planar, and the bond angles about C(2) have olefinic values. The methyl carboxylate substituents are also planar and have expected bond distances and angles.

The possibility of a general series of reactions between the relatively common $Pt(PR_3)_2$(alkyne) complexes and CO to give a dimetallacyclic product is interesting since it involves a formal one-electron oxidation of each metal. It is a reaction which is mediated by CO but where the alkyne ligand serves as the oxidizing agent. Bennett and Yoshida reported the formation of $Pt_2(PPh_3)_2(CO)_2(C_6H_8)$ by treating the platinum(0)–cyclohexyne complex with CO.[3] However, cyclic alkyne complexes prepared with less strained alkynes, cycloheptyne and cyclooctyne, were inert to CO addition. This was rationalized on the basis of the greater electrophilic character of the cyclohexyne ligand in complexes of form $Pt(PPh_3)_2$(alkyne). If complexes of electrophilic alkynes are indeed subject to CO addition and oxidation to Pt(I), the dimetallacyclic species may prove to be an important component of platinum–alkyne chemistry.

Registry No. $Pt_2(CO)_2(PPh_3)_2(C_2(CO_2CH_3)_2)$, 72207-39-7; $Pt(PPh_3)_2(C_2(CO_2CH_3)_2)$, 22853-55-0; $Pt(PPh_3)_2(CO)_2$, 15377-00-1.

Supplementary Material Available: A table of observed and calculated structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

Contribution from the Chemistry Department,
Monash University, Clayton, Victoria, 3168, Australia

Structure and Spectral and Redox Properties of a Dioxomolybdenum(VI) Chelate of *N*-Methyl-*p*-tolylthiohydroxamic Acid, a Complex Containing a $\{O_2MoO_2S_2\}$ Donor Set

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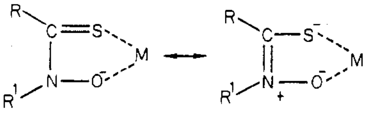
Keith S. Murray,* and Peter J. Newman

Received July 9, 1979

There is much current interest in complexes of molybdenum in which the metal is in oxidation states IV, V, and VI. Complexes with sulfur-containing ligands are of particular interest since they are useful for defining structural and spectroscopic features that can be used to understand the molybdenum active site in redox enzymes such as xanthine oxidase and sulfite oxidase. Recent comparisons of Mo–O and Mo–S distances in model systems (by crystallography or by extended X-ray absorption fine structure (EXAFS)) with those of the enzymes (by EXAFS) suggest that a number of sulfur atoms bind to an O_2Mo^{VI} moiety in the oxidized form of the enzymes.[1] In this paper we describe the first example of a mononuclear Mo(VI) chelate of the type MoO_2(chelate)$_2$ which possesses a donor set $MoO_2(S_2O_2)$. Other combinations such as $MoO_2(O_4)$, $MoO_2(N_2O_2)$, $MoO_2(S_2N_2)$, and $MoO_2(S_4)$ are known.[2] The ligand used in the present work is an N-substituted thiohydroxamic acid which binds to metals in the form of a uninegative bidentate anion via S and O donor atoms:



We have recently investigated a wide range of thiohydroxamate chelates of iron[3,4] and copper.[5] The present study is part of a systematic study of molybdenum complexes with thio ligands ranging from simple unidentate thiolates $\{RS^-\}$[6] to other chelate groups {SX}, where X = S, N, or O.

Experimental Section

The complex $MoO_2(p\text{-}CH_3C_6H_4C({=}S)N(CH_3)O)_2$ was obtained by reacting $(pyH)_2MoOCl_5$, ligand, and sodium methoxide in 1:2:2 mole ratio in dry methanol under nitrogen. The initial green/black solution lightened on stirring and a yellow/green solid deposited which formed yellow columnar crystals when recrystallized in the air from acetone; mp 140 °C. Anal. Calcd for $C_{18}H_{20}MoN_2O_4S_2$: C, 44.3; H, 4.1; N, 5.7. Found: C, 45.0; H, 4.4; N, 5.9.

