

respectively. In II both C-N distances have a high double-bond character. The unhybridized p orbital on C(30) in II may have some interaction with the two nitrogen atoms and the metal, so that considerable electronic delocalization occurs over the three atoms. This is the pattern observed in many carbenoid complexes and supports the carbenoid nature of C(30).



The C=N stretching frequencies of I and II parallel the structural data, indicating an increasing C=N double-bond character of the C(30)-N(1) unit passing from I to II. This and other features of the  $\eta^2$ -C,N-bonded amidinyl are highly reminiscent of  $\eta^2$ -C,O-bonded acyls<sup>26</sup> and  $\eta^2$ -C,N-bonded iminoacyls.<sup>27</sup> Amidinyl ligands in this form, like the ligands cited above, can be viewed as three-electron donors.

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V-C(30) bond distances fall in the range of the very few V-C ( $sp^2$ ) distances so far reported.<sup>24</sup> The counteranion  $I_3^-$  has the usual structural features (Table V)<sup>28</sup> and does not interact significantly with the macrocation, the shortest contact distance being 3.87 (13) Å [I(1)⋯N(2) ( $\bar{x}$ ,  $\bar{y}$ ,  $\bar{z}$ )].

### Conclusions

Besides the structural models for metal-bonded CO<sub>2</sub> and carboxylate esters, the present report describes the alkylation of a coordinated carbodiimide viewed as a reaction which can be considered a modeling study for the alkylation of metal-bonded CO<sub>2</sub>. Moreover, vanadocene can be proposed as a blocking agent for one double bond of a cumulene, so that it may promote a new kind of reactivity for the coordinated molecule.

**Acknowledgment.** We thank the CNR (Rome) for financial support.

**Registry No.** I, 75102-51-1; II, 75102-53-3; Cp<sub>2</sub>VI<sub>2</sub>, 75102-54-4; Cp<sub>2</sub>V, 1277-47-0; CH<sub>3</sub>I, 74-88-4.

**Supplementary Material Available:** Listings of structure factor amplitudes for complexes I and II, anisotropic thermal parameters (Tables VI and VII), and least-squares planes (Table VIII) (32 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405

## The Molybdenum-Molybdenum Triple Bond. 7.<sup>1</sup>

### Bis(1,3-di-*p*-tolyltriazenido)tetrakis(dimethylamido)dimolybdenum

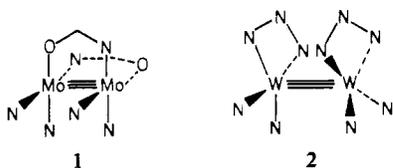
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Received May 14, 1980

Mo<sub>2</sub>(NMe<sub>2</sub>)<sub>6</sub> reacts in hydrocarbon solvents with 1,3-di-*p*-tolyltriazenine, C<sub>7</sub>H<sub>8</sub>NNNHC<sub>7</sub>H<sub>8</sub>, to give the title compound, Mo<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub>(C<sub>7</sub>H<sub>8</sub>N<sub>3</sub>C<sub>7</sub>H<sub>8</sub>)<sub>2</sub>, as a red, crystalline solid. An X-ray study shows that in the solid state each molybdenum atom is coordinated to four nitrogen atoms which lie in a plane; there is an unbridged molybdenum-to-molybdenum triple bond with a Mo-Mo distance of 2.212 (1) Å, and the molecule has crystallographically imposed C<sub>2</sub> symmetry. Variable-temperature <sup>1</sup>H NMR spectra recorded at 220 MHz support the view that this form of the molecule is present in solution. These observations are compared with other findings in dimolybdenum and ditungsten chemistry. Crystal data for Mo<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub>(C<sub>7</sub>H<sub>8</sub>N<sub>3</sub>C<sub>7</sub>H<sub>8</sub>)<sub>2</sub> are  $a = 27.529$  (7) Å,  $b = 8.728$  (2) Å,  $c = 18.294$  (4) Å,  $\beta = 58.34$  (1)°,  $V = 3741.58$  Å<sup>3</sup>,  $Z = 4$ ,  $d_{\text{calcd}} = 1.45$  g cm<sup>-3</sup>, and space group  $C2/c$ .

