the size and shape of the ligands, it seems necessary that the interconversion occur by a concerted shift of all four ligands.

Discussion

The investigation of the compound reported here did not come about by chance. The preparation was undertaken deliberately on the basis of the following considerations. It has been noted several times that attempts to introduce π -acceptor ligands into compounds containing M-M triple or quadruple bonds often leads to mononuclear products, the tendency for M-M bond rupture apparently increasing as the π acidity of the ligands increases. This is illustrated, for example, by the reactions of isocyanides with $\text{Mo}_2(\text{O}_2\text{CR})_4$, which lead¹⁷ to complexes such as $[\text{Mo}(\text{CNR})_7]^{2+}$, and by the reaction of CO with $\text{Re}_2\text{Cl}_4(\text{PR}_3)_4$ to give *trans*- $\text{Re}(\text{CO})_2\text{Cl}_2(\text{PR}_3)_2$ compounds.¹⁸ We believe that the tendency of π -acceptor ligands to cleave the M-M multiple bonds is due to their ability to draw M-M bonding electrons out of δ and π orbitals into their own empty π orbitals, thus seriously weakening the M-M bonding. On the other hand, it is well known that ligands with the general configuration **1** are well suited to span the closely



spaced, multiply bonded pairs of metal atoms, thus supporting the M-M bonding.

With these two concepts in mind, we wondered what would happen if both π -acceptor character and the type of structure represented by **1** were combined in the same ligand. Would the favorable structural character allow the retention of the M-M multiple bond in spite of the π acidity? A ligand that ideally meets the requirements was already at hand in the form of Nixon's $\text{F}_2\text{PN}(\text{CH}_3)\text{PF}_2$ molecule,⁴ which has marked π acidity and the right conformation, is stable and easily prepared, and is already known to form complexes⁵ readily. Its structure had also been thoroughly investigated.¹⁵

The result of reacting this ligand with $[\text{Mo}_2\text{Cl}_8]^{4-}$ was, in fact, a little more complicated, and a little more interesting, than expected. A simple replacement reaction giving $\text{Mo}_2\text{Cl}_4\text{L}_2$, somewhat analogous to the previously studied¹² $\text{Mo}_2(\text{NCS})_4(\text{DPPM})_2$ and $\text{Mo}_2\text{Cl}_4(\text{DPPM})_2$ compounds, had been considered likely, but instead reduction also occurred to give the Mo_2^{2+} complex described above.

The $\text{Mo}_2[(\text{F}_2\text{P})_2\text{NCH}_3]_4\text{Cl}_2$ molecule is both electronically and structurally a new type of $\text{M}\equiv\text{M}$ triple bond species. The previously known types have recently been reviewed in some detail.² Those of molybdenum in which there is fourfold (or quasi-fourfold) symmetry are represented by species such as $\text{Mo}_2(\text{OR})_6\text{L}_2$, which are adducts of the $\text{Mo}_2(\text{OR})_6$ molecules with the added ligands taking equatorial positions, or $\text{Mo}_2(\text{O}_2\text{COR})_2(\text{OR})_4$. These contain molybdenum atoms in the formal oxidation state III and the total number of electrons in the valence orbitals of each metal atom is 14.¹⁹ Mo-Mo bonds in these species are about 2.24 \AA in length.²⁰ A related type is represented by the $[\text{Mo}_2(\text{HPO}_4)_4]^{2-}$ ion.²¹ This is also a 14-electron case, but, if the electron pairs on weakly coor-

inated axial ligands, such as H_2O or Cl^- , are counted, it then becomes a 16-electron case.

The $\text{Mo}_2[(\text{F}_2\text{P})_2\text{NCH}_3]_4\text{Cl}_2$ molecule is clearly very different from these in several key respects. (1) The oxidation number of the metal is I rather than III. (2) The valence shell electron count is 18; this total is obtained by adding 6 for the molybdenum atom, 1 for the chlorine atom, 8 for the electron pairs donated by the phosphorus atoms, and 3 from the other molybdenum atom, assuming that there is an Mo-Mo triple bond. (3) The axial ligands, Cl, are strongly bonded (Mo-Cl = 2.47 \AA as contrasted to the Mo-Cl distance of 2.91 \AA in $[\text{Mo}(\text{HPO}_4)_4\text{Cl}_2]^{4-}$).