Cyclic voltammetric measurements were made on a PAR 170 instrument. $Et_4N(ClO_4)$ supporting electrolyte, Pt wire working electrode, and Ag/AgCl reference electrode were used with dry acetone as solvent. $Bu_4N(ClO_4)$ supporting electrolyte and the SCE were used with dichloromethane as solvent.

X-ray Crystallographic Data. For $Mo(C_{18}H_{20}N_2O_4S_2)$ (mol wt 488.5): monoclinic, $a = 12.674$ (7) Å, $b = 12.762$ (7) Å, $c = 13.058$ (8) Å, $\beta = 91.83$ (5)°, $V = 2111.0$ Å^3, $\rho_{obsd} = 1.53$ (2) g·cm^{-3}, $Z = 4$, $\rho_{calcd} = 1.54$ g·cm^{-3}, $F(000) = 991.7$, space group $P2_1/c$ (No. 14), systematic presences $h0l$, $l = 2n$, $0k0$, $k = 2n$, Mo Kα radiation, $\lambda = 0.7107$ Å, μ(Mo Kα) = 7.5 cm^{-1}.

Diffraction data were collected from a columnar crystal of approximate dimensions 0.08 × 0.08 × 0.27 mm at 290 K on a Philips PW 1100 diffractometer, using graphite-monochromated Mo Kα radiation. One quadrant of data was collected (6661 reflections) by the ω-scan technique, with a scan speed of 0.04° s^{-1}, with a symmetric scan range of ±0.65° in θ (with an allowance for dispersion) to the limit $2\theta < 60°$. The intensities of three standard reflections, monitored at regular intervals, showed no significant fluctuation during the data collection period. The raw intensity data were corrected for Lorentz, polarization, and absorption ($\mu = 7.5$ cm^{-1}) effects (absorption because of marked variation in crystal dimensions, transmission coefficients range from 0.88 to 0.95). After averaging of equivalent reflections, a total of 2170 independent reflections ($F^2 > 3\sigma(F^2)$) were used for solution and refinement. The estimated variances in the intensities (used to derive the weights for least-squares refinement) were obtained from counting statistics plus an additional term (0.04 × scan count)^2 to account for errors dependent upon intensity.

Solution and Refinement of the Structure. The position of the molybdenum atom was determined from a three-dimensional Patterson function calculated from intensity data; the remainder of the molecule was located from a difference Fourier map. Full-matrix least-squares refinement[7] was based on minimization of the function $\sum w(|F_o| - |F_c|)^2$, with the weights w taken as $(4F_o^2/\sigma^2(F_o^2))$, where F_o and F_c are the observed and calculated structure factor amplitudes, respectively. Atomic scattering factors and both the real, $\Delta f'$, and imaginary, $\Delta f''$, components of anomalous dispersion were taken from the "International Tables of X-ray Crystallography", Vol. 4. Anisotropic temperature factors were introduced for all nonhydrogen atoms. Hydrogen atoms were included in the refinement in their geometrically calculated positions, with the methyl groups free to rotate about the C–C$_{Me}$ bond (C–H = 1.08 Å).

The final agreement factors are

$$R = \sum||F_o| - |F_c||/\sum|F_o| = 0.047$$

and

$$R_w = \sum w^{1/2}(|F_o| - |F_c|)/\sum w^{1/2}|F_o| = 0.041$$

and the estimated standard deviation of an observation of unit weight is 1.47. The ratio of data to parameters is 8.4:1. Atomic coordinates and thermal parameters for all nonhydrogen atoms are listed in Table I. Some pertinent interatomic distances and angles are listed in Table II. A table of observed and calculated structure factor amplitudes is available.[8]

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0020-1669/80/1319-0773$01.00/0