### Introduction

Previously we have shown that 1,3-diphenyltriazenine and W<sub>2</sub>(NMe<sub>2</sub>)<sub>6</sub> react to give W<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub>(PhN<sub>3</sub>Ph)<sub>2</sub><sup>2</sup> and Mo<sub>2</sub>(NMe<sub>2</sub>)<sub>6</sub> and 2-hydroxy-6-methylpyridine react to give Mo<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub>(C<sub>6</sub>H<sub>6</sub>NO)<sub>2</sub>.<sup>1</sup> In both reactions, the replacement of two dimethylamido groups is accomplished by an increase in coordination number of the metal, since the triazenido and pyridine ligands act as bidentate ligands. However, the molybdenum and tungsten compounds adopt bridged and unbridged structures, respectively, as shown in 1 and 2. The



preference for the bridged or nonbridged structure could be determined by the subtle differences that exist within the coordination chemistry of molybdenum and tungsten. For example, in closely related compounds containing metal-to-metal triple bonds, the Mo-to-Mo distance is shorter by ca. 0.08 Å than the W-to-W distance, and the triazenido ligand is known to bridge the molybdenum-to-molybdenum quadruple bond in the compound Mo<sub>2</sub>(PhN<sub>3</sub>Ph)<sub>4</sub> which has a Mo-to-Mo distance of 2.083 (2) Å.<sup>3</sup> As part of our continuing program which is aimed at establishing the coordination chemistry surrounding the (M≡M)<sup>6+</sup> moiety (M = Mo, W), we decided to prepare and structurally characterize the related pair of molybdenum and tungsten compounds. We report here the preparation and characterization of Mo<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub>(C<sub>7</sub>H<sub>8</sub>N<sub>3</sub>C<sub>7</sub>H<sub>8</sub>)<sub>2</sub>.

### Results

**Synthesis.** In hydrocarbon solvents, Mo<sub>2</sub>(NMe<sub>2</sub>)<sub>6</sub> and 1,3-di-*p*-tolyltriazenine react upon mixing at room temperature

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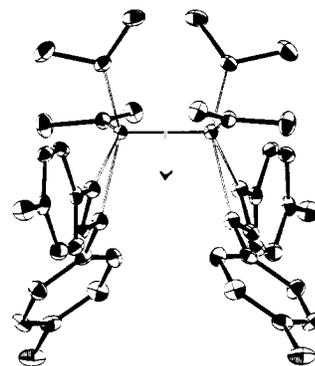
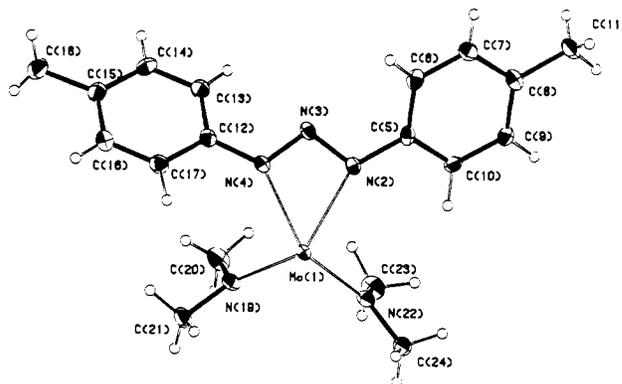
**Table I.** Fractional Coordinates for  $\text{Mo}_2\text{N}_{10}\text{C}_{36}\text{H}_{52}$ <sup>a, b</sup>

