has an appreciable amplitude near the center of the molecule.[9] Because of the importance of this conclusion, further experiments are being considered and a comparison with an extended basis set H–F calculation is to be made.

Acknowledgment. The authors thank Dr. E. D. Stevens and Mr. J. Rys for assistance with data collection and computations. Support of this work by the Petroleum Research Fund, administered by the American Chemical Society, and by the National Foundation (Grant CHE 7613342 A01) is gratefully acknowledged.

Registry No. S_4N_4, 28950-34-7.

Supplementary Material Available: A table listing observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

References and Notes

(1) D. Clark, *J. Chem. Soc.*, 1615 (1952).
(2) B. D. Sharma and J. Donohue, *Acta Crystallogr.*, **16**, 891 (1963).
(3) A. Hordvik, *Q. Rep. Sulfur Chem.*, **5**, 21 (1970).
(4) P. Coppens, Y. W. Yang, R. H. Blessing, W. F. Cooper, and F. K. Larsen, *J. Am. Chem. Soc.*, **99**, 760 (1977).
(5) D. M. P. Mingos, *Nature (London), Phys. Sci.*, **236**, 99 (1972).
(6) R. Gleiter, *J. Chem. Soc. A*, 3174 (1970).
(7) A. Banister, *Nature (London), Phys. Sci.*, **239**, 69 (1972).
(8) M. S. Gopinathan and M. A. Whitehead, *Can. J. Chem.*, **53**, 1343 (1975).
(9) D. R. Salahub and R. P. Messmer, *J. Chem. Phys.*, **64**, 2039 (1976).
(10) A. G. Turner and F. S. Mortimer, *Inorg. Chem.*, **5**, 906 (1966).
(11) W. Jolly, "The Synthesis and Characterization of Inorganic Compounds", Prentice-Hall, Englewood Cliffs, N.J., 1970, p 500.
(12) P. G. Lenhart, *J. Appl. Crystallogr.*, **8**, 568 (1975).
(13) P. Coppens, F. K. Ross, R. H. Blessing, W. F. Cooper, F. K. Larsen, J. G. Leipoldt, B. Rees, and R. Leonard, *J. Appl. Crystallogr.*, **7**, 315 (1974).
(14) F. K. Larsen, private communication.
(15) "International Tables for X-ray Crystallography", Kynoch Press, Birmingham, England: (a) Vol. III, 1965; (b) Vol. IV, 1974.
(16) Z. Iqbal, D. S. Downs, and C. W. Christoe, *J. Phys. Chem. Solids*, **38**, 263 (1977).
(17) P. Coppens, *Isr. J. Chem.*, **16**, 159 (1977); P. Coppens, T. N. Guru Row, P. Leung, E. D. Stevens, P. J. Becker, and Y. W. Yang, *Acta Crystallogr., Sect. A*, in press.
(18) A. M. Griffin, P. C. Minshall, and G. M. Sheldrick, *J. Chem. Soc., Chem. Commun.*, 809 (1976).
(19) M. L. DeLucia, Thesis, State University of New York at Buffalo, 1978.

Contribution from the Departments of Chemistry,
Princeton University, Princeton, New Jersey 08540,
and Texas A&M University, College Station, Texas 77843

The Molybdenum-to-Molybdenum Triple Bond. 5. Preparation and Structure of Dimethyltetrakis(dimethylamido)dimolybdenum[1]

M. H. Chisholm,*[2a] F. A. Cotton,*[2b] M. W. Extine,[2b] and C. A. Murillo[2a]

Received March 1, 1978

The existence of an extensive chemistry centering around the triply bonded Mo–Mo and W–W units is now well established and has recently been reviewed.[3,4] A firm structural base for interpreting this chemistry has been provided by more than a score of X-ray crystallographic structure determinations. Among these, however, there have been only a few pairs of molybdenum and tungsten compounds with the same or very similar sets of ligands. The comparisons afforded by such pairs are valuable in developing the comparative chemistry of the M–M multiple bonds in the second and third transition series.