Table I[a]

	x/a (σ)	y/b (σ)	z/c (σ)	U_{11} (σ)	U_{22} (σ)	U_{33} (σ)	U_{12} (σ)	U_{13} (σ)	U_{23} (σ)
Mo	3950 (1)	4068 (1)	3018 (1)	36 (1)	32 (1)	33 (1)	−3 (1)	−6 (1)	1 (1)
O(2)	3414 (4)	4933 (4)	3851 (4)	67 (4)	51 (4)	49 (3)	6 (3)	−1 (3)	−9 (3)
O(3)	4597 (4)	4853 (4)	2180 (4)	53 (3)	45 (3)	48 (3)	−14 (3)	−8 (3)	15 (3)
S(1)	2126 (1)	3804 (1)	2345 (2)	35 (1)	40 (1)	49 (1)	6 (1)	−3 (1)	−4 (1)
O(1)	4058 (3)	2760 (3)	1991 (3)	28 (2)	38 (3)	38 (3)	−4 (2)	−4 (2)	−5 (2)
N(1)	3206 (4)	2214 (4)	1661 (4)	28 (3)	31 (3)	36 (4)	2 (3)	−4 (3)	−1 (3)
C(1)	3466 (6)	1156 (5)	1328 (6)	48 (6)	35 (5)	44 (5)	8 (4)	−4 (4)	−5 (4)
C(2)	2270 (5)	2625 (6)	1715 (5)	32 (4)	36 (4)	35 (4)	0 (3)	−4 (3)	3 (3)
C(3)	1327 (5)	2144 (5)	1219 (5)	34 (4)	29 (4)	34 (4)	1 (3)	−5 (3)	3 (3)
C(4)	1300 (5)	1972 (6)	173 (6)	26 (4)	62 (5)	48 (5)	−7 (4)	0 (4)	9 (4)
C(5)	380 (6)	1585 (6)	−317 (6)	38 (5)	63 (5)	47 (5)	−8 (4)	−9 (4)	4 (4)
C(6)	−518 (5)	1377 (6)	221 (7)	26 (4)	48 (5)	61 (6)	−5 (4)	−6 (4)	−5 (5)
C(7)	−465 (6)	1541 (6)	1262 (7)	31 (4)	58 (6)	78 (7)	−11 (4)	16 (4)	−1 (5)
C(8)	422 (6)	1927 (6)	1765 (6)	41 (5)	65 (6)	54 (5)	−10 (4)	4 (4)	5 (5)
C(9)	−1494 (6)	991 (7)	−331 (7)	37 (5)	70 (6)	96 (7)	−12 (5)	−21 (5)	2 (6)
S′(1)	5704 (1)	3599 (2)	3730 (2)	36 (1)	49 (1)	52 (1)	−13 (1)	−9 (1)	16 (1)
O′(1)	3662 (3)	2759 (4)	4018 (4)	27 (3)	45 (3)	47 (3)	1 (2)	−0 (2)	11 (3)
N′(1)	4445 (4)	2147 (4)	4390 (4)	29 (3)	38 (4)	32 (3)	0 (3)	−1 (3)	−3 (3)
C′(1)	4078 (6)	1124 (5)	4760 (6)	47 (5)	26 (4)	49 (5)	−3 (3)	−1 (4)	9 (4)
C′(2)	5427 (5)	2451 (6)	4346 (5)	36 (4)	36 (4)	35 (4)	5 (4)	−5 (3)	3 (3)
C′(3)	6310 (5)	1854 (5)	4839 (6)	28 (4)	28 (4)	57 (5)	−5 (3)	−8 (4)	5 (4)
C′(4)	7062 (6)	1388 (6)	4237 (6)	48 (5)	53 (5)	51 (5)	5 (4)	−1 (4)	−6 (4)
C′(5)	7929 (6)	894 (7)	4698 (7)	38 (4)	57 (5)	75 (6)	17 (5)	−5 (4)	−14 (6)
C′(6)	8076 (6)	872 (7)	5738 (7)	33 (5)	59 (6)	78 (7)	6 (5)	−13 (4)	7 (6)
C′(7)	7314 (6)	1339 (7)	6331 (7)	43 (5)	79 (6)	50 (5)	0 (4)	−7 (4)	17 (5)
C′(8)	6451 (6)	1824 (7)	5900 (6)	42 (5)	80 (6)	40 (5)	15 (5)	−1 (4)	10 (5)
C′(9)	9027 (7)	330 (9)	6242 (8)	57 (6)	100 (8)	101 (8)	33 (6)	−21 (6)	7 (7)

[a] Coordinates have been multiplied by 10^4 and anisotropic thermal parameters by 10^3. The form of the thermal ellipsoids is $\exp[-2\pi^2\cdot(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)]$. Estimated standard deviations in the final digit are given in parentheses.