atom	x	y	z	B, Å <sup>2</sup>
Mo(1)	109.9 (1)	1373.9 (4)	1825.1 (2)	10
N(2)	-511 (1)	-211 (4)	1736 (2)	13
N(3)	-173 (1)	-1402 (4)	1418 (2)	12
N(4)	280 (1)	-1094 (4)	1458 (2)	13
C(5)	-1040 (2)	-392 (4)	1773 (2)	12
C(6)	-1296 (2)	-1815 (5)	1888 (3)	15
C(7)	-1804 (2)	-1942 (5)	1903 (3)	16
C(8)	7923 (2)	9346 (5)	1824 (2)	14
C(9)	-1820 (2)	751 (5)	1726 (2)	14
C(10)	-1306 (2)	892 (5)	1698 (2)	13
C(11)	-2622 (2)	-803 (6)	1822 (3)	20
C(12)	748 (2)	-2080 (4)	1010 (2)	13
C(13)	828 (2)	-2994 (5)	332 (3)	17
C(14)	1303 (2)	-3885 (5)	-116 (3)	19
C(15)	1727 (2)	-3916 (4)	79 (3)	17
C(16)	1642 (2)	-3015 (5)	768 (3)	19
C(17)	1166 (2)	-2099 (5)	1221 (3)	16
C(18)	2263 (2)	-4845 (6)	-439 (3)	24
N(19)	929 (1)	1715 (4)	1190 (2)	13
C(20)	1186 (2)	1585 (6)	263 (3)	21
C(21)	1366 (2)	1944 (5)	1399 (3)	17
N(22)	-237 (1)	3296 (4)	1751 (2)	14
C(23)	-123 (2)	3640 (6)	894 (3)	22
C(24)	-528 (2)	4572 (5)	2323 (3)	19

<sup>a</sup> The isotropic thermal parameters listed for those atoms refined anisotropically are the isotropic equivalents. <sup>b</sup> Numbers in parentheses in this and all following tables refer to the error in the least significant digits.

to give deep red solutions from which  $\text{Mo}_2(\text{NMe}_2)_4(\text{C}_7\text{H}_8\text{N}_3\text{C}_7\text{H}_8)_2$  can be obtained as red crystals from toluene-hexane solvent mixtures. The physical properties are analogous to those reported for the tungsten analogue.<sup>2</sup> Analytical data and other spectroscopic data are recorded in the Experimental Section.

**Solid-State Structure.** In the crystalline state, the compound is composed of discrete molecules of  $\text{Mo}_2(\text{NMe}_2)_4(\text{C}_7\text{H}_8\text{N}_3\text{C}_7\text{H}_8)_2$ . An ORTEP view of the molecule looking down the  $C_2$  axis of symmetry is shown in Figure 1 and the atomic numbering scheme is shown in Figure 2. Final atomic coordinates and thermal parameters are given in Tables I and II. Complete listings of bond distances and angles are given in Tables III and IV, respectively. A listing of least-squares

**Figure 1.** ORTEP view of the  $\text{Mo}_2(\text{NMe}_2)_4(\text{C}_7\text{H}_8\text{N}_3\text{C}_7\text{H}_8)_2$  molecule showing the  $C_2$  axis of symmetry. Thermal ellipsoids are drawn at the 40% probability level.**Figure 2.** ORTEP view of half the  $\text{Mo}_2(\text{NMe}_2)_4(\text{C}_7\text{H}_8\text{N}_3\text{C}_7\text{H}_8)_2$  molecule showing the atomic numbering scheme.

planes calculated for this molecule and the deviations of atoms from these planes, together with dihedral angles between planes, are available as supplementary material.

## Discussion

The molecule is in every way structurally akin to its tungsten analogue. The X-ray data for the molybdenum compound are superior and reveal certain trends which were alluded to in

