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## Monomeric Molybdenum(V) Complexes. 2. Comparison of the Structures of *cis*-Oxochlorobis(8-mercaptoquinolinato)molybdenum(V) and *cis*-Dioxobis(8-mercaptoquinolinato)molybdenum(VI)

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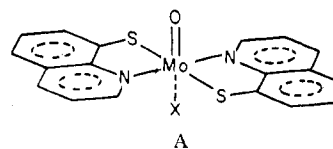
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The crystal and molecular structures of  $\text{MoOCl}(\text{tox})_2$  (**1**) and  $\text{MoO}_2(\text{tox})_2$  (**2**), where tox is the anion of 8-mercaptoquinoline, have been determined by X-ray crystallography. Crystal data for **1**: monoclinic; space group  $P2_1/c$ ;  $a = 15.144$  (2),  $b = 8.498$  (2),  $c = 13.840$  (3) Å;  $\beta = 100.436$  (15)°;  $Z = 4$ ;  $d_{\text{obsd}} = 1.765$  (10),  $d_{\text{calcd}} = 1.774$  g cm<sup>-3</sup>. Crystal data for **2**: orthorhombic; space group  $Pbca$ ;  $a = 9.038$  (3),  $b = 14.825$  (4),  $c = 25.210$  (7) Å;  $Z = 8$ ;  $d_{\text{obsd}} = 1.758$  (10),  $d_{\text{calcd}} = 1.763$  g cm<sup>-3</sup>. Full-matrix least-squares refinement of **1** by use of 1592 independent reflections with  $3.5^\circ < 2\theta \leq 45^\circ$  and  $I \geq 3\sigma(I)$  gave final discrepancy indices  $R_1 = 0.040$  and  $R_2 = 0.043$ . Refinement of **2** based on the 1398 unique data having  $3.5^\circ < 2\theta \leq 50^\circ$  and  $I \geq 3\sigma(I)$  converged at  $R_1 = 0.047$  and  $R_2 = 0.046$ . Compounds **1** and **2** have similar geometries. Both are monomeric with distorted octahedral geometry around each molybdenum atom. The  $\text{MoO}_2^{2+}$  grouping in **2** has the expected *cis* configuration with an O-Mo-O angle of 106.3 (3)°. The  $\text{MoOCl}^{2+}$  unit of **1** also has a *cis* configuration, contrary to earlier proposals, with a Cl-Mo-O angle of 103.0 (2)°. In **1** Mo-Cl = 2.342 (2) Å and Mo-O = 1.716 (4) Å. The average Mo-O distance in **2** is 1.703 (12) Å. The Mo-N bonds *trans* to the oxo groups (2.408 (6) Å in **1** and 2.374 (9) and 2.382 (9) Å in **2**) are ~0.2 Å longer than the Mo-N bond of **1** which is *trans* to the chlorine atom (2.210 (6) Å). The mean Mo-S distances are 2.409 (7) Å for **1** and 2.411 (1) Å for **2**, respectively. The 8-mercaptoquinolate ligands are folded along their S...N vectors in both compounds.

### Introduction

The molybdenum centers of a number of molybdenum-containing enzymes have been probed by EPR spectroscopy.<sup>1-4</sup> In particular, xanthine oxidase has been extensively studied.<sup>1</sup> During turnover, this enzyme shows a distinctive EPR spectrum with a relatively high  $g$  value ( $g = 1.977$ ) and a relatively small hyperfine splitting from <sup>95,97</sup>Mo ( $\langle A \rangle = 34$  G). The interpretation of such EPR spectra in terms of a specific molybdenum coordination environment in the enzyme has been hampered by a lack of definitive data from simple discrete mononuclear molybdenum complexes. Early solution EPR studies of molybdenum(V) in the presence of thiol ligands<sup>5</sup> led to the general assumption that sulfur ligation is important in the enzymes. However, few discrete mononuclear molybdenum(V) complexes of sulfur-containing ligands have been isolated and structurally characterized so that the stoichiometry and stereochemistry of the complex could be related to the observed spectrum.<sup>6-8</sup>

One of the most promising mimics of the EPR spectrum of xanthine oxidase is the species which is extracted into organic solvents when 8-mercaptoquinolate (tox) reacts with molybdenum(V) in aqueous acid.<sup>9</sup> The EPR parameters of this compound are similar to those observed for xanthine oxidase under certain conditions,<sup>1</sup> and structure A with X, a



unidentate monoanion, *trans* to an oxo ligand has been proposed for this complex. Recently  $\text{MoOCl}(\text{tox})_2$  (**1**) has been prepared in pure form and the kinetics of its oxidation by nitrate have been investigated.<sup>10</sup> Herein we show that the stereochemistry of  $\text{MoOCl}(\text{tox})_2$  is not A but that the Cl ligand is *cis* to the oxo group. The structure of the closely related molybdenum(VI) complex,  $\text{MoO}_2(\text{tox})_2$  (**2**), is also described. Compounds **1** and **2** are the first pair of monomeric molybdenum(V) and molybdenum(VI) compounds having common chelate ligands to be structurally characterized. The stereochemistries of such redox-related pairs are of fundamental interest for evaluating the consequences of electron transfer in molybdo enzymes.

### Experimental Section

**Preparation of Crystals.** All preparative manipulations were carried out in a dry nitrogen atmosphere. Solvents were dried and degassed by standard procedures. 8,8'-Diquinoyl disulfide was prepared as previously described.<sup>11</sup>

Table I. Crystallographic Data for MoOCl(tox)<sub>2</sub> (1) and MoO<sub>2</sub>(tox)<sub>2</sub> (2) at 24 °C<sup>a</sup>

	1	2
formula	C <sub>18</sub> H <sub>12</sub> ON <sub>2</sub> S <sub>2</sub> ClMo	C <sub>18</sub> H <sub>12</sub> O <sub>2</sub> N <sub>2</sub> S <sub>2</sub> Mo
mol wt	467.82	448.37
space group	P2 <sub>1</sub> /c (No. 14)	Pbca (No. 61)
cell dimens		
<i>a</i> , Å	15.144 (2)	9.038 (3)
<i>b</i> , Å	8.498 (2)	14.825 (4)
<i>c</i> , Å	13.840 (3)	25.210 (7)
β, deg	100.436 (15)	90.000
<i>V</i> , Å <sup>3</sup>	1751.8 (6)	3377.8 (16)
<i>Z</i>	4	8
<i>d</i> <sub>obsd</sub> , g cm <sup>-3</sup> <sup>b</sup>	1.765 (10)	1.758 (10)
<i>d</i> <sub>calcd</sub> , g cm <sup>-3</sup>	1.774	1.763
crystal shape	parallelepiped	rectangular parallelepiped
crystal dimens, mm	0.09 × 0.10 × 0.11	0.08 × 0.08 × 0.08
radiation (Mo Kα), Å	0.710 73	0.710 73
data collection method	θ-2θ scan	θ-2θ scan
scan speed (variable), <sup>c</sup> deg min <sup>-1</sup>	1.0-29.3	1.0-29.3 (3.5° ≤ 2θ ≤ 40°), 0.5-29.3 (40° ≤ 2θ ≤ 50°)
scan range (2θ), deg	Mo Kα <sub>1</sub> - 0.8 to Mo Kα <sub>2</sub> + 0.8	Mo Kα - 0.8 to Mo Kα + 0.8
total background time/peak scan time	1/2	1/2
std reflections	3 after every 47 readings	3 after every 47 readings
std dev of standards, %	1.77 for (002), <sup>d</sup> 1.78 for (312), 2.17 for (202)	1.91 for (023), 2.18 for (006), 2.34 for (102)
2θ limit, deg	3.5-45	3.5-50
no. of unique data	2302	2991
no. of obsd data ( <i>I</i> > 3σ( <i>I</i> ))	1592	1398
absorption coeff (Mo Kα), cm <sup>-1</sup>	11.25	10.17 <sup>e</sup>

<sup>a</sup> The estimated standard deviation of the least significant figure is given in parentheses in this table and in following tables. <sup>b</sup> Densities were determined by the flotation method using carbon tetrachloride-iodomethane solution. <sup>c</sup> Scan speed was determined as a function of peak intensity. <sup>d</sup> Correction for decomposition was applied (see text). <sup>e</sup> Empirical absorption correction was made (see text).