We believe that the most logical way to formulate the bonding in this molecule is in terms of a triple bond between the metal atoms. A convenient way to approach the formulation is to begin with the $[\text{Mo}_2(\text{HPO}_4)_4\text{Cl}_2]^{4-}$ species, in which there is a $\sigma^2\pi^4$ triple bond between the metal atoms, the δ and δ^* orbitals are empty (or, to put it in another way, the d_{xy} orbital on each metal atom is empty), and the axial Mo-Cl bonds are long and weak because the d_{z^2} orbitals are primarily involved in the Mo-Mo σ bond. If, now, four electrons are added to this configuration, thus reducing the oxidation state of each molybdenum atom from III to I, they would be expected to enter the d_{xy} orbitals on each of the two metal atoms (or, alternatively, the δ and δ^* MOs). This does not affect the Mo-Mo bond order of 3. It does, however, allow the axial Mo-Cl bonding to become stronger because the 5s orbitals of the molybdenum atoms, which are too high in energy in Mo(III) or even Mo(II) to be of much use in bonding, are considerably lowered in energy. Finally, the presence of the strongly π -accepting PF_2 groups allows considerable electron density to be removed from the Mo-Mo π -bonding orbitals, thus weakening the Mo-Mo bond to the extent that it increases about 0.24 \AA in length.

On the basis of this formulation, the $\text{Mo}_2[(\text{F}_2\text{P})_2\text{NCH}_3]_4\text{Cl}_2$ molecule has some kinship to the $\text{Re}_2\text{X}_4(\text{PR}_3)_4$ molecules, in which there is also a triple bond based on a $\sigma^2\pi^4\delta^2\delta^{*2}$ configuration. The two chief differences are that in the $\text{Re}_2\text{X}_4(\text{PR}_3)_4$ molecules there are no axial ligands and the equatorial ligands are not appreciably π acidic so that the Re-Re π bonding is not weakened.

Our success in obtaining the $\text{Mo}_2[(\text{F}_2\text{P})_2\text{NCH}_3]_4\text{Cl}_2$ molecule and its chemical and thermal stability clearly suggest that other dinuclear complexes with M-M multiple bonds may be obtainable using the Nixon ligand.

Acknowledgments. We thank the National Science Foundation for financial support. W.K. thanks the Verband der Chemischen Industrie for a Liebig stipend.

Supplementary Material Available: A table of observed and final calculated structure factors (15 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) Cotton, F. A. *Chem. Soc. Rev.* **1975**, *4*, 25.
- (2) Chisholm, M. H.; Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 2.
- (3) Brencic, J. V.; Cotton, F. A. *Inorg. Chem.* **1970**, *9*, 346.
- (4) Nixon, J. F. *J. Chem. Soc. A* **1968**, 2689; **1969**, 1087.
- (5) King, R. B.; Gimeno, J. *Inorg. Chem.* **1978**, *17*, 2390.
- (6) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227.
- (7) Calculations were performed using the Molecular Structure Corp. PDP-11/45 computer and the Enraf-Nonius Structure Determination Package with programs written chiefly by Frenz and Okaya.
- (8) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography", Vol. IV; Kynoch Press: Birmingham, England, 1974; Table 2.3.1.
- (9) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.
- (10) Klingler, R. J.; Butler, W.; Curtis, M. D. *J. Am. Chem. Soc.* **1975**, *97*, 3535.
- (11) Cotton, F. A.; Lay, D. G.; Millar, M. *Inorg. Chem.* **1978**, *17*, 172.
- (12) Abbott, E. H.; Bose, K. S.; Cotton, F. A.; Hall, W. T.; Sekutowski, J. C. *Inorg. Chem.* **1978**, *17*, 3240.
- (13) Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Murillo, C. A.