**Table II.** Anisotropic Thermal Parameters for  $\text{Mo}_2\text{N}_{10}\text{C}_{36}\text{H}_{52}$ <sup>a</sup>

atom	$b_{11}$	$b_{22}$	$b_{33}$	$b_{12}$	$b_{13}$	$b_{23}$
Mo(1)	3.95 (7)	34.9 (5)	10.7 (2)	-0.5 (1)	-3.8 (1)	0.3 (2)
N(2)	6 (1)	47 (5)	17 (1)	1 (1)	-7 (1)	-1 (2)
N(3)	5 (1)	43 (4)	15 (1)	-3 (1)	-5 (1)	8 (2)
N(4)	5 (1)	48 (5)	15 (1)	-1 (2)	-6 (1)	-1 (2)
C(5)	5 (1)	56 (5)	10 (1)	4 (1)	-3 (1)	-2 (2)
C(6)	7 (1)	47 (5)	16 (2)	2 (2)	-5 (1)	6 (2)
C(7)	7 (1)	53 (5)	17 (2)	-3 (2)	-6 (1)	2 (2)
C(8)	5 (1)	69 (6)	10 (1)	-3 (2)	-3 (1)	5 (2)
C(9)	6 (1)	41 (5)	15 (2)	2 (2)	-5 (1)	2 (2)
C(10)	7 (1)	35 (5)	15 (2)	2 (2)	-6 (1)	-5 (2)
C(11)	7 (1)	66 (6)	28 (2)	-5 (2)	-9 (1)	3 (3)
C(12)	5 (1)	41 (5)	15 (2)	-4 (2)	-3 (1)	8 (2)
C(13)	8 (1)	61 (6)	20 (2)	2 (2)	-9 (1)	-8 (3)
C(14)	10 (1)	50 (6)	19 (2)	4 (2)	-7 (1)	-14 (3)
C(15)	6 (1)	40 (5)	21 (2)	-1 (2)	-4 (1)	5 (2)
C(16)	7 (1)	65 (6)	24 (2)	1 (2)	-7 (1)	-3 (3)
C(17)	8 (1)	59 (6)	16 (2)	-0 (2)	-7 (1)	-3 (3)
C(18)	9 (1)	47 (6)	35 (2)	2 (2)	-7 (1)	-2 (3)
N(19)	6 (1)	48 (5)	12 (1)	-5 (2)	-4 (1)	2 (2)
C(20)	7 (1)	100 (7)	13 (2)	-6 (2)	-4 (1)	-1 (3)
C(21)	5 (1)	74 (6)	18 (2)	-3 (2)	-4 (1)	-2 (3)
N(22)	7 (1)	40 (5)	18 (1)	-4 (1)	-8 (1)	7 (2)
C(23)	12 (1)	69 (6)	27 (2)	-6 (2)	-13 (1)	17 (3)
C(24)	9 (1)	41 (6)	31 (2)	0 (2)	-12 (1)	4 (3)

<sup>a</sup> The form of the exponent is  $\exp[-(h^2b_{11} + k^2b_{22} + l^2b_{33} + 2hk_{12} + 2hl_{13} + 2kl_{23})]$ .

**Table III.** Bond Distances (Å) for the  $\text{Mo}_2(\text{NMe}_2)_4(\text{C}_7\text{H}_8\text{N}_3\text{C}_7\text{H}_8)_2$  Molecule

A	B	dist	A	B	dist
Mo(1)	Mo(1)'	2.212 (1)	C(5)	C(6)	1.387 (6)
Mo(1)	N(2)	2.271 (3)	C(5)	C(10)	1.385 (5)
Mo(1)	N(4)	2.231 (3)	C(6)	C(7)	1.388 (6)
Mo(1)	N(19)	1.943 (3)	C(7)	C(8)	1.402 (6)
Mo(1)	N(22)	1.970 (3)	C(8)	C(9)	1.380 (6)
N(2)	N(3)	1.310 (4)	C(8)	C(11)	1.507 (5)
N(2)	C(5)	1.431 (5)	C(9)	C(10)	1.393 (5)
N(3)	N(4)	1.316 (4)	C(12)	C(13)	1.390 (6)
N(4)	C(12)	1.400 (5)	C(12)	C(17)	1.394 (5)
N(19)	C(20)	1.459 (5)	C(13)	C(14)	1.364 (6)
N(19)	C(21)	1.454 (5)	C(14)	C(15)	1.388 (6)
N(22)	C(23)	1.460 (5)	C(15)	C(16)	1.397 (6)
N(22)	C(24)	1.449 (5)	C(15)	C(18)	1.504 (6)
			C(16)	C(17)	1.381 (6)

the tungsten structure. For example, there are short (1.943 (3) Å) and long (1.970 (3) Å) Mo–N bond distances associated with the two types of Mo–NMe<sub>2</sub> groups, and these are, respectively, trans to long (2.271 (3) Å) and short (2.231 (3) Å) Mo–N distances of the triazenido ligand.