Table II. Some Bond Lengths (Å) and Angles (Deg)

	Metal Distances		
Mo-O(2)	1.706 (5)	M-O′(1)	2.158 (5)
-O(3)	1.713 (5)	-S(1)	2.469 (2)
-O(1)	2.148 (5)	-S′(1)	2.456 (2)
	Ligand Distances		
O(1)-N(1)	1.345 (7)	O′(1)-N′(1)	1.341 (7)
N(1)-C(1)	1.460 (9)	N′(1)-C′(1)	1.473 (9)
-C(2)	1.301 (8)	-C′(2)	1.307 (9)
C(2)-S(1)	1.726 (7)	C′(2)-S′(1)	1.713 (7)
-C(3)	1.475 (9)	-C′(3)	1.484 (10)
C(3)-C(4)	1.383 (10)	C′(3)-C′(4)	1.389 (11)
C(4)-C(5)	1.402 (10)	C′(4)-C′(5)	1.387 (11)
C(5)-C(6)	1.383 (11)	C′(5)-C′(6)	1.366 (13)
C(6)-C(7)	1.375 (12)	C′(6)-C′(7)	1.390 (12)
C(7)-C(8)	1.375 (11)	C′(7)-C′(8)	1.363 (11)
C(3)-C(8)	1.398 (10)	C′(3)-C′(8)	1.392 (11)
C(6)-C(9)	1.496 (11)	C′(6)-C′(9)	1.522 (13)
	Coordination Angles about Molybdenum		
O(2)-Mo-O(3)	103.7 (2)	O(3)-Mo-S(1)	108.3 (2)
O(2)-Mo-O(1)	159.3 (2)	O(1)-Mo-O′(1)	78.0 (2)
O(2)-Mo-O′(1)	92.1 (2)	O(1)-Mo-S′(1)	88.4 (1)
O(2)-Mo-S′(1)	106.9 (2)	O(1)-Mo-S(1)	75.5 (1)
O(2)-Mo-S(1)	85.9 (2)	O′(1)-Mo-S′(1)	75.6 (1)
O(3)-Mo-O(1)	90.8 (2)	O′(1)-Mo-S(1)	86.3 (1)
O(3)-Mo-O′(1)	158.9 (2)	S(1)-Mo-S′(1)	157.98 (7)
O(3)-Mo-S′(1)	86.5 (2)		

Table III. IR, UV, and NMR Features of $MoO_2(p\text{-}CH_3C_6H_4C(=S)N(CH_3)O)_2$

$\nu(Mo\text{-}O_t)$,[a] cm^{-1}	913 s, 887 s
λ_{max}, cm^{-1} (ϵ),[b] in $CHCl_3$	26 315 (2465) metal ligand, 40 000 (41 550) intraligand
^1H NMR in $CDCl_3$ (ppm)	2.40 CH_3 (tolyl), 3.67 $CH_3\text{-}N\text{-}$, 7.2–7.4 aromatic

[a] O_t are terminal oxygens O(2) and O(3) in Figure 2. [b] Units are L mol^{-1} cm^{-1}.

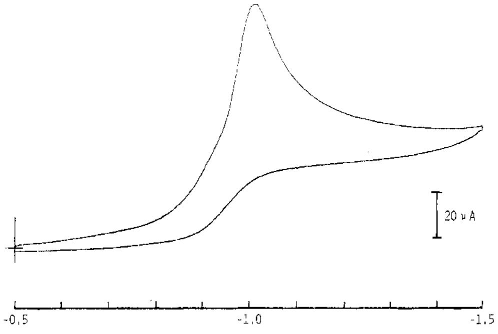

Figure 1. Cyclic voltammogram of $MoO_2(p\text{-}CH_3C_6H_4C(=S)N(CH_3)O)_2$ in acetone at a platinum electrode: scan rate 100 mV s^{-1}, reference electrode Ag/AgCl/0.1 M LiCl–acetone, supporting electrolyte 0.1 M Et_4NClO_4, temperature 25 °C.