- Inorg. Chem.* **1977**, *16*, 2407.
 (14) Cotton, F. A.; Lahuerta, P.; Stults, B. R. *Inorg. Chem.* **1976**, *15*, 1866.
 (15) Hedberg, E.; Hedberg, L.; Hedberg, K. *J. Am. Chem. Soc.* **1974**, *96*, 4417.
 (16) San Filippo, Jr., J. *Inorg. Chem.* **1972**, *11*, 3140.
 (17) Brant, P.; Cotton, F. A.; Sekutowski, J. C.; Walton, R. A.; Wood, T. E. *J. Am. Chem. Soc.*, **1979**, *101*, 6588.
 (18) Hertzler, C. A.; Myers, R. E.; Brant, P.; Walton, R. A. *Inorg. Chem.* **1978**, *17*, 2383.
 (19) The number 14 is obtained by counting six for the Mo–Mo triple bond and two from each Mo–O or Mo–L bond.
 (20) Chisholm, M. H.; Cotton, F. A.; Exline, M. W.; Reichert, W. W. *J. Am. Chem. Soc.* **1978**, *100*, 153, 1727.
 (21) Bino, A.; Cotton, F. A. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 332.

Enthalpy of Formation of Dicesium Octabromodirhenium(III), $\text{Cs}_2\text{Re}_2\text{Br}_8$, and a Thermochemical Estimate of the Energy of the Re–Re Quadruple Bond

Lester R. Morss,*^{1a} Robert J. Porcja,^{1a} James W. Nicoletti,^{1a}
 Joseph San Filippo, Jr.,*^{1a} and H. Donald B. Jenkins^{1b}

Contribution from the Department of Chemistry, Rutgers, the State University, New Brunswick, New Jersey 08903, and the Department of Chemistry & Molecular Sciences, University of Warwick, Coventry CV47AL, United Kingdom. Received July 30, 1979

Abstract: The enthalpy of formation of $\text{Cs}_2\text{Re}_2\text{Br}_8(\text{c})$ has been determined to be -1171 ± 35 kJ/mol at 298 K by measuring its heat of oxidation by aqueous bromate. The enthalpy of formation of $\text{Re}_2\text{Br}_8^{2-}(\text{g})$ has been calculated to be -1046 ± 40 kJ/mol by calculating the lattice enthalpy of $\text{Cs}_2\text{Re}_2\text{Br}_8$ in conjunction with other thermodynamic data. From estimates of enthalpies of formation of various Re–Br species, and from estimates of the Re–Br bond energy, the Re–Re quadruple bond strength in $\text{Re}_2\text{Br}_8^{2-}$ has been estimated to be 408 ± 50 kJ/mol (98 kcal/mol). This value is discussed in comparison with other recent estimates.

The explosive growth in the chemistry of compounds containing metal–metal bonds within the past 15 years has challenged many chemists to characterize these materials. Naturally, the strongest of these bonds have attracted the most interest: the multiple Cr–Cr, W–W, Mo–Mo, and Re–Re bonds are well-characterized, remarkably stable entities. Early and more recent estimates have focused on theoretical molecular-orbital interpretations of the bonding and electronic spectra in these species.^{2–4} Observations drawn from the photochemistry of $\text{Re}_2\text{Cl}_8^{2-}$ led to alternative estimates for the strength of this metal–metal bond.⁵ In one instance an effort was made to apply classical vibrational spectroscopic techniques to estimate the Re–Re quadruple bond strength.⁶ Most recently there have been attempts to answer this question by the application of traditional thermochemical techniques. Thus, Skinner, Cotton, and co-workers⁷ have reported on their attempts to assess the strength of the Mo–Mo and W–W multiple bonds found in several organometallic compounds, but

their efforts were hampered by uncertainties in ligand enthalpies of formation and metal–ligand bond strengths.

Several years ago in a report detailing the single-crystal structure determination of dicesium octabromodirhenium(III), $\text{Cs}_2\text{Re}_2\text{Br}_8$, Cotton and co-workers⁸ made the perspicacious observation that this particular substance might prove suitable for the necessary thermochemical measurements and lattice-energy calculations required to produce a thermochemical cycle leading to the enthalpy of the Re–Re bond. We report here the results of our determination of this and related quantities for $\text{Cs}_2\text{Re}_2\text{Br}_8$.

Our investigation centered on three problems. The first task was to determine a calorimetric standard enthalpy of formation of $\text{Cs}_2\text{Re}_2\text{Br}_8(\text{c})$, and the second was to calculate the lattice energy (or, more precisely, the lattice enthalpy U_{pot} at 298 K) of this compound. The sum of these two enthalpies would then yield $\Delta H_f^\circ(\text{Re}_2\text{Br}_8^{2-}, \text{g})$ (eq 1) by the thermochemical cycle⁹ shown in Scheme I. The third problem—and by far the least

Scheme I