The Mo–Mo distance is 2.212 (1) Å which is slightly shorter than the average of the two crystallographically independent Mo–Mo distances found for Mo<sub>2</sub>(NMe<sub>2</sub>)<sub>6</sub> which were 2.211 (2) and 2.217 (2) Å.<sup>4</sup> By contrast, the W–W distance in W<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub>(PhN<sub>3</sub>Ph)<sub>2</sub> is 2.314 (1) Å which is longer than the three crystallographically independent W–W distances found for the W<sub>2</sub>(NMe<sub>2</sub>)<sub>6</sub> molecule.<sup>5</sup> These were 2.294 (1) Å found for the W<sub>2</sub>(NMe<sub>2</sub>)<sub>6</sub> molecule which cocrystallized with W(NMe<sub>2</sub>)<sub>6</sub> and 2.290 (2) and 2.294 (2) Å found in crystals of pure W<sub>2</sub>(NMe<sub>2</sub>)<sub>6</sub>.

For a closely related series of compounds containing the central (M≡M)<sup>6+</sup> unit, we have found that the W–W distance is longer by 0.08 Å than the Mo–Mo distance.<sup>6</sup> Here the distances differ by 0.10 Å which is a small but crystallographically significant deviation from what we expected. However, little chemical significance can be attached to this observation, and the bonding in Mo<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub>(C<sub>7</sub>H<sub>8</sub>N<sub>3</sub>C<sub>7</sub>H<sub>8</sub>)<sub>2</sub> may be viewed as previously described for the tungsten dimer.

Variable-temperature <sup>1</sup>H NMR studies reveal the two types of Mo–NMe<sub>2</sub> groups with quite different energies of activation for proximal ⇌ distal methyl exchange. There are two tolyl methyl signals, consistent with the maintenance of the C<sub>2</sub> axis of symmetry in solution. Thus, the triazenido moiety is rigidly bound on the NMR time scale: The <sup>1</sup>H NMR data do not allow one to distinguish between a bridged structure akin to **1** or the nonbridged structure **2**. However, only one isomer is present in solution (one pair of enantiomers, to be precise), and so one can rule out a rapid equilibrium between bridged and nonbridged structures, since this would cause the tolyl methyl groups to become equivalent on the NMR time scale. Thus, we are inclined to the view that the structure found in the solid state is maintained in solution.

This raises the question: Why does the 2-oxy-6-methylpyridine ligand favor a bridged structure, **1**, while the 1,3-diaryltriazenido ligands favor the nonbridged structure **2**? We propose that the reason rests solely on the relative ordering of steric repulsive interactions within the molecules (**1**). The 2-oxy-6-methylpyridine ligand acts as a strong O donor and a weak N donor, as evidenced by the short Mo–O (2.08 Å) and long Mo–N (2.31 Å) bond distances. Furthermore, the

**Table IV.** Angles (Deg) for the  $\text{Mo}_2(\text{NMe}_2)_4(\text{C}_7\text{H}_8\text{N}_3\text{C}_7\text{H}_8)_2$  Molecule

A	B	C	angle
Mo(1)'	Mo(1)	N(2)	107.8 (1)
Mo(1)'	Mo(1)	N(4)	103.1 (1)
Mo(1)'	Mo(1)	N(19)	102.6 (1)
Mo(1)'	Mo(1)	N(22)	102.6 (1)
N(2)	Mo(1)	N(4)	55.8 (1)
N(2)	Mo(1)	N(19)	137.0 (1)
N(2)	Mo(1)	N(22)	95.9 (1)
N(4)	Mo(1)	N(19)	88.4 (1)
N(4)	Mo(1)	N(22)	146.5 (1)
N(19)	Mo(1)	N(22)	106.3 (1)
Mo(1)	N(2)	N(3)	97.4 (2)
Mo(1)	N(2)	C(5)	148.2 (3)
N(3)	N(2)	C(5)	113.8 (3)
N(2)	N(3)	N(4)	106.7 (3)
Mo(1)	N(4)	N(3)	99.1 (2)
Mo(1)	N(4)	C(12)	138.9 (2)
N(3)	N(4)	C(12)	116.6 (3)
Mo(1)	N(19)	C(20)	112.6 (3)
Mo(1)	N(19)	C(21)	136.5 (3)
C(20)	N(19)	C(21)	110.7 (3)
Mo(1)	N(22)	C(23)	114.2 (3)
Mo(1)	N(22)	C(24)	135.2 (3)
C(23)	N(22)	C(24)	110.1 (3)
N(2)	C(5)	C(6)	121.9 (3)
N(2)	C(5)	C(10)	119.0 (3)
C(6)	C(5)	C(10)	119.1 (3)
C(5)	C(6)	C(7)	120.0 (4)
C(6)	C(7)	C(8)	121.5 (4)
C(7)	C(8)	C(9)	117.4 (3)
C(7)	C(8)	C(11)	121.3 (4)
C(9)	C(8)	C(11)	121.3 (4)
C(8)	C(9)	C(10)	121.6 (4)
C(5)	C(10)	C(9)	120.3 (4)
N(4)	C(12)	C(13)	122.9 (3)
N(4)	C(12)	C(17)	118.9 (3)
C(13)	C(12)	C(17)	118.2 (4)
C(12)	C(13)	C(14)	121.1 (4)
C(13)	C(14)	C(15)	121.8 (4)
C(14)	C(15)	C(16)	117.1 (4)
C(14)	C(15)	C(18)	121.8 (4)
C(16)	C(15)	C(18)	121.1 (4)
C(15)	C(16)	C(17)	121.6 (4)
C(12)	C(17)	C(16)	120.2 (4)

