the reaction conditions, 6-bromofulvene was converted very slowly to IV.

A third possible route, path c, to VI entails the cis 1,2-elimination of the halogen at C_6 to form a severely distorted 2-halogenated bicyclo[3.1.0]hexa-3,5-diene. Nucleophilic addition of dimethylamine at C_6 with concurrent loss of halogen would generate VI and subsequently III after an [1,5]-sigmatropic migration. To establish the feasibility of such a cis elimination, *exo*-6-bromobicyclo[3.1.0]hex-2-ene[5] was prepared and found to react sluggishly even at 25° with potassium *tert*-butoxide. Since the inductive effect of an allylic halogen at C_2 is unlikely to so drastically alter the rate of the cis elimination, path c was no longer considered viable.

In the absence of any alternative mechanisms leading to III, or to 6-*tert*-butoxyfulvene itself, path a, entailing the intermediacy of *m*-benzyne, provides the best explanation of these results.

We have attempted to determine the nature of the ground state of *m*-benzyne. If the C_1–C_5 bond were a weak or nonexistent bond (i.e., structure Ia), hydrogen abstraction would be favored over nucleophilic addition.[16] When II was treated as above but in the presence of cumene (0.4 *M*) III was isolated in the same yield as in the absence of cumene. These experimental data are consistent with the reaction proceeding via a singlet ground state of *m*-benzyne best represented by structure Ib.

In order to gain some insight into which geometrical conformation best represented singlet *m*-benzyne, we performed ab initio SCF calculations utilizing the minimal STO-3G basis functions in the GAUSSIAN 70 series of computer programs.[18] To simplify the undertaking, I was assumed to possess C_{2v} symmetry and carbon-hydrogen bond lengths of 1.08 Å. The total energy was optimized as a function of geometry and bond length. Particular emphasis was placed on the C_1–C_5 bond length as it was varied from 1.4 to 2.41 Å.

Only one minimum, Ic, was found in which the C_1–C_5 bond length was 1.5 Å.[19] The calculated difference in energy between Ic and the hexagonal conformation Ia was 54 kcal. Dewar, using a semiempirical approach (MINDO/3), had similarly found one minimum but the C_1–C_5 separation corresponded to 1.97 Å. For comparative purposes, the total energy of the conformation of I predicted by MINDO/3 to be of lowest energy was calculated using the STO-3G basis set and found to be 21 kcal less stable than Ic.

Our theoretical prediction of a "real" bond as opposed to a reactive weak long bond bridging the dehydrocarbons of I is substantiated by the chemistry of I. In conclusion, we suggest that *m*-benzyne, or 1,3-dehydrobenzene is a misnomer. Instead, bicyclo[3.1.0]hexa-1,3,5-triene more aptly describes the molecule in question. We are continuing our investigations of bicyclo[3.1.0]hexa-1,3,5-triene.

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William N. Washburn
Department of Chemistry, University of California, Berkeley
Berkeley, California 94720

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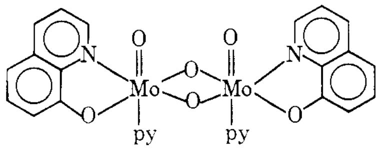
Reactions of Bisoxinato Complexes of $[Mo_2O_4]^{2+}$. I. The Preparation and Structure of the Novel Coordination Compound μ-(2-Mercaptoethanolato-*S:O*)-μ-oxo-bis[oxo-8-hydroxyquinolinatomolybdenum(V)]

Sir:

A variety of chemical and physical studies suggest that Mo(V) coordinated by one or more S atoms may be an important feature of molybdoenzymes.[1] The current interest in molybdoenzymes and the paucity of data for well-characterized molybdenum complexes of sulfur-containing ligands have led to systematic studies of such complexes in our laboratories. Herein we show that the reaction of di-μ-oxo-bis-[oxo-8-hydroxyquinolinatopyridinemolybdenum(V)] (**1**)[2] with 2-mercaptoethanol produces a novel coordination compound (**2**) in which two $[MoO]^{3+}$ units are bridged by *three* donor atoms.