**Oxochlorobis(8-mercaptoquinolinato)molybdenum(V), MoOCl(tox)<sub>2</sub> (1).** Potassium hexachloromolybdate(III) (2.2 g, 5 mmol) was added to 25 mL of dimethylformamide. The mixture was stirred at ca. 90 °C for 12 h and filtered to remove precipitated potassium chloride. 8,8'-Diquinolyl disulfide (1.6 g, 5 mmol) in 1,2-dichloroethane (40 mL) was added to the reddish orange filtrate, and the solution was refluxed with stirring for 2 h. The resulting dark brown solution was concentrated to about 30 mL under reduced pressure. The purplish brown microcrystals which precipitated were removed by filtration, washed with a small amount of 1,2-dichloroethane and hexane, and dried in vacuo; yield 1.6 g (68%).

The IR, UV, visible, and EPR spectra of the product were identical with those of the sample obtained by the reaction of ammonium oxopentachloromolybdate(V) with 8-mercaptoquinoline in dry ethanol.<sup>10</sup> Crystals of 1 suitable for X-ray study were obtained by slow liquid diffusion of hexane into a saturated solution of 1 in 1,2-dichloroethane.

**Dioxobis(8-mercaptoquinolinato)molybdenum(VI), MoO<sub>2</sub>(tox)<sub>2</sub> (2).** The compound was isolated as dark red crystals from a solution of 1 when insufficiently dried and degassed dichloromethane and pentane were employed as solvents.

**Collection and Refinement of the X-ray Data.** The crystallographic data for the two compounds are summarized in Table I. Intensity data were collected on a Syntex P2<sub>1</sub> autodiffractometer<sup>12</sup> equipped with a scintillation counter and a graphite monochromator by using conditions shown in Table I. The data were reduced to *F*<sub>o</sub><sup>2</sup> and σ(*F*<sub>o</sub><sup>2</sup>) by the procedures previously described.<sup>7</sup> Lorentz-polarization factors were calculated on the assumption of 50% mosaic and 50% perfection of the monochromator crystal. Additional details concerning data collection and data processing for each compound are given below.

**MoOCl(tox)<sub>2</sub> (1).** A well-formed crystal was mounted with its longest dimension (011 axis) approximately parallel to the φ axis of the diffractometer. The axial photographs showed the crystal system to be monoclinic. Examination of a preliminary data set collected in the 2θ range 15-25° revealed the systematic absences 0*kl* for *k* = 2*n* + 1 and 0*0l* for *l* = 2*n* + 1, consistent with the space group P2<sub>1</sub>/c. The cell dimensions given in Table I and the orientation matrix were obtained from a least-squares refinement of the setting angles of 25 automatically centered reflections in this 2θ range.

During the data collection, all three standard reflections showed a steady decline in intensity. Plots of intensity vs. exposure time indicated that the decomposition was linear. The maximum decreases in intensity for the (002), (202), and (312) reflections were 18, 17,

and 21% of the initial intensity, respectively. The data were corrected for decomposition by assuming an isotropic and linear decay with exposure time. Estimated standard deviations of the corrected intensities for the three standard reflections are shown in Table I. The variation in the absorption correction factors (1.09-1.12) is small, and no absorption correction was applied.

**MoO<sub>2</sub>(tox)<sub>2</sub> (2).** A small uniform crystal was examined on the diffractometer. A preliminary data set (15° ≤ 2θ ≤ 25°) together with axial photographs indicated Laue symmetry *mmm* and the systematic absence of 0*kl* when *k* = 2*n* + 1, *h*0*l* when *l* = 2*n* + 1, and *hk*0 when *h* = 2*n* + 1. The observations are uniquely consistent with the orthorhombic space group *Pbca*. The cell parameters shown in Table I were determined from a least-squares refinement of the setting angles of 25 strong reflections with 15° < 2θ < 23°. None of the standard reflections showed any noticeable change in intensity throughout the data collection.

An empirical correction for absorption was made with the program TAPER<sup>12</sup> as previously described.<sup>7</sup> Five strong reflections having χ values of ca. 90° and having 7° < 2θ < 30° were measured by the ψ-scan technique to define the absorption curves. The maximum absorption correction factor was 1.19.

**Solution and Refinement of Structures.** Neutral atomic scattering factors of Cromer and Waber<sup>13a</sup> were used for all atoms except hydrogen, for which the values of Stewart, Davidson, and Simpson<sup>14</sup> were taken. The effects of the real and imaginary components of anomalous dispersion for the molybdenum, sulfur, and chlorine atoms were included in the calculated structure factors by using the values from the tabulation of Cromer.<sup>13b</sup>

The structures were refined by full-matrix, least-squares techniques,<sup>15</sup> minimizing the function ∑w(|*F*<sub>o</sub> - |*F*<sub>c</sub>||)<sup>2</sup>; the weights were assigned as w = 4*F*<sub>o</sub><sup>2</sup>/[σ<sup>2</sup>(*F*<sub>o</sub><sup>2</sup>) + (*pF*<sub>o</sub><sup>2</sup>)<sup>2</sup>] where *p*, the factor to prevent overweighting strong reflections, was set equal to 0.03.<sup>16</sup> The discrepancy indices, *R*<sub>1</sub> and *R*<sub>2</sub>, are defined as *R*<sub>1</sub> = ∑||*F*<sub>o</sub> - |*F*<sub>c</sub>||/∑|*F*<sub>o</sub>| and *R*<sub>2</sub> = [∑w(|*F*<sub>o</sub> - |*F*<sub>c</sub>||)<sup>2</sup>/∑w*F*<sub>o</sub><sup>2</sup>]<sup>1/2</sup>. The "goodness of fit" is defined by GOF = [∑w(|*F*<sub>o</sub> - |*F*<sub>c</sub>||)<sup>2</sup>/(*n* - *m*)]<sup>1/2</sup> where *n* is the number of reflections used in the refinement and *m* is the number of refined parameters.