pyridine nitrogen accommodates a considerable pyramidal distortion in its coordination to molybdenum in the Mo<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub>(2-oxy-6-methylpyridine)<sub>2</sub> molecule. In this way, the Mo<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub> portion of the molecule adopts a skew geometry which reduces the unfavorable steric repulsions which otherwise would result from the eclipsed geometry. A Mo<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub>(ArN<sub>3</sub>Ar)<sub>2</sub> molecule having two bridging triazenido groups has no inherent asymmetry and would, therefore, favor a more rigorously eclipsed geometry (**2**). If the 2-oxy-6-methylpyridine ligand is placed as a bidentate, but nonbridging group such that each MoN<sub>3</sub>O moiety is at least roughly planar, then the methyl group of the pyridine ligand is also confined to this plane. This is clearly unfavorable from steric considerations. In the M<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub>(ArN<sub>3</sub>Ar)<sub>2</sub> structures, the phenyl groups are free to rotate about the N–C<sub>sp<sup>2</sup></sub> bonds and may, as they indeed do, orientate the phenyl blades to reduce this steric repulsion in the MoN<sub>4</sub> plane.

While the above arguments offer a qualitative explanation for the choice of bridging vs. nonbridging structures, the structural characterization of the Mo<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub>(2-oxy-6-methylpyridine)<sub>2</sub> and Mo<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub>(C<sub>7</sub>H<sub>8</sub>N<sub>3</sub>C<sub>7</sub>H<sub>8</sub>)<sub>2</sub> molecules provide further support for the view that the favored geometry for d<sup>3</sup>–d<sup>3</sup> dimers L<sub>4</sub>M≡ML<sub>4</sub> has the four ligand atoms, which are directly bonded to each metal, in a plane.

#### Experimental Section

General procedures, including the preparation of Mo<sub>2</sub>(NMe<sub>2</sub>)<sub>6</sub>,<sup>4</sup> have been described previously.

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(6) For a table listing M≡M distances, see M. H. Chisholm, *Transition Met. Chem.*, **3**, 321 (1978).