Results and Discussion

The complex dioxobis(*N*-methyl-*p*-tolylthiohydroxamato)molybdenum(VI) (I) was obtained by an oxidative route starting from $MoOCl_5^{2-}$. The mechanism of the reaction and isolation of Mo(V) intermediates are being investigated and will be described separately. Other *N*-methyl-substituted complexes with substituents on carbon such as $p\text{-}CH_3OC_6H_4$, $p\text{-}ClC_6H_4$, and C_6H_5 could be obtained by the same route. If ligands were used which contained R′ = H, i.e., non-N-substituted, solid species were obtained which decomposed slowly to yield the appropriate nitrile, RCN. Complex I shows spectroscopic features typical of *cis*-dioxomolybdenum(VI) species (Table III). The single resonances of the $N\text{-}CH_3$ and CH_3(*p*-tolyl) protons in the ^1H NMR spectrum measured in $CDCl_3$ solution show that at ambient temperature the two bidentate ligands are equivalent. The resonances are shifted to slightly lower field compared to their free ligand positions.

A well-defined Mo(VI) → Mo(V) reduction peak, shown in Figure 1, is observed at −1.02 V (relative to Ag/AgCl) in the cyclic voltammogram measured in acetone. A similar peak was observed at −1.18 V (relative to SCE) in CH_2Cl_2 solution. The peak did not shift with increasing scan rate (up to 5 V s^{-1}) and no reoxidation peak was observed even at scan rates

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(8) Supplementary material.

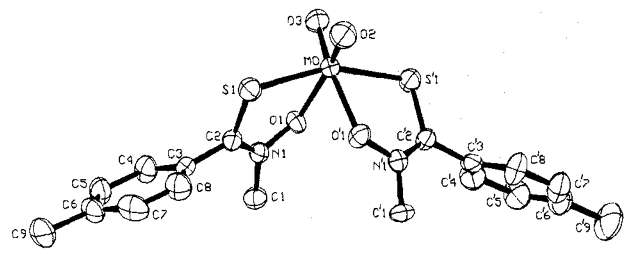

Figure 2. General view and labeling scheme of the molecule (ORTEP-II diagram; 50% ellipsoids). Hydrogen positions have been omitted for clarity.

up to 100 V s^{-1}. This behavior suggests either that the Mo(VI) → Mo(V) electron transfer is irreversible or that the Mo(V) species is rapidly decomposing. The temperature of the cell was gradually reduced to −60 °C to try to slow down any such chemical change but no alteration in the cyclic voltammogram was detected. Electrochemical studies on other MoO_2(chelate)$_2$ systems have generally shown irreversible or quasi-reversible behavior, the E_{pc} values being similar in magnitude to the present value.[9-12] Recently, a reversible Mo(VI) → Mo(V) couple has been observed by cyclic voltammetry[13] in a complex with a tetradentate $\{S_2N_2\}$ aminothiol. The fate of the present Mo(V) species, obtained on reduction, has yet to be ascertained with certainty. There is a lack of detail concerning the Mo(V) species in the electrochemical studies cited above. Spence et al.[12] have suggested that monomeric Mo(V) species produced on reduction of MoO_2(chelate)$_2$ (where chelate = 8-hydroxyquinoline, 8-mercaptoquinoline, and the $\{S_2N_2\}$ tetradentate aminoethanethiol) will spontaneously reduce further because of the relative E_{pc} values for related Mo(V) monomers. It is also possible that the dinuclear Mo(V) species, $Mo^{V}{}_2O_3$(chelate)$_4$, is formed which disproportionates to give $Mo^{IV}O$(chelate)$_2$ and $Mo^{VI}O_2$(chelate)$_2$, a reaction which is now well authenticated for a number of chelated derivatives.[14]

