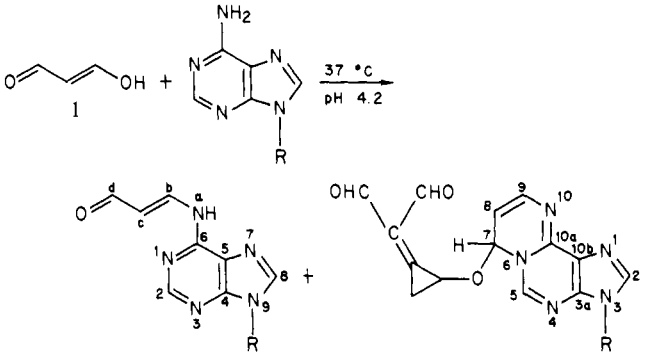
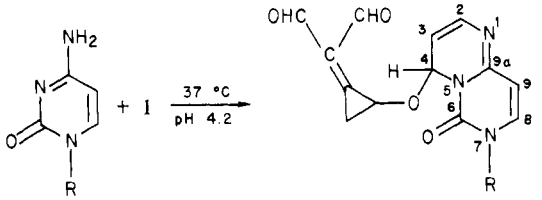


2, R = ribosyl
3, R = Et

4, R = ribosyl
5, R = Et

237 nm (ϵ = 27 060). The EI and FAB mass spectral data and elemental analysis suggested a molecular formula of $C_{19}H_{19}N_5O_7$. The delayed-decoupled high-field ^{13}C NMR spectrum (in Me_2SO-d_6) revealed the presence in the structure of the following proton substitution pattern: 2 CH_2, 12 CH, 5 C. An unusual feature in the ^{13}C spectrum was the presence of a CH at δ 16.2 and a CH_2 at δ 24.1. This information in conjunction with other ^{13}C and ^1H NMR data led to the conclusion that a methylidene cyclopropane moiety was present within the structure. Two aldehyde carbons were seen at δ 187.9 and 187.1, with the corresponding protons appearing as singlets at δ 9.38 and 9.21. The cyclopropyl CH appeared as a broadened quartet at δ 4.03 and the geminal protons at δ 2.08 and 1.97 (J_{gem} = 13.5 Hz). The ^{13}C and ^1H NMR data were also consistent with the formation of a new six-membered ring with carbon resonances at δ 77.2, 142.9, and 162.4 and corresponding proton resonances at δ 7.72 (brs), 7.63 (brd, J = 6.8 Hz), and 9.21 (brd, J = 6.8 Hz). The purine and ribose components were intact and gave expected ^{13}C and ^1H peaks. The spectral data were completely consistent with **4**, a 3:1 adduct of MDA and adenosine.

Modified bases identical with those present in **2** and **4** were formed in the reaction of 9-ethyladenine[14] with MDA. When cytidine and 1-methylcytosine[15] were treated with MDA, adducts **6** and **7** were isolated as the sole products.



6, R = ribosyl
7, R = Me

A plausible mechanism for the formation of the intriguing 3:1 adducts is shown in Scheme I for the adenine case. The mechanism implies the intermediacy of the enaminal **2** (or **3**). Thus, cyclization of this enaminal gives a tricyclic base **8**. Reaction of **8** with another molecule of MDA followed by elimination of water results in the formation of the ether **9**. Intermediate **9** can be attacked further by a molecule of MDA to give **10**, which can undergo cyclization and 1,2-hydrogen shifts to give the observed products **4** (and **5**). Although in the formation of the 3:1 adducts two new chiral centers are introduced, the relative stereochemistry of the resulting diastereoisomeric structures is not readily discernible from the high-field NMR data.

We conclude that MDA is capable of modifying both adenine and cytosine bases at the amino group. Subsequent cyclization of these primary products followed by further reaction with MDA results in the formation of hypermodified bases with methylene cyclopropane rings. The alteration of adenine and cytosine by MDA has not been reported previously. The formation of cyclopropane rings in the degenerative chemistry of MDA is also novel. The toxic effects of MDA that involve nucleic acids could be mediated by the formation of such bicyclic and tricyclic bases or interstrand and intrastrand crosslinking involving enaminal structures.

Acknowledgment. Support of these investigations by a grant (CHE-8200818) from the NSF is gratefully acknowledged. The Bruker WM-360 high-field NMR spectrometer used in this work was purchased in part from a grant (CHE-8201836) from the NSF. We thank Dr. Curt S. Cooper for some preliminary experiments with MMDA.

Supplementary Material Available: NMR (^1H and ^{13}C), UV, and mass spectral data for all adducts (6 pages). Ordering information is given on any current masthead page.