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**Synthesis of  $\text{Mo}_2(\text{NMe}_2)_4(\text{C}_7\text{H}_8\text{N}_3\text{C}_7\text{H}_8)_2$ .**  $\text{Mo}_2(\text{NMe}_2)_6$  (0.4477 g, 0.98 mmol) and 1,3-di-*p*-tolyltriazine (0.52 g, 1.96 mmol) were placed in a 100-mL round-bottomed flask. Dry toluene (50 mL) was added, yielding a deep red solution which was stirred at room temperature for  $1/2$  h. Hexane (10 mL) was added, and the flask was placed in the refrigerator at  $-10^\circ\text{C}$ . Rust red crystals were obtained. Elemental analyses were erratic and unsatisfactory. IR data obtained from Nujol mull using CsI plates ( $\nu$  in  $\text{cm}^{-1}$ ): 1596 m, 1380 s, 1340 s, 1293 vs, 1272 vs, 1240 s, 1170 w, 1155 w, 1144 m, 1115 w, 1105 w, 1044 m, 950 s, 935 s, 931 s, 820 s, 759 m, 727 m, 652 m, 624 m, 540 m, 503 m, 366 m.  $^1\text{H}$  NMR data obtained from toluene- $d_6$  at 220 MHz and  $+16^\circ\text{C}$ :  $\delta$  (NMe-proximal) 4.45 (br), 4.28 (sh);  $\delta$  (NMe-distal) 2.09 (br), 2.53 (sh);  $\delta$  (tolyl methyls) 2.29 and 2.22;  $\delta$  (aromatic protons) 7.03, 7.24, 7.42, 7.59 (all doublets with splittings of ca. 7.5 Hz).

**X-ray Structural Determination.** A crystal of dimensions  $0.08 \times 0.11 \times 0.34$  mm was mounted in a nitrogen-filled glovebag and transferred to the liquid-nitrogen boil-off cooling system of the diffractometer.<sup>8</sup> The diffractometer used for data collection was designed and constructed locally. A Picker four-circle goniostat equipped with a Furnas monochromator (HOG crystal) and Picker X-ray generator is interfaced to a TI980 minicomputer, with Slo-Syn stepping motors to drive the angles. Centering is accomplished by using automated top/bottom-left/right slit assemblies. The minicomputer is interfaced by slow-speed data lines to a CYBER 172-CDC 6600 multiframe system where all computations are performed.

(8) J. C. Huffman, Ph.D. Thesis, Indiana University, Bloomington, Ind., 1974.

The cell dimensions obtained from 20 reflections at  $-17^\circ\text{C}$  with Mo K $\alpha$  ( $\lambda = 0.71069 \text{ \AA}$ ) were  $a = 27.529 (7) \text{ \AA}$ ,  $b = 8.728 (2) \text{ \AA}$ ,  $c = 18.294 (4) \text{ \AA}$ ,  $\beta = 58.34 (1)^\circ$ ,  $V = 3741.58 \text{ \AA}^3$ ,  $Z = 4$ ,  $d_{\text{calcd}} = 1.45 \text{ g cm}^{-3}$ , and space group  $C2/c$ .

A total of 3730 reflections were collected by using standard moving-detector techniques with the following values: Scan speed =  $3^\circ \text{ min}^{-1}$ ; scan width =  $2^\circ + \text{dispersion}$ ; single background time at extremes of scan = 5 s; aperture size =  $2.5 \times 3.5 \text{ mm}$ . The limits of data collection were  $5^\circ < 2\theta < 50^\circ$ . The number of reflections with  $F > 2.33\sigma(F)$  was 2853.

For the final refinement, all nonhydrogen atoms were allowed to vary anisotropically. The hydrogen positional parameters were also varied, while their isotropic thermal parameters were kept fixed.

The structure was solved by direct methods and Patterson techniques and refined by full-matrix least-squares techniques to yield final residues:  $R_F = 0.039$  and  $R_{wF} = 0.040$ . The goodness of fit for the last cycle was 1.01, and the maximum  $\Delta/\sigma$  was 0.1.

**Acknowledgment.** We thank the Office of Naval Research, the Marshall H. Wrubel Computing Center, and the taxpayers of the State of Indiana for financial support of this work.

**Registry No.**  $\text{Mo}_2(\text{NMe}_2)_4(\text{C}_7\text{H}_8\text{N}_3\text{C}_7\text{H}_8)_2$ , 75067-37-7;  $\text{Mo}_2(\text{NMe}_2)_6$ , 51956-20-8.

**Supplementary Material Available:** A table of observed and calculated structure factors (31 pages). Ordering information is given on any current masthead page. The complete structural report, MSC Report 8001, is available upon request in microfiche form only from the Indiana University Chemical Library.