**MoOCl(tox)<sub>2</sub> (1).** The 1238 significant reflections (2θ ≤ 40°), uncorrected for decomposition, were used for the structure determination and the preliminary least-squares refinement. The structure was solved by direct methods<sup>15</sup> by use of the 400 reflections with the largest values of |*E*|. An "E map" based on the solution with the highest combined form value (2.00) and the lowest residual index

Table II. Atomic Parameters for MoOCl(tox)<sub>2</sub>

Atom	x	y	z	10 <sup>4</sup> β <sub>11</sub> <sup>a</sup>	10 <sup>4</sup> β <sub>22</sub>	10 <sup>4</sup> β <sub>33</sub>	10 <sup>4</sup> β <sub>12</sub>	10 <sup>4</sup> β <sub>13</sub>	10 <sup>4</sup> β <sub>23</sub>
Mo	.22154(5)	.82723(8)	.03990(5)	39.4(4)	102.2(11)	53.4(4)	1.8(6)	10.99(29)	3.1(7)
Cl	.27971(16)	1.03053(28)	.14697(16)	56.6(13)	193.(4)	73.4(16)	-15.9(20)	5.7(12)	-33.4(21)
S(1)	.14144(14)	.74546(26)	.16618(14)	44.4(11)	144.(3)	48.3(13)	-2.2(17)	13.7(10)	-15.4(17)
S(2)	.33368(13)	.86496(24)	-.06161(14)	40.0(11)	142.(4)	52.4(12)	-3.8(16)	8.6(9)	20.8(18)
O	.1449(3)	.9226(5)	-.0470(13)	29.7(25)	104.(8)	53.(3)	8.(4)	-11.0(23)	17.(4)
N(1)	.1768(4)	.5914(7)	-.0161(4)	27.(3)	106.(10)	39.(4)	-3.(5)	1.0(27)	9.(5)
N(2)	.3453(4)	.6648(7)	.1151(4)	32.(3)	121.(10)	38.(3)	-7.(5)	2.8(26)	3.(6)
C(1)	.1936(4)	.5396(9)	-.1017(5)	27.(4)	148.(15)	36.(5)	5.(6)	6.(3)	7.(7)
C(2)	.1663(5)	.3922(10)	-.1385(5)	41.(5)	147.(15)	46.(5)	-7.(7)	6.(4)	-27.(7)
C(3)	.1223(5)	.2950(9)	-.0874(6)	42.(4)	132.(16)	53.(5)	-5.(6)	3.(4)	-17.(7)
C(4)	.1017(4)	.3444(9)	.0033(5)	30.(4)	100.(13)	47.(5)	5.(6)	-1.(3)	12.(7)
C(5)	.0543(5)	.2515(9)	.0603(6)	38.(4)	116.(13)	62.(6)	-1.(6)	0.(4)	8.(7)
C(6)	.0341(5)	.3081(10)	.1463(6)	34.(4)	162.(17)	55.(5)	-2.(7)	8.(4)	34.(8)
C(7)	.0622(5)	.4587(10)	.1790(5)	36.(4)	154.(15)	40.(5)	8.(7)	4.(4)	17.(7)
C(8)	.1086(5)	.5549(8)	.1261(5)	28.(4)	125.(13)	35.(4)	13.(6)	1.(3)	12.(6)
C(9)	.1301(4)	.4970(8)	.0373(5)	19.(3)	109.(13)	37.(4)	9.(5)	-1.(3)	13.(6)
C(10)	.3410(5)	.5660(9)	.1871(5)	43.(5)	146.(15)	49.(5)	3.(7)	13.(4)	11.(8)
C(11)	.4135(6)	.4711(10)	.2327(5)	51.(5)	164.(15)	42.(5)	20.(8)	5.(4)	25.(7)
C(12)	.4940(5)	.4887(10)	.2058(5)	42.(5)	153.(16)	45.(5)	22.(7)	-9.(4)	-3.(7)
C(13)	.5027(5)	.5949(9)	.1296(5)	42.(5)	112.(13)	42.(5)	-8.(7)	7.(4)	-22.(7)
C(14)	.5847(5)	.6198(10)	.0971(6)	35.(5)	151.(16)	62.(6)	11.(7)	0.(4)	-26.(8)
C(15)	.5902(5)	.7194(10)	.0227(7)	31.(4)	154.(17)	74.(6)	-4.(7)	17.(4)	-18.(8)
C(16)	.5129(6)	.7970(9)	-.0254(5)	53.(5)	114.(14)	50.(5)	-13.(7)	11.(4)	-9.(7)
C(17)	.4315(5)	.7784(8)	.0031(5)	33.(4)	100.(13)	50.(5)	-11.(5)	14.(4)	-12.(6)
C(18)	.4253(5)	.6802(9)	.0840(5)	35.(4)	103.(12)	43.(4)	-4.(6)	7.(3)	-12.(7)

<sup>a</sup> Anisotropic thermal parameters are in the form:  $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$ .

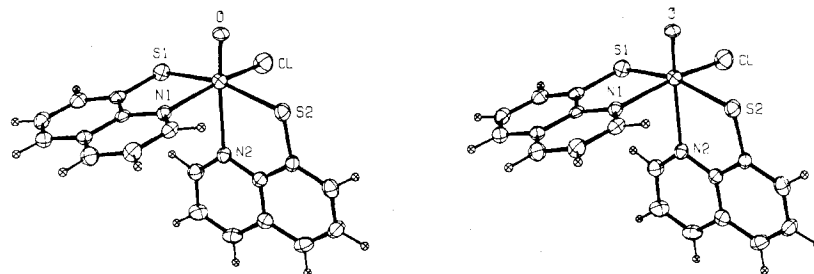


Figure 1. Stereoview of the MoOCl(tox)<sub>2</sub> molecule. The hydrogen atoms have been assigned arbitrarily small thermal parameters for clarity. Thermal ellipsoids are drawn to enclose 30% of the probability distribution.

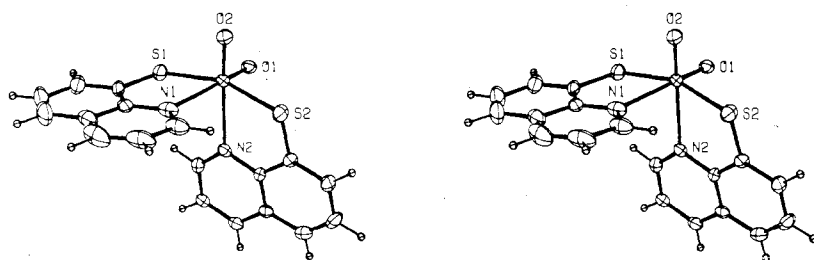


Figure 2. Stereoview of the MoO<sub>2</sub>(tox)<sub>2</sub> molecule. The hydrogen atoms have been assigned arbitrarily small thermal parameters for clarity. Thermal ellipsoids are drawn to enclose 30% of the probability distribution.

(31.1%) clearly showed the positions of 22 atoms of the 25 nonhydrogen atoms of **1**. The three remaining carbon atoms were readily located by a difference electron-density map.

Least-squares refinement of the structure utilized the 1592 data which had  $I \geq 3\sigma(I)$  and  $3.5^\circ < 2\theta \leq 45^\circ$  and which had been corrected for decomposition. Refinement of the model with anisotropic thermal parameters for all nonhydrogen atoms converged with  $R_1 = 0.048$ ,  $R_2 = 0.054$ , and GOF = 1.952. A difference electron-density map calculated at this stage revealed the positions of all 12 hydrogen atoms. The hydrogen atoms were included as fixed contributions in subsequent cycles of refinement. The positions of the hydrogen atoms were idealized by assuming trigonal geometry about the carbon atoms and C-H = 0.95 Å.<sup>17</sup> Each hydrogen atom was assigned an isotropic thermal parameter 1 Å<sup>2</sup> greater than the value for its bonded carbon atom. In the final cycle of full-matrix least-squares refinement, 226 parameters were allowed to vary. All shifts were less than  $0.3\sigma$ . Final discrepancy indices were  $R_1 = 0.040$ ,  $R_2 = 0.043$ , and GOF = 1.538; the overdetermination ratio ( $n/m$ ) was 7.0. An analysis of  $w(\Delta F)^2$  showed no appreciable dependence upon either  $(\sin \theta)/\lambda$  or  $|F_o|$ . The largest residual in the final difference electron-density map was 1.17

e Å<sup>-3</sup> near the molybdenum atom. All other peaks were less than 0.5 e Å<sup>-3</sup>. A structure factor calculation for all 2302 independent reflections yielded  $R_1 = 0.072$  and  $R_2 = 0.049$ .