To further this structural basis we report here the preparation and structural characterization of dimethyltetrakis(dimethylamido)dimolybdenum, $Mo_2Me_2(NMe_2)_4$. The structure may be compared to that of the close ditungsten analogue, $W_2Me_2(NEt_2)_4$, the structure of which has already been reported.[5] The preparation of this new compound was accomplished by taking advantage of our recently published route[6] to substitution products of the readily available $Mo_2(NMe_2)_6$, viz., reaction 1, and then replacing Cl by methyl by means of the methyllithium reagent, reaction 2. At a later time we shall report further studies of reactions of type 2 which have also allowed the isolation of alkyls, such as $M_2Et_2(NMe_2)_4$, for which β-H elimination is not impossible.

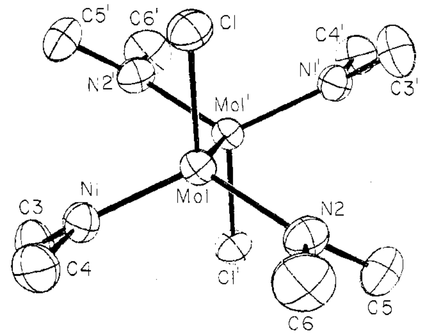

Figure 1. ORTEP view of molecule I using 50% probability ellipsoids and showing the atom labeling scheme.

$$Mo_2(NMe_2)_6 + 2Me_3SiCl \rightarrow Mo_2Cl_2(NMe_2)_4 + 2Me_3SiNMe_2 \quad (1)$$

$$Mo_2Cl_2(NMe_2)_4 + 2MeLi \rightarrow Mo_2Me_2(NMe_2)_4 + 2\ LiCl \quad (2)$$

Results and Discussion

Synthesis. The compounds $M_2Cl_2(NMe_2)_4$, where M = Mo and W, react with ether and tetrahydrofuran: reaction 2 was carried out in toluene. $Mo_2Me_2(NMe_2)_4$ was isolated from (2) as a yellow, crystalline, diamagnetic, air-sensitive compound in greater than 70% yield. It is thermally stable and may be sublimed at 100 °C (10^{-2} Torr). In the mass spectrometer a molecular ion $Mo_2Me_2(NMe_2)_4^+$ together with many other Mo_2-containing ions were observed. IR, NMR, and analytical data are recorded in the Experimental Section.

Structural Results. $Mo_2(NMe_2)_4Me_2$ is isostructural with $M_2(NMe_2)_4Cl_2$. The asymmetric unit consists of half of each of two independent dinuclear molecules, each molecule having crystallographically imposed C_i symmetry but deviating only slightly from C_{2h}. Atomic thermal and positional parameters are given in Table I. An ORTEP drawing of molecule I is shown in Figure 1. Bond distances and angles are given in Table II. The atom labeling scheme used for molecule II parallels that used for molecule I with Mo(2), N(3)–N(4), and C(7)–C(12) replacing Mo(1), N(1)–N(2), and C(1)–C(6), respectively.

Discussion of Structure. The crystal structure of $Mo_2(NMe_2)_4Me_2$ is closely similar to those[6] of $Mo_2(NMe_2)_4Cl_2$ and $W_2(NMe_2)_4Cl_2$. In all of these, the presence of four molecules in a unit cell belonging to the space group $P2_1/c$ does not correspond, as is usually the case, to the molecule being the asymmetric unit, with the four molecules then being related by the two types of crystallographic inversion center at 0, 0, 0 and $^1/_2$, 0, $^1/_2$. In these structures the asymmetric unit is composed of halves of two different molecules. This means that there are two crystallographically independent, centrosymmetric molecules, each type located on a crystallographic center of inversion. However, as Table II shows, the differences between the two molecules of $Mo_2(NMe_2)_4Me_2$ are completely insignificant, not only chemically but in terms of the statistical validity of the differences.