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## Synthesis, Structure, and Properties of the Cluster Complex $[\text{MoFe}_4\text{S}_4(\text{SC}_2\text{H}_5)_3(\text{C}_6\text{H}_4\text{O}_2)_3]^{3-}$ , Containing a Single Cubane-Type $\text{MoFe}_3\text{S}_4$ Core

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Received May 15, 1980

Reaction of the Fe(III)-bridged complex  $[\text{Mo}_2\text{Fe}_7\text{S}_8(\text{SEt})_{12}]^{3-}$  with catechol in acetonitrile solution at ambient temperature results in cleavage of this "double-cubane" cluster and formation of a new Mo-Fe-S cluster compound of the formulation  $(\text{Et}_4\text{N})_3[\text{MoFe}_4\text{S}_4(\text{SEt})_3(\text{C}_6\text{H}_4\text{O}_2)_3]$ . This compound crystallizes in the monoclinic space group  $P2_1/c$  with  $a = 16.844 (4) \text{ \AA}$ ,  $b = 13.016 (3) \text{ \AA}$ ,  $c = 29.362 (7) \text{ \AA}$ ,  $\beta = 91.57 (2)^\circ$ , and  $Z = 4$ . The anion consists of a single  $\text{MoFe}_3\text{S}_4(\text{SEt})_3$  cluster with a trigonally distorted  $\text{MoFe}_3\text{S}_4$  core. Coordination of the Mo atom is completed by an unprecedented structural feature, viz., attachment via Mo-O-Fe bridges of a  $\text{Fe}^{\text{III}}(\text{C}_6\text{H}_4\text{O}_2)_3$  subunit functioning as a tridentate ligand. This arrangement causes distortions of the unperturbed  $[\text{Fe}(\text{C}_6\text{H}_4\text{O}_2)_3]^{3-}$  structure which include a shift of the Fe-O<sub>6</sub> coordination polyhedron (twist angle  $\phi = 35^\circ$ ) toward the trigonal-prismatic limit ( $\phi = 45^\circ$  in the free trianion). Mean dimensions of the cluster are virtually identical with those of individual clusters in the species  $[\text{Mo}_2\text{Fe}_6\text{S}_9(\text{SR})_8]^{3-}$ ,  $[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{SR})_9]^{3-}$ , and  $[\text{Mo}_2\text{Fe}_7\text{S}_8(\text{SR})_{12}]^{3-}$ . This result, together with  $^{57}\text{Fe}$  isomer and Fe-SCH<sub>2</sub>CH<sub>3</sub>  $^1\text{H}$  NMR isotropic shifts, suggests that the mean oxidation state of core Fe in all clusters thus far prepared with a net 3- charge is the same. Cyclic voltammetry reveals three redox processes. That with  $E_{1/2} \approx -1.31 \text{ V}$  corresponds to cluster electron transfer, while the two others at more and less negative potentials are tentatively ascribed to  $\text{Fe}(\text{C}_6\text{H}_4\text{O}_2)_3$  subunit metal-centered reduction and ligand-based oxidation, respectively. At present  $[\text{MoFe}_3\text{S}_4(\text{SEt})_3(\text{C}_6\text{H}_4\text{O}_2)_3]^{3-}$  is the only cluster species proven to contain a single  $\text{MoFe}_3\text{S}_4$  cubane-type core, a matter of current interest in view of the possible relevance of this unit as a model for some structural properties of the nitrogenase FeMo cofactor.

### Introduction

Recently synthesized molybdenum-iron-sulfur cluster complexes are of substantial interest in view of their possible relevance as models for some structural features of the iron-molybdenum cofactor of nitrogenase. Compositional and physicochemical properties of the latter<sup>2-7</sup> are consistent with

a unique type of Mo-Fe-S cluster whose structure is unknown. From the reaction system  $\text{FeCl}_3/\text{MS}_4^{2-}/\text{RS}^-$  in methanol or ethanol ( $M = \text{Mo}, \text{W}$ ), we have isolated the polynuclear species  $[\text{M}_2\text{Fe}_6\text{S}_9(\text{SR})_8]^{3-}$ ,  $[\text{M}_2\text{Fe}_6\text{S}_8(\text{SR})_9]^{3-}$ , and  $[\text{M}_2\text{Fe}_7\text{S}_8(\text{SR})_{12}]^{3-}$ <sup>4</sup> and have determined their structures and

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