The structure of I is shown in Figure 2. It can be seen that the complex is a monomeric Mo(VI) species with distorted octahedral geometry. The ligand geometry is similar to that observed in a related Fe(III) tris chelate.[15] The MoO_2 moiety has the cis configuration common to dioxomolybdenum(VI) compounds with Mo–O$_t$ distances, 1.706 (5) and 1.713 (5) Å, and O$_t$–Mo–O$_t$ angle, 103.7 (2)°, occurring within the range previously observed.[2] The Mo–O bonds trans to the terminal oxygens have been significantly lengthened and are similar in length to those in MoO_2(diketone)$_2$ chelates.[16-18] The Mo–S bonds cis to the terminal oxygens are similar in length to those found in other thio complexes, e.g., 2.45 Å (average) in $MoO_2((C_3H_7)_2NCS_2)_2$,[8] and are also close to those in the non-oxo molybdenum(VI) complex $Mo(C_6H_5CSN_2H)_3$, 2.400 (5) Å.[19]

It has been noted that the weakest π donors are normally trans to the terminal oxygen atoms.[20] This effect is also apparent in the present structure. The thiolate donor atoms will undoubtedly lie cis to the two oxo groups in some recently studied $\{SN\}$ chelate complexes.[21,22] In Figure 3 the average Mo–ligand bond distances are compared for a representative range of distorted octahedral dioxomolybdenum(VI) species. There are no discernible trends as the ligands are varied, other than the features mentioned above. The MoO_2 moiety appears to dominate the bonding and stereochemistry. The range of structures do, however, provide a rich source of data for comparison with EXAFS results on the oxidized enzymes.

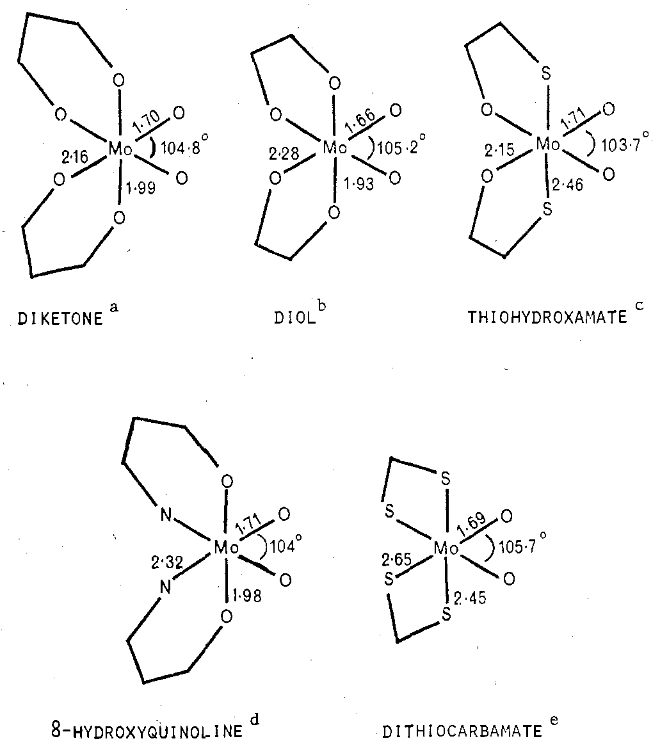

Figure 3. Representation of molybdenum–ligand geometries in a range of MoO_2(chelate)$_2$ complexes showing average Mo–ligand bond lengths: (a) ref 16, 17; (b) ref 20; (c) this work; (d) L. O. Atovmyan and Y. A. Sokolova, *Chem. Commun.*, 649 (1969); (e) ref 18.

The MoO_2 group in compounds of this general type also show novel chemical reactivity toward a variety of substrates, the extent and rate of reactivity being affected by the nature of the coligand.[23-25] A comparison of such reactivity between the present thiohydroxamate complex and other sulfur and non-sulfur-containing Mo(VI) compounds will be particularly interesting.

Acknowledgment. We wish to thank Dr. A. G. Wedd and Mr. D. Brockway for valuable discussion.

Registry No. $MoO_2(p\text{-}CH_3C_6H_4C({=}S)N(CH_3)O)_2$, 72174-98-2; $(pyH)_2MoOCl_5$, 17871-01-1.

Supplementary Material Available: A table of observed and calculated structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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