0020-1669/78/1317-2338$01.00/0

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

atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo(1)	0.45070 (4)	0.05707 (5)	0.46198 (8)	0.00292 (3)	0.00341 (3)	0.0109 (1)	0.00098 (5)	0.00134 (9)	0.0007 (1)
Mo(2)	−0.02775 (4)	0.07171 (5)	0.02880 (8)	0.00299 (3)	0.00361 (3)	0.0128 (1)	−0.00063 (5)	0.00145 (10)	−0.0014 (1)
N(1)	0.3605 (4)	0.0385 (5)	0.6069 (8)	0.0031 (3)	0.0058 (4)	0.014 (1)	−0.0002 (6)	0.001 (1)	−0.001 (1)
N(2)	0.5181 (5)	0.1797 (5)	0.4644 (8)	0.0049 (4)	0.0040 (4)	0.015 (1)	0.0001 (6)	0.001 (1)	0.001 (1)
N(3)	0.0732 (5)	0.1602 (5)	0.0640 (9)	0.0050 (4)	0.0039 (4)	0.018 (1)	−0.0020 (6)	0.001 (1)	−0.003 (1)
N(4)	−0.1224 (4)	0.0931 (5)	−0.1481 (8)	0.0030 (3)	0.0054 (4)	0.014 (1)	−0.0002 (6)	−0.002 (1)	−0.000 (1)
C(1)	0.4037 (5)	0.0110 (7)	0.214 (1)	0.0039 (4)	0.0066 (6)	0.012 (1)	−0.0004 (8)	−0.002 (1)	−0.002 (1)
C(2)	−0.0798 (6)	0.0370 (7)	0.255 (1)	0.0050 (5)	0.0076 (6)	0.016 (1)	0.0008 (9)	0.007 (1)	−0.001 (2)
C(3)	0.3548 (6)	−0.0209 (8)	0.752 (1)	0.0049 (5)	0.0084 (6)	0.018 (2)	0.0003 (10)	0.006 (1)	0.008 (2)
C(4)	0.2888 (6)	0.1139 (7)	0.590 (1)	0.0032 (4)	0.0077 (6)	0.023 (2)	0.0032 (8)	0.001 (1)	−0.005 (2)
C(5)	0.6087 (6)	0.2072 (7)	0.523 (1)	0.0049 (5)	0.0065 (6)	0.022 (2)	−0.0034 (9)	0.000 (2)	−0.001 (2)
C(6)	0.4637 (7)	0.2666 (7)	0.424 (1)	0.0087 (6)	0.0039 (5)	0.029 (2)	0.0039 (10)	0.006 (2)	0.005 (2)
C(7)	0.1688 (6)	0.1489 (8)	0.050 (1)	0.0032 (4)	0.0080 (7)	0.026 (2)	−0.0034 (8)	0.003 (1)	−0.000 (2)
C(8)	0.0523 (7)	0.2645 (7)	0.086 (1)	0.0072 (6)	0.0040 (5)	0.030 (2)	−0.0014 (9)	−0.001 (2)	−0.005 (2)
C(9)	−0.1507 (6)	0.0454 (8)	−0.306 (1)	0.0054 (5)	0.0078 (6)	0.017 (2)	0.0013 (10)	−0.002 (2)	−0.004 (2)
C(10)	−0.1733 (6)	0.1866 (7)	−0.134 (1)	0.0055 (5)	0.0065 (6)	0.028 (2)	0.0033 (9)	0.001 (2)	−0.000 (2)

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Table II. Bond Distances (A) and Angles (deg) for $Mo_2(NMe_2)_4Me_2$[a]

atoms	molecule I	molecule II
Distances		
Mo(1)-Mo(1)′	2.201 (1)	2.201 (1)
-N(1)	1.958 (6)	1.952 (6)
-N(2)	1.959 (6)	1.948 (6)
-C(1)	2.173 (7)	2.176 (8)
N(1)-C(3)	1.46 (1)	1.49 (1)
-C(4)	1.50 (1)	1.47 (1)
N(2)-C(5)	1.46 (1)	1.47 (1)
-C(6)	1.46 (1)	1.50 (1)
Angles		
Mo(1)′-Mo(1)-N(1)	104.4 (2)	104.8 (2)
-N(2)	104.7 (2)	104.0 (2)
-C(1)	101.6 (2)	100.9 (2)
N(1)-Mo(1)-N(2)	121.1 (2)	121.4 (3)
-C(1)	111.3 (3)	112.1 (3)
N(2)-Mo(1)-C(1)	111.5 (3)	111.0 (3)
Mo(1)-N(1)-C(3)	134.0 (5)	133.9 (5)
-C(4)	115.1 (5)	115.5 (5)
C(3)-N(1)-C(4)	109.6 (6)	109.9 (6)
Mo(1)-N(2)-C(5)	134.4 (5)	135.1 (5)
-C(6)	113.5 (5)	114.5 (5)
C(5)-N(2)-C(6)	111.2 (7)	110.0 (6)

[a] Atoms are labeled as shown for molecule I in Figure 1. Molecules I and II lie on inversion centers at 1/2, 0, 1/2 and 0, 0, 0, respectively.