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Preparation of Thiolate-Bridged Dimolybdenum Complexes from Mo-Mo Quadruple Bonds by Both Conventional and Unconventional Reactions

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Transition-metal chemistry with thiolate ligands, SR or SAr, is an important field, with special pertinence to some biochemical problems.[1] It is not always an easy field for the preparative chemist since thiols and thiolate anions are capable of a variety of reactions with metal atoms. We wish to report here some new synthetic chemistry together with structural characterization of representative products. Our synthetic reactions are novel in several ways, but generally in that they employ oxidative addition to quadruple M-M bonds. Other examples of oxidative addition to metal-metal quadruple bonds have appeared in the literature. Compounds containing Mo$\equiv$Mo,[2,3] W$\equiv$W,[4] Re$\equiv$Re,[5] and Mo$\equiv$W[6] cores have been shown to oxidatively add acids (HCl, HBr) and/or halogens. In most cases, extensive ligand rearrangement occurs with concomitant reduction of bond order.

We have found that compounds of the general class $Mo_2X_4L_4$ react with alkyl and aryl disulfides, RSSR, to yield $Mo_2X_4(\mu\text{-}SR)_2L_4$ species. The first such product was serendipitously discovered by the reaction of $K_4Mo_2Cl_8$[7] and 3,6-dithiaoctane (dto) in methanol. Initially, it appeared as if no reaction occurred, but after several weeks large green crystals of $Mo_2Cl_4(\mu\text{-}SEt)_2(dto)_2$, **1**, formed in 12% yield. The reaction is presumably the very novel one shown in eq 1, whereby EtS and ethylene are formed from

$$[Mo_2Cl_8]^{4-} + 3EtSCH_2CH_2SEt \xrightarrow{dto} [MoCl_2(dto)]_2(\mu\text{-}SEt)_2 + C_2H_4 \quad (1)$$

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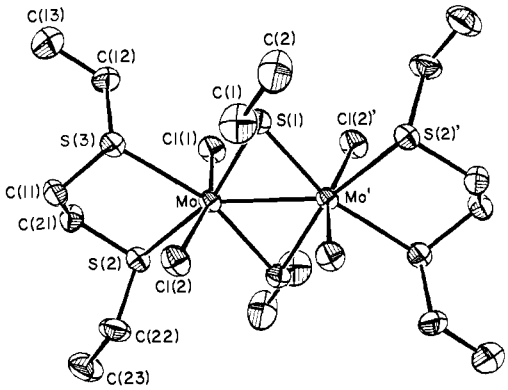

Figure 1. Molecular geometry and atom-labeling scheme for $Mo_2Cl_4(\mu\text{-}SEt)_2(dto)_2$ (**1**). The molecule resides on a center of inversion. Thermal ellipsoids represent 50% of the electron density. Selected bond distances and angles are Mo–Mo = 2.682 (1) Å, average $Mo\text{–}S_{bridging}$ = 2.402 [2] Å, average $Mo\text{–}S_{terminal}$ = 2.579 [1] Å, average Mo–Cl = 2.403 [1] Å, $Mo\text{–}S_b\text{–}Mo$ = 67.90 (3)°, average Mo–Mo–S_t 138.8 [8]°, average Mo–Mo–Cl = 98.46 [4]°.

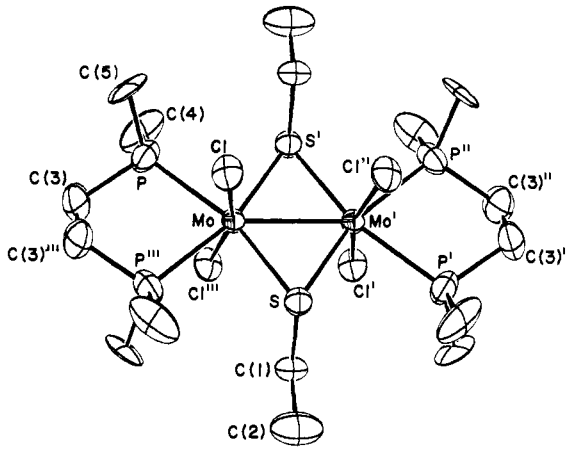

Figure 2. ORTEP view of $Mo_2Cl_4(\mu\text{-}SEt)_2(dmpe)_2$ (**3**) at the 50% probability level. The crystallographic symmetry of the molecule is $2/m$; singly primed, doubly primed, and triply primed atoms are related to unprimed atoms by an inversion center, a mirror plane, and a twofold axis, respectively. Selected bond distances and angles are Mo–Mo = 2.712 (3) Å, Mo–S = 2.411 (4) Å, Mo–P = 2.541 (3) Å, Mo–Cl = 2.417 (3)°, Mo–S–Mo = 68.5 (1)°, Mo–Mo–P = 140.25 (9)°, Mo–Mo–Cl = 98.55 (8)°.

dto.[8] Higher yields (40–45%) of **1** as a green-brown precipitate are obtained when a 1:2:1 ratio of $(NH_4)_5Mo_2Cl_9\cdot H_2O$,[9] dto, and ethyl disulfide (EtSSEt) are refluxed together in methanol for 3–5 h; an IR spectrum[10a] is identical with that of the product from the first procedure. A similar reaction between $(NH_4)_5Mo_2Cl_9\cdot H_2O$, dto, and phenyl disulfide (PhSSPh) yields a yellow-green solid which is probably $Mo_2Cl_4(\mu\text{-}SPh)_2(dto)_2$ (**2**) since its IR spectrum[10b] is similar to that of **1**.