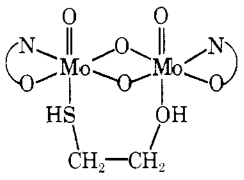


1

Compound (**1**) (1 mmol in 200 ml of absolute ethanol) was combined with 2-mercaptoethanol (1 mmol in 2 ml of ethanol) and the mixture heated slowly to 75° and stirred for 20 min. The air-stable amber yellow powder (**2**) was filtered and washed with ethanol. Compound **2** was insoluble in water, slightly soluble in DMSO and DMF, and soluble in CH_2Cl_2 and $CHCl_3$. **2** decomposed at ~200° and upon treatment with strong acids and bases.

Anal. Calcd for $C_{20}H_{16}SN_2Mo_2O_6$: C, 39.86; H, 2.65; N, 4.65; S, 5.32; Mo, 31.60. Found: C, 39.80; H, 2.67; N, 4.61; S, 5.37; Mo, 31.62

The analyses established that the metal-ligand stoichiometry of **2** was Mo_2(oxine)$_2$(mercaptoethanol), but did not define the Mo:O ratio. Initially **2** was formulated as **3**, a simple substitution product of **1**. Two pieces of negative evidence, however, suggested that structure **3** might not be



3

correct. The ir spectrum showed no O-H or S-H stretching frequencies. The mass spectrum showed no peak corresponding to **3** but did exhibit a mass peak corresponding to **3** less one molecule of water.

Single crystals of **2** were obtained as rhombohedral plates by slow evaporation of a dichloromethane solution. Preliminary precession photographs (Mo Kα) established that the crystals were monoclinic with a = 34.188 (5) Å, b = 7.863 (3) Å, c = 15.335 (9) Å, and β = 93.67 (5)°. The systematic absences hkl for $h + k \neq 2n$ and $h0l$ for $l \neq 2n$ are consistent with space groups Cc or $C2/c$. The latter space group was assumed and verified by successful solution and refinement of the structure. The experimental density of 1.96 (1) g cm^{-3} determined by flotation in aqueous $ZnBr_2$ solution yielded a molecular weight of 607 for eight molecules per unit cell.[3] The intensities of 3746 independent reflections having $2\theta \leq 50°$ were collected on a Picker FACS-1 diffractometer using graphite monochromated Mo Kα radiation and the θ-2θ scan technique.[4] Solution and refinement of the structure utilized the 2807 reflections with $F_o{}^2 \geq 3\sigma(F_o{}^2)$. The positions of the Mo atoms were determined from a Patterson function. The remaining nonhydrogen atoms were located by successive structure factor calculations and difference electron density maps. In the final refinement cycles all atoms except the C atoms of the oxinate ligands were refined anisotropically and H atoms were included as fixed contributions in their calculated positions. The final agreement factors are R_1 = 0.037 and R_2 = 0.049.[5,6]

The structure of **2** is shown in Figure 1. It is evident from Figure 1 that the reaction of **1** with 2-mercaptoethanol does not produce **3** but rather a novel dimeric coordination compound in which the two Mo atoms are bridged by *three* donor atoms. Two of the bridging atoms are the O and S atoms of the 2-mercaptoethanolato dianion. To our knowledge this is the first example of two $[MoO]^{3+}$ units bridged by three donor atoms and the first example of symmetric briging by both the donor atoms of 2-mercaptoethanolate.[7] The average terminal Mo-O distance is 1.693 (4) Å and the Mo-Mo distance is 2.628 (1) Å. Other selected distances and angles appear in Table I. The overall coordination geometry of **2** can be described as two distorted octahedra sharing a face. The two oxinato ligands are cis to one another, and the N atom of each ligand is trans to the bridging S atom. The terminal O atom of each Mo atom is trans to O7, the bridging O atom of the 2-mercaptoethanolato ligand.

The ir spectrum of **2** shows bands at 1376 cm^{-1} (C—O), 949 (Mo═O), 755, and 532 (Mo-O-Mo). The electronic spectrum of **2** is the same in the solid (Nujol mull) and in CH_2Cl_2 solution. The solution spectrum shows a broad band at 390 nm (ϵ ~600) and a peak at 252 nm (ϵ ~2000). Similar bands have been observed in other dimeric Mo(V) complexes.[8] The mass spectrum exhibits several peaks, including a parent ion peak (m/e 604) and peaks which can be assigned to the loss of C_2H_4O and C_2H_4S from **2**. The most prominent peak is m/e 28 (C_2H_4). There is no evidence for fragmentation involving loss of the entire 2-mercaptoethanolate ligand. The compound is diamagnetic in the solid and does not give an ESR signal in solution.