Table III. Lengths of M-M Triple Bonds in Compounds of the Types M_2L_6 and $M_2L_4X_2$ and Some of Their Adducts

compd	M-M, Å	
	M = Mo	M = W
$M_2(CH_2SiMe_3)_6$	2.167 (?)[a]	2.255 (2)[b]
$M_2(NMe_2)_6$	2.214 (3)[c]	2.294 (2)[d]
$M_2(OCH_2CMe_3)_6$	2.222 (2)[e]	
$M_2(OSiMe_3)_6(NHMe_2)_2$	2.242 (1)[f]	
$M_2(O\text{-}t\text{-}Bu)_4(O_2CO\text{-}t\text{-}Bu)_2$	2.241 (1)[g]	
$M_2(O_2CNMe_2)_6$		2.279 (1)[h]
$M_2Me_2(O_2CNEt_2)_4$		2.272 (1)[h]
$M_2Me_2(NMe_2)_4$	2.201 (1)[i]	
$M_2Me_2(NEt_2)_4$		2.291 (1)[j]
$M_2Cl_2(NMe_2)_4$	2.201 (2)[k]	2.285 (2)[k]
$M_2Cl_2(NEt_2)_4$		2.301 (1)[l]
$M_2Br_2(NEt_2)_4$		2.301 (2)[m]
$M_2I_2(NEt_2)_4$		2.300 (4)[m]

[a] F. Huq, W. Mowat, A. Shortland, A. C. Skapski, and G. Wilkinson, *Chem. Commun.*, 1079 (1971). [b] M. H. Chisholm, F. A. Cotton, M. W. Extine, and B. R. Stults, *Inorg. Chem.*, **15**, 2252 (1976). [c] M. H. Chisholm, F. A. Cotton, B. Frenz, W. W. Reichert, and L. Shive, *J. Am. Chem. Soc.*, 98, 4469 (1976). [d] M. H. Chisholm, F. A. Cotton, M. W. Extine, and B. R. Stults, *J. Am. Chem. Soc.*, 98, 4477 (1976). [e] M. H. Chisholm, F. A. Cotton, C. A. Murillo, and W. W. Reichert, *J. Am. Chem. Soc.*, **99**, 1652 (1977); *Inorg. Chem.*, **16**, 1801 (1977). [f] M. H. Chisholm, F. A. Cotton, M. W. Extine, and W. W. Reichert, *J. Am. Chem. Soc.*, **100**, 153 (1978). [g] Reference 1. [h] M. H. Chisholm, F. A. Cotton, M. W. Extine, and B. R. Stults, *Inorg. Chem.*, **16**, 603 (1977). [i] This work. [j] M. H. Chisholm, F. A. Cotton, M. W. Extine, M. Millar, and B. R. Stults, *Inorg. Chem.*, 15, 2244 (1976). [k] Reference 6. [l] M. H. Chisholm, F. A. Cotton, M. W. Extine, M. Millar, and B. R. Stults, *J. Am. Chem. Soc.*, 98, 4486 (1976). [m] M. H. Chisholm, F. A. Cotton, M. W. Extine, M. Millar, and B. R. Stults, *Inorg. Chem.*, 16, 320 (1977).