**MoO<sub>2</sub>(tox)<sub>2</sub> (2).** The structure of **2** was solved by direct methods using the 350 reflections with the largest  $|E|$  values. The solution using the highest combined form value (2.09) and the lowest residual index (64.4%) gave the position of the molybdenum atom in an "E map". Two cycles of least-squares refinement on the scale factor and the positional parameters of the molybdenum atom led to  $R_1 = 0.400$  and  $R_2 = 0.459$ . A series of least-squares refinements and difference electron-density maps revealed the remaining 24 nonhydrogen atoms. Least-squares refinement of the structure utilized the 1398 data with  $I \geq 3\sigma(I)$ . Refinement of the model with anisotropic thermal parameters for all nonhydrogen atoms converged with  $R_1 = 0.051$ ,  $R_2 = 0.052$ , and GOF = 1.441. A difference electron-density map revealed all six hydrogen atoms of one of the tox ligands (H(1)–H(3), H(5)–H(7)). Hydrogen atoms could not be determined for the other tox ring which has relatively larger thermal motion for the carbon atoms. Idealized positions were calculated for all hydrogen atoms and these atoms were included as fixed contributions in subsequent

Table III. Atomic Parameters for MoO<sub>2</sub>(tox)<sub>2</sub>

Atom	x	y	z	10 <sup>4</sup> β <sub>11</sub> <sup>a</sup>	10 <sup>4</sup> β <sub>22</sub>	10 <sup>4</sup> β <sub>33</sub>	10 <sup>4</sup> β <sub>12</sub>	10 <sup>4</sup> β <sub>13</sub>	10 <sup>4</sup> β <sub>23</sub>
Mo	.13638(10)	.10607(5)	.10062(4)	77.4(9)	31.2(4)	11.36(13)	4.7(8)	-.2(5)	3.50(28)
S(1)	.0199(3)	-.03872(19)	.11290(12)	110.(4)	38.5(13)	16.5(6)	-8.5(21)	3.3(13)	2.4(7)
S(2)	.31940(29)	.22431(17)	.10226(16)	111.(4)	28.4(11)	22.0(6)	-.4(18)	10.4(16)	-1.3(9)
O(1)	.1009(7)	.0962(5)	.03488(24)	83.(10)	52.(4)	11.2(12)	9.(6)	-3.4(27)	2.4(21)
O(2)	.0115(8)	.1825(5)	.12483(28)	102.(11)	42.(4)	16.8(15)	8.(6)	7.(3)	1.4(20)
N(1)	.1892(10)	.0710(6)	.1909(3)	109.(14)	57.(6)	11.7(17)	23.(7)	-5.(4)	-5.4(27)
N(2)	.3641(10)	.0291(5)	.08824(29)	87.(10)	27.(4)	10.8(16)	2.(7)	-8.(4)	.8(18)
C(1)	.2638(15)	.1260(9)	.2211(4)	138.(19)	72.(9)	14.8(22)	20.(11)	-16.(6)	-6.(4)
C(2)	.2767(17)	.1120(13)	.2766(5)	176.(26)	114.(13)	15.0(27)	51.(17)	-24.(7)	-11.(5)
C(3)	.2183(21)	.0392(14)	.2987(6)	266.(36)	123.(15)	10.4(26)	86.(19)	-4.(8)	-1.(5)
C(4)	.1390(18)	-.0241(11)	.2681(5)	158.(21)	97.(10)	12.3(23)	65.(15)	12.(8)	11.(4)
C(5)	.0700(21)	-.1068(14)	.2867(7)	269.(38)	113.(15)	22.(4)	51.(20)	34.(9)	29.(7)
C(6)	-.0014(25)	-.1602(11)	.2559(8)	276.(37)	82.(12)	32.(5)	50.(18)	33.(11)	33.(6)
C(7)	-.0214(15)	-.1398(8)	.2020(6)	161.(22)	48.(7)	22.(3)	10.(11)	23.(7)	8.(4)
C(8)	.0438(12)	-.0638(7)	.1797(5)	110.(18)	31.(5)	18.1(24)	11.(8)	16.(5)	9.(3)
C(9)	.1257(15)	-.0051(8)	.2130(4)	95.(15)	57.(7)	12.5(21)	33.(11)	12.(6)	7.(3)
C(10)	.3771(13)	-.0603(6)	.0874(4)	106.(15)	34.(5)	11.9(21)	-9.(9)	0.(5)	1.4(23)
C(11)	.5036(11)	-.1060(7)	.0710(4)	94.(14)	37.(5)	13.8(19)	12.(10)	-2.(4)	5.(3)
C(12)	.6239(13)	-.0590(7)	.0535(4)	95.(15)	47.(6)	10.5(19)	21.(9)	-1.(5)	1.6(25)
C(13)	.6175(12)	.0363(7)	.0547(4)	84.(15)	40.(5)	9.8(18)	-3.(9)	-10.(5)	1.2(25)
C(14)	.7337(12)	.0909(8)	.0362(4)	91.(15)	55.(8)	11.8(20)	14.(10)	-2.(5)	-3.(3)
C(15)	.7230(13)	.1824(9)	.0378(5)	83.(17)	60.(7)	16.2(25)	-27.(10)	1.(5)	1.(3)
C(16)	.5936(12)	.2242(7)	.0575(5)	109.(18)	40.(6)	16.3(24)	-27.(8)	-12.(5)	3.(3)
C(17)	.4765(11)	.1734(7)	.0753(4)	77.(14)	30.(5)	14.7(21)	-20.(8)	-14.(5)	-.7(28)
C(18)	.4860(11)	.0784(6)	.0727(4)	73.(14)	28.(5)	10.1(18)	-4.(7)	2.(4)	1.3(25)

<sup>a</sup> Anisotropic thermal parameters are in the form:  $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$ .

Table VIII. Interatomic Distances (Å) in MoOCl(tox)<sub>2</sub> (1) and MoO<sub>2</sub>(tox)<sub>2</sub> (2)

	1	2		1	2
Mo-X <sup>a</sup>	2.342 (2)	1.694 (6)	Mo-Y <sup>a</sup>	1.716 (4)	1.712 (7)
Mo-S(1)	2.403 (2)	2.411 (3)	Mo-S(2)	2.414 (2)	2.411 (3)
Mo-N(1)	2.210 (6)	2.382 (9)	Mo-N(2)	2.408 (6)	2.374 (9)
S(1)-C(8)	1.754 (8)	1.738 (12)	S(2)-C(17)	1.748 (7)	1.746 (11)
N(1)-C(9)	1.371 (8)	1.383 (14)	N(2)-C(18)	1.363 (8)	1.379 (12)
N(1)-C(1)	1.331 (8)	1.305 (14)	N(2)-C(10)	1.313 (9)	1.331 (11)
C(1)-C(2)	1.387 (10)	1.419 (16)	C(10)-C(11)	1.415 (10)	1.391 (14)
C(2)-C(3)	1.340 (10)	1.325 (22)	C(11)-C(12)	1.346 (11)	1.365 (14)
C(3)-C(4)	1.411 (10)	1.412 (22)	C(12)-C(13)	1.412 (10)	1.415 (14)
C(4)-C(5)	1.403 (10)	1.453 (22)	C(13)-C(14)	1.411 (10)	1.405 (15)
C(5)-C(6)	1.369 (10)	1.284 (25)	C(14)-C(15)	1.347 (11)	1.361 (16)
C(6)-C(7)	1.397 (11)	1.405 (21)	C(15)-C(16)	1.402 (11)	1.414 (16)
C(7)-C(8)	1.373 (10)	1.390 (15)	C(16)-C(17)	1.370 (10)	1.374 (14)
C(8)-C(9)	1.415 (9)	1.418 (16)	C(17)-C(18)	1.413 (9)	1.413 (13)
C(9)-C(4)	1.419 (10)	1.422 (15)	C(18)-C(13)	1.425 (10)	1.417 (14)
S(1)-N(1)	2.976 (6)	2.975 (10)	S(2)-N(2)	2.958 (6)	2.944 (18)
S(1)-N(2)	3.361 (6)	3.327 (10)	S(2)-N(1)	3.462 (6)	3.398 (10)
S(1)-X	3.244 (3)	2.899 (7)	S(2)-Y	2.943 (5)	2.907 (8)
S(1)-Y	3.322 (5)	3.294 (8)	S(2)-X	3.440 (3)	3.224 (7)
X-N(2)	3.317 (7)	2.908 (10)	Y-N(1)	2.874 (7)	2.844 (11)
X-Y	3.198 (5)	2.726 (10)	N(1)-N(2)	2.919 (7)	3.095 (12)