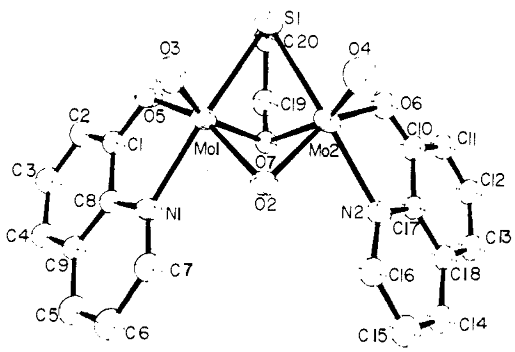


Figure 1. Perspective view of **2**. Hydrogen atoms have been omitted for clarity.

Table I. Selected Interatomic Distances and Angles[a]

Atoms	Distance (Å)	Atoms	Angle (deg)
Mo1–Mo2	2.628 (1)	Mo1–O2–Mo2	85.5 (2)
Mo1–S	2.484 (2)	Mo1–O7–Mo2	73.8 (2)
Mo2–S	2.484 (2)	Mo1–S–Mo2	63.9 (1)
Mo1–O2	1.943 (5)	S–Mo1–O7	70.2 (1)
Mo2–O2	1.930 (5)	S–Mo2–O7	70.6 (1)
Mo1–O7	2.201 (5)	S–Mo1–O2	104.3 (2)
Mo2–O7	2.178 (5)	S–Mo2–O2	104.7 (2)
Mo1–O5	2.021 (5)	O2–Mo1–O7	74.2 (2)
Mo2–O6	2.039 (5)	O2–Mo2–O7	75.0 (2)
Mo1–N1	2.201 (6)	O3–Mo1–O7	158.6 (2)
Mo2–N2	2.209 (6)	O4–Mo2–O7	159.1 (3)
Mo1–O3	1.693 (5)	O5–Mo1–N1	76.8 (2)
Mo2–O4	1.693 (6)	O6–Mo2–N2	75.5 (2)

[a] The standard deviation of the least significant figure is given in parentheses.

Dimeric Mo(V) complexes bridged by one[9] or two[10] donor atoms are well-established. The isolation and characterization of **2** suggest that triply bridged dimeric complexes may also be a common feature of the chemistry of oxomolybdenum(V) and clearly open for reconsideration many structures which have been proposed[11] for Mo(V) complexes of thiol ligands. Our results also underscore the difficulty of deducing the number of oxygen atoms in Mo complexes from chemical analysis and routine spectroscopic measurements.

Reactions of protic reagents with the oxo bridges of complexes of the $[Mo_2O_4]^{2+}$ unit have been previously observed,[12] and conversion of **1** to **2** probably proceeds by reaction 1.

$$\mathrm{Mo_2O_4(oxine)_2(py)_2 + HSCH_2CH_2OH \longrightarrow Mo_2O_3(oxine)_2(SCH_2CH_2O) + 2py + H_2O} \quad (1)$$

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Supplementary Material Available. Final atomic parameters will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm) 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JACS-75-1616.

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(6) Final atomic parameters are available, see note at the end of this communication.

(7) If the bridging ligand were 2-mercaptoethanol itself rather than the 2-mercaptoethanolate dianion, then **2** would be a dimeric Mo(IV) complex. The similarity of the electronic spectrum of **2** to other dimeric oxomolybdenum(V) species[8] and the absence of O–H and S–H bands in the infrared spectrum of **2** support the Mo(V) formulation. Meaningful proton magnetic resonance spectra of **2** could not be obtained because of its low solubility in suitable solvents.

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John I. Gelder, John H. Enemark*
Department of Chemistry, University of Arizona
Tucson, Arizona 85721

G. Wolterman, D. A. Boston, G. P. Haight
Department of Chemistry, University of Illinois
Urbana, Illinois 61801

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Absolute Rate Constants for Reaction of the *tert*-Butylperoxy Radical with 1-Bromo-2-methylpropane and 1-Chloro-2-methylpropane. Kinetic Evidence for Anchimeric Assistance in the Abstraction of a β-Hydrogen Atom for Alkyl Bromides and Chlorides[1]

Sir:

A large amount of effort has been expended to prove[2] and disprove[3] the concept that H-atom transfer reactions can be accelerated by a β substituent via a bridged intermediate. Most of the experimental evidence has, however, been obtained from free radical brominations of alkyl bromides, reactions that may be complicated by the reversibility of the H-atom transfer reactions, and elimination of Br· from β-bromoalkyl radicals.[3]