The structure takes the form of the anti rotamer, as has been the case in every $M_2(NR_2)_4X_2$ structure so far examined. The Mo–Mo distance is entirely typical for Mo≡Mo bonds in compounds of this class, as Table III makes clear. The mean Mo–N distance, 1.954 (5) Å, is not significantly different from those found in other structures of the $Mo_2(NR_2)_{6-n}X_n$ type, which have always been in the range 1.94–1.97 Å. It is interesting that once again the Mo–X and W–X distances in molecules where $n = 2$ are practically identical. Thus, for example, in the two $M_2(NMe_2)_4Cl_2$ molecules[6] the Mo–Cl and W–Cl distances are 2.348 (5) and 2.329 (5) Å. The Mo–C distance found here, 2.175 (6) Å, is indistinguishable from that in $W_2Me_2(NEt_2)_4$, namely, 2.171 (11) Å.

Table III shows the M≡M distances in all compounds of this general class that have been structurally characterized and gives references to the detailed reports. It is clear that there is a consistent difference of about 0.08 Å between the Mo≡Mo and W≡W bond lenghts in compounds with identical or similar sets of ligands and different metal atoms.

Experimental Section

General chemical procedures and the preparation of $Mo_2Cl_2(NMe_2)_4$ have been described previously.[6]

Preparation. Methyllithium (8.34 mmol) in ether (4.53 mL) was placed in a dried, round-bottom flask (100 mL) under a nitrogen atmosphere. The ether was removed in vacuo. The resulting white solids (MeLi) and $Mo_2Cl_2(NMe_2)_4$ (4.17 mmol) were then dissolved in toluene (40 mL). The solution so formed was initially cooled to ca. 0 °C (ice bath) for 0.5 h and then warmed to room temperature for 1.5 h with stirring. The solvent was removed under vacuum and the solids were dried at 25 °C (10^{-2} Torr) for 1 h. Hexane (40 mL) was added and the solution was filtered under a nitrogen atmosphere using standard Schlenk techniques. The yellow filtrate was collected, reduced in volume to ca. 8 mL, and cooled to ca. −10 °C, yielding a yellow crystalline product $Mo_2Me_2(NMe_2)_4$ (1.20 g; 73% yield based on eq 2), which was collected by filtration and dried in vacuo (25 °C (10^{-2} Torr)). Anal. Calcd for $C_{10}H_{30}N_4Mo_2$: C, 30.16; H, 7.59; N, 14.07. Found: C, 29.9; H, 7.46; N, 13.8. ^1H NMR data (60 MHz, 40 °C, toluene-d_8 solvent): $\delta(Me) = 1.17$, $\delta(NMe_2) = 3.29$ (δ relative to Me_4Si). IR data (Nujol mull, CsI plates (1500–200 cm^{-1} region)): 1422 (w), 1310 (w), 1242 (m), 1172 (w), 1150 (m), 1122 (w), 1042 (m), 950 (s), 940 (vs), 590 (m), 500 (s), 335 (m, br).

X-ray Crystallography. A crystal of $Mo_2(NMe_2)_4Me_2$ measuring ca. 0.2 × 0.25 × 0.4 mm was mounted in a thin-walled glass capillary embedded in epoxy resin with the major crystal axis nearly coincident with the ϕ axis of the goniometer. Crystal quality was checked with ω scans of several intense low-angle reflections which had peak widths at half-height of ca. 0.2°. Cell constants and axial photographs indicated that the crystal belonged to the monoclinic system with $a = 15.342$ (2) Å, $b = 13.578$ (2) Å, $c = 8.264$ (1) Å, $\beta = 97.26$ (1)°, and $V = 1707.7$ (4) Å^3. The observed volume is consistent with that expected for $Z = 4$.

Data were collected at 22 ± 2 °C on a Syntex $P\bar{1}$ autodiffractometer equipped with a graphite crystal monochromator in the incident beam and using M Kα (λ 0.710730 Å) radiation. The θ–2θ scan technique was used with scans ranging from 1.1° above and 1.1° below the calculated $K\alpha_1$, $K\alpha_2$ doublet, with variable scan speeds from 4.0 to 24.0°/min, and with a scan to background time ratio of 2.0. The intensities of three standard reflections were monitored frequently throughout data collection and showed no decrease in intensity. The integrated intensities of 2240 unique, nonsystematically absent reflections having $0° < 2\theta < 45°$ were recorded. The data were reduced to a set of relative $|F_o|^2$ values and were not corrected for absorption ($\mu = 14.3$ cm^{-1}). The 1716 reflections having $|F_o|^2 > 3\sigma(|F_o|^2)$ were used in subsequent structure solution and refinement. Systematic absences on $0k0$ ($k = 2n + 1$) and $h0l$ ($l = 2n + 1$) uniquely determined the space group to be $P2_1/c$ (No. 14).