<sup>a</sup> X = Cl and Y = O for 1. X = O(1) and Y = O(2) for 2.

refinements (vide supra). Two additional cycles of full-matrix least-squares refinement (226 variables) led to final convergence with  $R_1 = 0.047$ ,  $R_2 = 0.046$ , and  $\text{GOF} = 1.268$  ( $n/m = 6.2$ ). All parameter shifts during the final cycle of refinement were less than  $0.4\sigma$ . The value of  $w(\Delta F)^2$  was not significantly dependent upon either  $(\sin \theta)/\lambda$  or  $|F_o|$ . The final difference electron-density map showed no peak greater than  $0.64 \text{ e } \text{Å}^{-3}$ . A structure factor calculation for all 2991 unique data gave  $R_1 = 0.135$  and  $R_2 = 0.063$ . The large values of the discrepancy indices result from the large number of unobserved reflections due to the small size of the crystal.

The final nonhydrogen atomic parameters with their estimated standard deviations for MoOCl(tox)<sub>2</sub> are given in Table II. The corresponding parameters for MoO<sub>2</sub>(tox)<sub>2</sub> are listed in Table III. Tables IV and V give the root-mean-square amplitudes of vibration for the anisotropic atoms.<sup>18</sup> The fixed positional and thermal parameters for hydrogen atoms appear in Tables VI and VII.<sup>18</sup> Tables of  $10|F_o|$  and  $10|F_c|$  values for the two compounds are available.<sup>18</sup>

### Comparison of Structures

Interatomic distances and angles with their estimated

standard deviations for the MoOCl(tox)<sub>2</sub> (1) and MoO<sub>2</sub>(tox)<sub>2</sub> (2) compounds are listed in Tables VIII and IX. Figure 1 shows a stereoview of one molecule of 1 together with the labeling scheme, while the corresponding drawing of 2 appears in Figure 2.

The geometries of the two compounds are strikingly similar. In the monomeric molecules of 1 and 2, the individual molybdenum atoms are in a severely distorted octahedral environment and coordinated to two bidentate 8-mercaptoquinolate ligands and two unidentate ligands. These unidentate ligands, an oxo ligand and a chloride ligand in 1 and two oxo ligands in 2, occupy *cis* positions in both molecules. The sulfur atoms from the 8-mercaptoquinolate ligands are *trans* to each other.

As expected, the molybdenum atom is displaced from the center of each octahedron toward the terminal oxygen atom. The displacements of the molybdenum atom are  $0.25 \text{ Å}$  from the respective (O, S, N, S) planes in 2, and  $0.33 \text{ Å}$  from the

Table IX. Interatomic Angles (deg) in MoOCl(tox)<sub>2</sub> (1) and MoO<sub>2</sub>(tox)<sub>2</sub> (2)

	1	2		1	2
S(1)-Mo-N(1) <sup>a</sup>	80.21 (16)	76.7 (3)	S(2)-Mo-N(2) <sup>a</sup>	75.69 (14)	75.9 (2)
X-Mo-S(1)	86.26 (8)	88.1 (3)	Y-Mo-S(2)	89.24 (17)	88.0 (3)
X-Mo-S(2)	92.67 (8)	102.1 (3)	Y-Mo-S(1)	106.28 (18)	104.8 (3)
X-Mo-N(1)	161.28 (15)	162.4 (3)	Y-Mo-N(2)	161.53 (21)	159.5 (3)
X-Mo-N(2)	88.57 (15)	89.7 (3)	Y-Mo-N(1)	93.27 (21)	86.3 (3)
S(1)-Mo-N(2)	88.62 (14)	88.1 (2)	S(2)-Mo-N(1)	96.86 (16)	90.3 (3)
S(1)-Mo-S(2)	164.30 (7)	160.9 (1)	N(1)-Mo-N(2)	78.29 (19)	81.2 (3)
X-Mo-Y	102.96 (17)	106.3 (3)			
Mo-S(1)-C(8)	100.86 (24)	105.1 (4)	Mo-S(2)-C(17)	105.44 (24)	103.7 (3)
Mo-N(1)-C(9)	119.8 (5)	118.7 (7)	Mo-N(2)-C(18)	118.4 (5)	118.4 (6)
Mo-N(1)-C(1)	121.1 (5)	121.7 (8)	Mo-N(2)-C(10)	123.5 (5)	123.9 (8)
C(9)-N(1)-C(1)	119.1 (6)	119.3 (10)	C(18)-N(2)-C(10)	118.0 (6)	116.9 (9)
N(1)-C(1)-C(2)	122.2 (7)	121.8 (14)	N(2)-C(10)-C(11)	124.2 (7)	124.2 (10)
C(1)-C(2)-C(3)	120.5 (7)	120.1 (15)	C(10)-C(11)-C(12)	118.8 (7)	120.1 (9)
C(2)-C(3)-C(4)	119.8 (7)	120.9 (14)	C(11)-C(12)-C(13)	119.3 (7)	118.1 (10)
C(3)-C(4)-C(5)	123.4 (7)	127.0 (15)	C(12)-C(13)-C(14)	122.7 (8)	122.5 (10)
C(3)-C(4)-C(9)	117.7 (7)	116.5 (15)	C(12)-C(13)-C(18)	118.4 (7)	118.7 (10)
C(9)-C(4)-C(5)	118.9 (7)	116.6 (15)	C(18)-C(13)-C(14)	118.9 (7)	118.7 (9)
C(4)-C(5)-C(6)	120.6 (7)	122.7 (16)	C(13)-C(14)-C(15)	121.2 (7)	120.8 (10)
C(5)-C(6)-C(7)	120.0 (7)	121.2 (16)	C(14)-C(15)-C(16)	119.8 (7)	120.4 (11)
C(6)-C(7)-C(8)	121.9 (7)	120.7 (14)	C(15)-C(16)-C(17)	121.8 (7)	120.8 (10)
C(7)-C(8)-C(9)	118.4 (7)	118.7 (11)	C(16)-C(17)-C(18)	119.2 (7)	119.0 (10)
S(1)-C(8)-C(7)	121.6 (6)	120.8 (11)	S(2)-C(17)-C(16)	121.8 (6)	121.1 (8)
S(1)-C(8)-C(9)	119.9 (5)	120.5 (8)	S(2)-C(17)-C(18)	118.9 (5)	119.9 (8)
N(1)-C(9)-C(8)	119.1 (6)	118.6 (9)	N(2)-C(18)-C(17)	119.8 (6)	117.8 (9)
N(1)-C(9)-C(4)	120.7 (6)	121.3 (13)	N(2)-C(18)-C(13)	121.2 (7)	121.9 (8)
C(4)-C(9)-C(8)	120.2 (6)	120.1 (13)	C(13)-C(18)-C(17)	119.0 (6)	120.3 (10)

<sup>a</sup> X = Cl and Y = O for 1. X = O(1) and Y = O(2) for 2.