Alkylperoxy radicals (ROO·) and the bromine atom have similar selectivities to H-atom transfer even though Br· is about 10^6 times more reactive.[4] An alkylperoxy radical should, therefore, be a better probe for anchimeric assistance because accurate rate constants for H-atom abstraction can easily be obtained at very low extents of reaction where the reaction can not be reversible.[5] Furthermore, complications due to β-scission of β-bromoalkyl radicals can be eliminated by performing the reaction in the presence of a substantial concentration of hydroperoxide (ROOH).[6]

In this communication we report the results of a kinetic study of the liquid-phase autoxidation of 1-bromo-2-methylpropane (**1**) and 1-chloro-2-methylpropane (**2**) at 30°. This work provides kinetic evidence in support of anchimeric assistance to H-atom transfer by β-chloro and β-bromo substituents.

Kinetic data for the autoxidation of **1** and **2** in the absence and presence of *tert*-butyl hydroperoxide are summarized in Table I. Overall rates of autoxidation ($-d[O_2]/dt$) were determined from the consumption of oxygen as described previously[6] while rates of chain initiation (R_i) were determined for each run by the induction period method using 2,6-di-*tert*-butyl-4-methoxyphenol as the inhibitor.[7] Oxidizabilities, $k_p/(2k_t)^{1/2}$, were calculated from the kinetic expression

$$\frac{-d[O_2]}{dt} = \frac{k_p[RH]R_i^{1/2}}{(2k_t)^{1/2}} \qquad (I)$$

where k_p and $2k_t$ are the rate controlling propagation and termination rate constants.

1-Bromo-2-methyl-2-hydroperoxypropane and 1-chloro-2-methyl-2-hydroperoxypropane were the only reaction products that could be detected.[8]

Absolute values of $2k_t$ were determined by kinetic electron spin resonance spectroscopy[10] and values of k_p were calculated from eq I.

Both **1** and **2** undergo autoxidation relatively rapidly (i.e., relative to a hydrocarbon with an unactivated tertiary hydrogen, such as 2-methylpropane). The rate of autoxidation of **1** in the absence of $(CH_3)_3COOH$ does, however, increase as the partial pressure of oxygen above the liquid is reduced. This may be because some of the β-bromoalkyl radicals formed during autoxidation undergo β-scission to give isobutylene and a bromine atom (reaction 1) rather than combine with oxygen to give a peroxy radical (reaction 2). The enhanced rate of autoxidation of **1** may, therefore, be because of the involvement of Br· in rate controlling

Table I. Kinetic Data for the Autoxidation of $(CH_3)_2CHCH_2Br$ 1 and $(CH_3)_2CHCH_2Cl$ 2 in the Absence and Presence of *tert*-Butyl Hydroperoxide at 30°

Substrate	Concen (*M*)	$[(CH_3)_3COOH]$ (*M*)	10^7R_i ($M\ sec^{-1}$)	$10^7(-d[O_2]/dt)$ ($M\ sec^{-1}$)	$10^3(k_p/(2k_t)^{1/2})$ ($M^{-1/2}\ sec^{-1/2}$)	k_p ($M^{-1}\ sec^{-1}$)	$10^{-6}(2k_t)$ ($M^{-1}\ sec^{-1}$)
1	9.2		0.2	1.5	0.12	0.07	0.36
1^a	9.2		0.2	3.4	0.27		
1^b	9.2		0.2	145	11		
1	8.3	0.5	1.6	16	0.48	0.017	0.0012^c
1	7.4	2.0	1.7	16	0.52	0.018	0.0012^c
1^a	7.4	2.0	6.0	30	0.52	0.018	
1^b	7.4	2.0	4.0	24	0.52		
2	9.4		0.2	~0.3^d	~0.02^d	~0.02^d	1.2
2	8.5	1.0	0.2	1.25	0.11	0.004	0.0012^c
2	7.5	2.0	0.2	0.85	0.08	0.003	0.0012^c

^{a} O_2 pressure = 140 Torr. ^{b} Containing 0.04 *M* HBr. ^{c} Calculated from the kinetic expression $\log(2k_t/M^{-1}\ sec^{-1}) = 9.2 - 8.5/\theta$, where $\theta = 2.3RT$(kcal mol^{-1}),[11] the measured rate constants in these systems agreed with this value within experimental error. ^{d} Approximate values because of the low kinetic chain length.