Since the cell constants of $Mo_2(NMe_2)_4Me_2$ were very similar to those of $Mo_2(NMe_2)_4Cl_2$ and both compounds crystallized in the same space group, the starting atomic positions for $Mo_2(NMe_2)_4Me_2$ were taken from the $Mo_2(NMe_2)_4Cl_2$ structure,[6] assuming Mo–Me = Mo–Cl. The positions were sufficiently close to allow refinement to proceed smoothly to convergence. In the final stages of refinement anisotropic thermal parameters were used for all atoms. The final unweighted and weighted residuals were $R_1 = 0.037$ and $R_2 = 0.060$, respectively. A value of 0.07 was used for p in the calculation of the weights. The esd of an observation of unit weight was 1.412. The largest peaks in a final difference Fourier map were about where some methyl-group hydrogen atoms might be expected, but no attempt was made to introduce or refine these.

Acknowledgment. We thank the Office of Naval Research for support of this work at Princeton University and the National Science Foundation for support at Texas A&M University.

Registry No. $Mo_2Me_2(NMe_2)_4$, 67030-82-4; $Mo_2Cl_2(NMe_2)_4$, 63301-82-6.

Supplementary Material Available: A table of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Part 4: M. H. Chisholm, F. A. Cotton, M. W. Extine and W. W. Reichert, *J. Am. Chem. Soc.*, **100** 1727 (1978).

(2) (a) Princeton University. (b) Texas A&M University.

(3) M. H. Chisholm and F. A. Cotton, *Acc. Chem. Res.*, in press.

(4) F. A. Cotton, *Acc. Chem. Res.*, **11**, 224 (1978).

(5) M. H. Chisholm, F. A. Cotton, M. W. Extine, M. Millar, and B. R. Stults, *Inorg. Chem.*, **15**, 2244 (1976).

(6) M. Akiyama, M. H. Chisholm, F. A. Cotton, M. W. Extine, and C. A. Murillo, *Inorg. Chem.*, **16**, 2407 (1977).

Additions and Corrections

1977, Volume 16

Stephen D. Robinson* and Arvind Sahajpal: Complexes of the Platinum Metals. 10. Dithioformato Derivatives of Ruthenium, Osmium, and Iridium.

Page 2718. An unfortunate mistake appears in the abstract to this paper because of a computer system error which occurred in a recycling process after proof had been approved by the author. The correct version of the abstract should read: "Insertion" of carbon disulfide into platinum metal–hydrogen bonds has been employed to synthesize a range of new dithioformato complexes. Products prepared in this manner include the species $[MX(S_2CH)(CO)(PPh_3)_2]$ (two isomers; M = Ru or Os; X = Cl, Br, or $OCOCF_3$), $[M(S_2CH)_2(PPh_3)_2]$, $[IrCl_2(S_2CH)(PPh_3)_2]$, and $[IrH_2(S_2CH)(PPh_3)_2]$. Phosphine substitution reactions have been employed to prepare the species $[MCl(S_2CH)(CO)(PMe_2Ph)_2]$ and $[MCl(S_2CH)(CO)(PMePh_2)_2]$. The stereochemistry of each new complex has been assigned by reference to the ^1H NMR spectrum of the dithioformate (S_2CH) ligands and has been confirmed where appropriate by use of high-field (metal hydride) resonances, virtual coupling patterns of the PMe_nPh_{3-n} (n = 1 or 2) ligands, or the ^{31}P NMR pattern of the phosphine ligands.—Stephen D. Robinson

R. E. Noftle,* R. R. Smardzewski, and W. B. Fox: Gas-Phase Raman Spectrum of Pentafluorosulfur Chloride, SF_5Cl.

Page 3380. In Table I under ν, cm^{-1}, 951.4 should read 851.4. The number is correct in the text.—R. E. Noftle