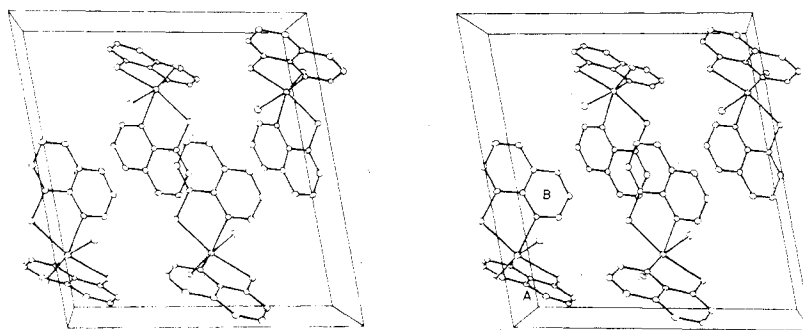


Figure 3. Stereoview of the packing of MoOCl(tox)<sub>2</sub>. The positive direction of the *b* axis is perpendicular to the paper toward the reader. The positive direction of the *c* axis is horizontal to the right. The chloride ligand has a bigger thermal ellipsoid than the oxo ligand: A, S(1), C(1)-C(9), N(1); B, S(2), C(10)-C(18), N(2).

equatorial (Cl, S, N, S) plane in 1.

The Mo-O distance of 1.716 (4) Å in 1 is nearly identical with the mean Mo-O distance of 1.703 (13) Å for 2. The Mo-Cl distance in 1 is 2.342 (2) Å. The *cis*-MoOCl<sup>2+</sup> grouping of 1 has a Cl-Mo-O angle of 102.96 (17)°, slightly smaller than the O-Mo-O angle of 106.3 (3)° for the *cis*-MoO<sub>2</sub><sup>2+</sup> group of 2. The Mo-S bond lengths in both compounds are little different from each other; the mean of the four Mo-S bonds is 2.410 (5) Å. Significant differences, however, are observed among the Mo-N bonds. In 1 the Mo-N(1) bond (2.210 (6) Å) is trans to the chlorine atom and is ca. 0.2 Å shorter than Mo-N(2) (2.408 (6) Å) which is trans to the oxo group. The latter distance is slightly longer than the average of the corresponding Mo-N distances (2.378 (6) Å) in 2.

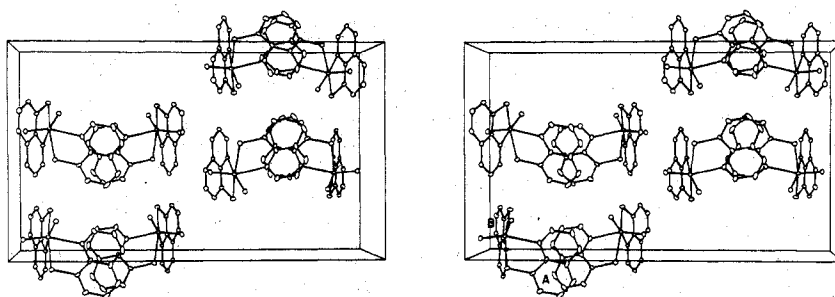
Another significant deviation is found among S-Mo-N chelate bite angles. The S(1)-Mo-N(1) bite angle of 1 (80.2 (2)°) which involves the nitrogen atom that is trans to the chlorine atom is significantly larger than the average (76.1 (5)°) of other three bite angles which involve the nitrogen atoms in the trans positions of the oxo groups. Since the Mo-S distances and the chelate bite distance are nearly the same for all of the tox ligands in 1 and 2 (Table VIII), the shorter Mo-N distance results in a larger bite angle.

Table X. Dihedral Angles (deg) of MoOCl(tox)<sub>2</sub> (1) and MoO<sub>2</sub>(tox)<sub>2</sub> (2)

plane 1	plane 2	1	2
Mo, S(1), N(1)	Mo, S(2), N(2)	78.4	81.2
Mo, S(1), N(1)	Mo, X, Y <sup>a</sup>	106.3	105.0
Mo, S(2), N(2)	Mo, X, Y	92.7	102.2
Mo, S(1), N(1)	ligand A <sup>b</sup>	2.6	6.0
Mo, S(2), N(2)	ligand B	11.1	18.2
ligand A <sup>b</sup>	ligand B	95.9	98.5

<sup>a</sup> X = Cl and Y = O for 1. X = O(1) and Y = O(2) for 2. <sup>b</sup> Ligand A: S(1), C(1)-C(9), N(1). Ligand B: S(2), C(10)-C(18), N(2).

Compound 1 has no symmetry, whereas the coordination polyhedron of 2 has an approximate C<sub>2</sub> axis which bisects the O...O edge. Close examination of the structure of 2, however, reveals that the 8-mercaptoquinolate ligands are unequally folded toward the terminal oxygen atoms along their S...N vectors. Ligand A makes a dihedral angle of 6.0° with its coordination plane, while the dihedral angle between ligand B and its coordination plane is 18.2° (Table X). As a result, the overall structure significantly departs from C<sub>2</sub> point symmetry. The structure of 1 also exhibits a similar pattern



**Figure 4.** Stereoview of the packing of  $\text{MoO}_2(\text{tox})_2$ . The positive direction of the  $a$  axis is perpendicular to the paper away from the reader. The positive direction of the  $c$  axis is horizontal to the right: A, S(1), C(1)–C(9), N(1); B, S(2), C(10)–C(18), N(2).

of ligand foldings; that is, ligand B is folded toward the chlorine atom, whereas ring A is nearly coplanar with its coordination plane.

Inspection of the packing diagrams and the intra- and intermolecular contacts of both compounds suggests that the folding of ligand B in **1** and **2** arises from the intermolecular repulsions between ligand rings in the solid. Figure 3 shows a stereoview of the crystal structure of compound **1** projected down the  $a$  axis. The crystal packing of compound **2** viewed along the  $b$  axis is shown in Figure 4. Selected intermolecular contacts in **1** and **2** are given in Tables XI and XII,<sup>18</sup> respectively.

The molecules of **1** pack with the planes of A ligands being nearly parallel to the  $b$  axis. The planes of B ligands, which are related to each other by inversion centers, stack along this axis with two distinct contact distances: (1) the distance between two "top" faces; (2) the distance between the "bottom" faces (the top face of a plane is the side adjacent to a unidentate ligand). As shown in Table XI,<sup>18</sup> most of the nonbonded contacts of ligand B occur on the bottom side. In the absence of folding the separation between the bottom faces of B ligands would be only 2.55 Å. Consequently, ligand B is folded along its S...N vector toward the chlorine atom so as to relieve the strong interactions between the bottom faces. Observed distances are 3.45 Å, between the bottom faces, and 3.19 Å, between the top faces. The folding of ligand B also decreases the edge-to-face interactions between A and B; the shortest C...H contact is 2.77 Å between C(1) and H(14). The minimum contact between the planes of two A ligands in the absence of folding would be 3.50 Å, comparable to van der Waals contacts of phenyl rings.<sup>19</sup> Hence, the observed deviation of ligand A from planarity is small.