Both **1** and **2** are most likely produced by initial formation of $Mo_2Cl_4(dto)_2$[11] followed by oxidative addition of RSSR. This pathway is supported by the fact that if $(NH_4)_5Mo_2Cl_9\cdot H_2O$ and EtSSEt are refluxed together for a few hours before adding dto, a compound with an IR spectrum quite different from that of **1** is formed. Moreover, the reaction of $\beta\text{-}Mo_2Cl_4(dmpe)_2$[12] with EtSSEt in refluxing toluene yields $Mo_2Cl_4(\mu\text{-}SEt)_2(dmpe)_2\cdot C_7H_8$ (**3**). Interestingly, $Mo_2Cl_4(PMe_2Ph)_4$[13] fails to react with EtSSEt in refluxing toluene, allowing for the recovery of starting material in ca. 95% yield.

The structures of **1** and **3** have been determined by X-ray crystallography[14] and are illustrated in Figures 1 and 2, respectively. Both structures may be described as edge-sharing bioctahedrons, with metal–metal distances (ca. 2.7 Å) indicative of a Mo–Mo bond order of at least 1. Both **1** and **3** are diamagnetic.[15]

To our knowledge, these are the first examples of Mo(III) dimers doubly bridged by alkyl sulfide groups. Efforts are under way to obtain crystals of **2** and related species as we continue to investigate oxidative addition of various reagents to quadruply bonded bimetallic compounds.

Acknowledgment. We are grateful to the National Science Foundation for support.

Supplementary Material Available: Tables of crystallographic data and atomic positional parameters (3 pages). Ordering information is given on any current masthead page.

(8) The fate of the C_2H_4 has not been established and it may not appear as such but rather in some other, as yet unidentified product. Since this procedure generates **1** slowly, it has the virtue of producing it in crystalline form whereas the reaction of $Mo_2Cl_8^{4-}$ with EtSSEt and dto does not.

(9) Brencic, J. V.; Cotton, F. A. *Inorg. Chem.* **1970**, *9*, 346.

(10) Selected infrared absorption frequencies (cm^{-1}) for Nujol mulls. (a) $Mo_2Cl_4(\mu\text{-}SEt)_2(dto)_2$: 1400 s, 1247 m, 1170 w–m, 1145 w–m, 1059 m, 1048 sh, 1039 m, 1005 w, 962 m, 900 m–s, 840 m, 770 sh, 758 m. (b) $Mo_2Cl_4(\mu\text{-}SPh)_2(dto)_2$(?): 1400 s, 1258 m, 1241 m, 1150 sh, 1141 m, 1058 s, 1020 s, 970 m, 898 m, 836 w–m, 800 m, 757 sh, 751 s, 691 m–s.

(11) $Mo_2Cl_4(dto)_2$ was previously shown to form $Mo_2Cl_6(dto)_2$ spontaneously in CH_2Cl_2: Cotton, F. A.; Fanwick, P. E.; Fitch, J. W. III. *Inorg. Chem.* **1978**, *17*, 3254.

(12) Cotton, F. A.; Powell, G. L. *Inorg. Chem.* **1983**, *22*, 1507.

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(14) Tables of crystallographic data and atomic positional parameters (3 pages) are available as supplementary material.

(15) Detailed magnetic measurements on **1** have shown that it has a partially populated triplet state.

Peroxide Coordination to a Dicopper(II) Center. Dioxygen Binding to a Structurally Characterized Phenoxide-Bridged Copper(I) Complex

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There is considerable effort being undertaken to understand the binding, interaction, and subsequent reactivity of dioxygen at copper ion centers. This is in part due to the occurrence of copper-containing enzymes such as hemocyanin[1,2] that bind and transport O_2 and the monooxygenases tyrosinase[1,2b,3] and dopamine β-hydroxylase[3] that incorporate oxygen (from O_2) into organic substrates. Studies of biomimetic chemical models can be useful in elucidating structural and spectroscopic properties of the enzyme active sites as well as reactions occurring at these centers.[4] In addition, information gained in such model studies may apply to the development of useful synthetic systems for oxidation reactions.[5]

We have recently developed a model system which mimics the dioxygen reactivity found in the copper monooxygenases.[6,7] In

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