In the molecular packing of **2**, on the other hand, an edge-to-face interaction plays an important role. Molecules related to each other by an  $a$  glide plane interact weakly through their A planes (carbon atoms in this ligand show relatively larger thermal motions). The dihedral angle between these planes is 22°. The A ligands stack along the  $a$  axis, whereas the rings of the B ligands are aligned approximately perpendicular to the  $c$  axis. A strong edge-to-face contact occurs between the top face of ligand B and the edge of ligand A in an  $a$ -glide-related molecule. The stereochemistry of these inter-ring interactions favors deformation of the ligand skeleton of B away from the edge of ligand A.<sup>20</sup> The shortest distance among the edge-to-face contacts is 2.76 Å between C(11) and H(5), and the distance between inversion-related B ligand planes is 3.28 Å.

Little variation is observed among the chemically equivalent angles and distances of the four 8-mercaptoquinolinate ligands in **1** and **2**. The average S–C distance is 1.746 (7) Å. One of the two N–C distances in the chelate is consistently shorter than the other; the average for the shorter distance is 1.320 (13) Å and that for the longer distances is 1.374 (9) Å. The mean C–C distance is 1.392 (28) Å for **1** and 1.394 (40) Å for **2**, in good agreement with that of aromatic rings,<sup>21</sup> although

the individual C–C distances vary widely in the chelate.

## Discussion

To our knowledge, oxochlorobis(8-mercaptoquinolinate)-molybdenum(V),  $\text{MoOCl}(\text{tox})_2$ , is the first six-coordinate monomeric molybdenum(V) compound containing both a terminal oxo grouping and coordinated thiolate ligand to be definitively characterized by X-ray crystallography. The structures of two five-coordinate oxomolybdenum(V) complexes containing sulfur donors,  $\text{MoOCl}_3(\text{SPPH}_3)$ <sup>6</sup> and  $[\text{MoO}(\text{SPh})_4]^-$ ,<sup>8</sup> have been determined. Moreover, no other structural study has been reported on a monomeric pair of oxomolybdenum(V) and dioxomolybdenum(VI) compounds with common organic ligands. It is noteworthy, therefore, that in the present study a *cis* configuration has been found not only for the  $\text{MoO}_2^{2+}$  group in  $\text{MoO}_2(\text{tox})_2$  (**2**) but also for the  $\text{MoOCl}^{2+}$  grouping in  $\text{MoOCl}(\text{tox})_2$  (**1**). Earlier solution ESR studies suggested a *trans* configuration for the latter group.<sup>9</sup> Our serial studies<sup>22–24</sup> on the structures of monomeric oxomolybdenum(V) compounds reveal that chlorine atoms in  $\text{MoOCl}_4^-$ ,  $\text{MoOCl}_3$ , and  $\text{MoOCl}_2^+$  groups are all *cis* to the terminal oxo group as in the present  $\text{MoOCl}^{2+}$  group. These findings are consistent with those obtained for other structures with  $\text{MoOCl}_4^-$  and  $\text{MoOCl}_3$  groups.<sup>6,25–27</sup>

The Mo–O bond lengths observed in compounds **1** and **2** (Table VIII) are in good agreement with previously reported values, ranging from 1.65 to 1.72 Å, for six-coordinate oxomolybdenum compounds.<sup>2,28</sup> The short Mo–O distance suggests significant  $d\pi-p\pi$  bonding interaction in this bond. The Mo–Cl distance of 2.342 (2) Å in **1** is comparable to those found in several oxomolybdenum(V) compounds.<sup>25,28</sup> For example, the unique Mo–Cl bond of the  $\text{MoOCl}_3$  grouping is 2.353 (2) Å,<sup>26</sup> 2.368 (2) Å<sup>27</sup> for  $\text{MoOCl}_3(\text{OP}(\text{NMe}_2)_3)_2$ , 2.358 (3) Å for  $[\text{MoOCl}_3(\text{ox})]^-$ <sup>23</sup> (ox = 8-hydroxyquinolinate) and 2.342 (2) Å for  $\text{MoOCl}_3(\text{SPPH}_3)$ .<sup>6</sup> Slightly longer Mo–Cl distances (2.38–2.42 Å) are observed for Mo–Cl bonds *trans* to each other in the  $[\text{MoOCl}_2(\text{salphO})]^-$  anion<sup>24</sup> (salphO = *N*-(2-hydroxyphenyl)salicylideneiminato dianion) and in six-coordinate compounds containing the  $\text{MoOCl}_3$  group.<sup>23,26,27</sup>

The four Mo–S distances averaging 2.410 (5) Å in **1** and **2** are slightly longer than those for 1,2-dithiolate compounds (2.35–2.38 Å)<sup>29–31</sup> but significantly shorter than the Mo–S distance of 2.460 (1) Å in  $\text{MoOCl}_3(\text{SPPH}_3)$ <sup>6</sup> and the average Mo–S distances (ca. 2.46 Å) for the coordinated dithiocarbamate ligands.<sup>7,28</sup> Similar average Mo–S distances have been recently observed for coordinated benzenethiolate ligands in the  $[\text{MoO}(\text{SPh})_4]^-$  anion (2.403 (5) Å),<sup>8</sup> for tetradentate dithiolate ligands in dioxomolybdenum(VI) compounds (2.406 and 2.415 Å),<sup>32</sup> and for the 2-aminobenzenethiolate dianion in a trigonal-prismatic molybdenum(VI) compound (2.418 (6) Å).<sup>33</sup> The relatively short Mo–S distances in the present compounds indicate a charge delocalization over both ligand and metal.

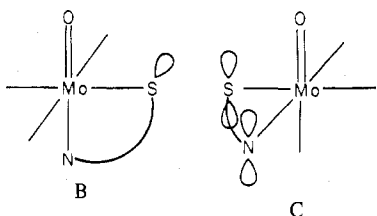
The Mo–N(1) distance of 2.210 (6) Å *trans* to the chlorine atom in **1** is similar to the Mo–N distance (2.198 (8) Å) for

8-hydroxyquinolate ligand in the  $[\text{MoOCl}_3(\text{ox})]^-$  anion<sup>23</sup> in which the nitrogen atom is also cis to the terminal oxo group and trans to a chlorine atom. On the other hand, the Mo–N bonds trans to the oxo group (2.408 (6) Å in **1** and 2.378 (6) Å (average) in **2**) are longer than the above Mo–N distances, as expected. Furthermore, these values are ca. 0.05 Å larger than those usually observed for the Mo–N bond trans to a terminal oxo group: 2.32 (2) Å in  $\text{MoO}_2(\text{ox})_2$ ,<sup>34</sup> 2.298 (8) Å in  $[\text{MoOCl}_2(\text{salphO})]^-$ ,<sup>24</sup> and 2.341 (6) Å (mean) in  $\text{MoO}_2(\text{salme})_2$ <sup>35</sup> (salme = *N*-methylsalicylideneimine). These Mo–N distances trans to an oxo group may be related to the size of the atoms in the equatorial plane, although other factors are also important (vide infra).

The coordination angles (Table IX) show that the geometries about the molybdenum atom in **1** and **2** are severely distorted from an ideal octahedron. For example, in structure **1** the O–Mo–S(1) angle of 106.28 (18)° significantly deviates from the ideal angle of 90° whereas the O–Mo–S(2) angle, another angle involving O and S atoms, is 89.24 (17)°. The difference between the two angles is 17° (100σ). The intramolecular nonbonded contacts in the coordination spheres shown in Table VIII also emphasize the irregularity of the coordination polyhedra. The O...S distances in the above example are 3.322 (5) Å for the O...S(1) edge and 2.943 (5) Å for the O...S(2) edge. The latter distance is significantly shorter than the sum of van der Waals radii (3.25 Å).<sup>19</sup> Two kinds of distances are also observed for the Cl...S edges in **1**, although the difference is smaller (Table VIII).

Ligand–ligand repulsion<sup>36</sup> is a major factor in determining the shape of coordination polyhedron of oxomolybdenum(V) and dioxomolybdenum(VI) compounds. In the  $[\text{MoOCl}_4(\text{OH}_2)]^-$  anion nonbonded contacts of the terminal oxo group with chloride atoms in the equatorial plane are identical with the corresponding contacts of the coordinated water.<sup>22,25</sup> Naturally the short Mo–O<sub>t</sub> distance requires a displacement of the molybdenum atom toward the terminal oxo group which is equal to the lengthening of the trans Mo–O<sub>t</sub> bond. The same conclusion has been obtained from the intramolecular contacts in the  $[\text{MoOCl}_3(\text{ox})]^-$  anion.<sup>23</sup> However, the O<sub>t</sub>...N distance of 2.654 (9) Å in this anion is again shorter than the van der Waals distance (2.90 Å). In general, in oxomolybdenum(V) and dioxomolybdenum(VI) compounds a relatively short contact is commonly observed between a donor atom from a chelate and the oxo group which is in the chelate plane.

The irregular shapes of **1** and **2** and related compounds are explicable by considering repulsions between the π-electron density in the short Mo–O<sub>t</sub> bond and the electrons in the two types of orbitals of the chelates: (1) a ligand “horizontal” orbital which lies in the plane of the chelate (primarily sp<sup>2</sup>-type orbital on the sulfur atom in the tox ligand); (2) orbitals of the ligand π system which are perpendicular to the plane of the ligand skeleton. Repulsions between the Mo–O<sub>t</sub> bond and electrons in the “horizontal” orbitals will be large when the Mo–O<sub>t</sub> group and the chelating ligand are coplanar (B). Repulsions between Mo–O<sub>t</sub> bond and the π orbitals will be large when the Mo–O<sub>t</sub> vector is perpendicular to the plane of the chelating ligand (C). In **1** the π-electron density on the



S(1) atom and the “horizontal” electron density on the S(2) atom can strongly interact with the Mo–O<sub>t</sub> bond, but the “horizontal” orbital on the S(1) atom and the π orbital on the

S(2) atom cannot. The fact that the O...S(2) distance is shorter than the O...S(1) edge in **1** indicates that the repulsions involving the “horizontal” orbital are weaker than those involving the π orbital. The shortening of the O...S(2) distance also reduces the repulsive interactions of the N(2) atom with the equatorial atoms, especially with the chlorine atom in **1** (the other oxo group in **2**) which is strongly compressed toward the N(2) atom by the interaction with the oxo group.

An extensive discussion of the distorted stereochemistries of other compounds containing both chelating ligands and strongly bound unidentate ligands is beyond the scope of this paper.<sup>37</sup> However, it should be noted that in general the anisotropy of the ligand–ligand repulsions between strongly bound unidentate ligands and spatially localized orbitals of the chelate ligands, taking into account the constraints of the chelate bite, can explain the irregular stereochemistries of compounds such as *cis*- $\text{MoO}_2(\text{S}_2\text{CNPr}_2)_2$ <sup>38</sup> and *cis*- $\text{Mo}(\text{NPh})_2(\text{S}_2\text{CNET}_2)_2$ .<sup>39</sup> Extension of these concepts to higher coordination numbers allows the unique distortions observed in the structure of  $\text{MX}(\text{AA})_3$  type compounds such as  $\text{TaS}(\text{S}_2\text{CNET}_2)_3$ <sup>40</sup> to be rationalized.

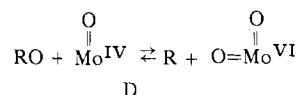
#### Implications for Molybdo Enzymes

The EPR spectrum of xanthine oxidase was first reported in 1959.<sup>41a</sup> From comparison of the spectral parameters from the enzyme to those<sup>5</sup> from molybdenum(V) species in aqueous solutions of thiols it was suggested that one or more sulfur atoms were ligated to the molybdenum atom in xanthine oxidase.<sup>41b</sup> An early report<sup>41b</sup> concluded that “a complete understanding of this system still eludes us, ...[but]... the solution to this problem is near at hand.” In the intervening years, however, progress in developing a suitable catalog of EPR data for relevant mononuclear molybdenum(V) complexes of known structure has been frustratingly slow.<sup>2</sup>

Marov and co-workers<sup>9</sup> proposed that complexes of structure A were present in solutions of Mo(V) and the tox ligand on the basis of the nearly axial EPR spectrum and from an analysis of the line widths. Subsequently  $\text{MoOCl}(\text{tox})_2$  has been prepared.<sup>10</sup> Its EPR spectrum in solution is nearly axial,<sup>10,42,43</sup> but the parameters are somewhat different from those reported earlier.<sup>9</sup> Figure 1 shows that the Cl and O atoms are actually cis to one another in the solid state and that the stereochemistry about the molybdenum is rather irregular. It is possible, of course, that the stereochemistry of **1** is different in the solid state and in solution.<sup>50</sup> Clearly, a much larger catalog of spectral and structural data for mononuclear molybdenum(V) complexes is needed before the EPR data from enzymes can be correlated with a specific molybdenum environment. The present study also reemphasizes the danger of attempting to deduce the stereochemistry about a transition-metal center solely from EPR data.

The present study as well as several previous studies<sup>2,6–8</sup> on discrete molybdenum(V) complexes are consistent with sulfur ligation of molybdenum in xanthine oxidase and other enzymes. Recent EXAFS (extended X-ray absorption fine structure) studies on xanthine oxidase<sup>44</sup> and sulfite oxidase<sup>45</sup> also support thiolate ligands coordinated to molybdenum.

The structures of **1** and **2**, which are the first pair of molybdenum(V) and molybdenum(VI) complexes to be structurally characterized, provide some support for one proposed pathway for the reaction of certain molybdo enzymes with substrates (D).<sup>46,47</sup> In the forward reaction of D an



oxomolybdenum(IV) center reduces the substrate by abstracting an oxygen atom to form a *cis*-dioxomolybdenum(VI) center. The reverse reaction, substrate oxidation, involves

transfer of an oxygen atom from a *cis*-dioxomolybdenum(VI) center to the substrate leaving an oxomolybdenum(IV) center. Such oxo-transfer reactions have been observed for the oxidation of the phosphines by molybdenum(VI)<sup>48</sup> but have not yet been generally observed in model systems. The *cis* stereochemistry of **1** and **2** and the facile reductions of nitrate by a number of *cis*-oxochloromolybdenum(V) complexes<sup>10,49</sup> suggest that such a pathway is feasible for molybdo enzymes. However, additional studies on the stereochemistry and reactions of monomeric molybdenum(IV), -(V), and -(VI) complexes of biologically relevant ligands are needed to provide further insight concerning this and other possible mechanisms for the action of molybdo enzymes.

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**Registry No.** **1**, 67650-71-9; **2**, 69779-05-1; K<sub>3</sub>MoCl<sub>6</sub>, 13600-82-3; 8,8'-diquinolyl disulfide, 1160-28-7.

**Supplementary Material Available:** Tables IV and V, the root-mean-square amplitudes of vibration, Tables VI and VII, the fixed positional and thermal parameters for hydrogen atoms, Tables XI and XII, selected intermolecular contacts, and listings of the observed and calculated structure factor amplitudes for MoOCl(tox)<sub>2</sub> and MoO<sub>2</sub>(tox)<sub>2</sub> (18 pages). Ordering information is given on any current masthead page.

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