Inorganica Chimica Acta, *85* (1984) 129–135

Monomeric Molybdenum(V) Complexes.
4. The Structure of Tetraphenylarsonium Oxodichloro(N-2-oxophenylsalicylideniminato)molybdate(V), $[Ph_4As][MoOCl_2(SalphO)]$

KATSUMOTO YAMANOUCHI[‡,§] SHOICHIRO YAMADA[§] and JOHN H. ENEMARK[‡,*]

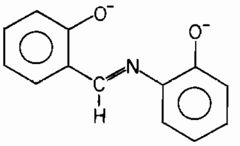
Department of Chemistry, University of Arizona, Tucson, Ariz. 85721, U.S.A. and Institute of Chemistry, College of General Education, Osaka University, Toyonaka, Osaka 560, Japan

Received September 27, 1983

The structure of $[Ph_4As][MoOCl_2(SalphO)]$, where SalphO is N-2-oxophenylsalicylideniminate dianion, has been determined by X-ray crystallography. The complex crystallizes in the monoclinic space group $P2_1/n$ *with* $a = 11.829(2)$, $b = 16.149(3)$, $c = 17.410(3)$ *Å,* $\beta = 97.485(15)^\circ$ *and* $Z = 4$. *The calculated and observed densities and 1.566 and 1.573(10) g cm*$^{-3}$*, respectively. Block-diagonal least-squares refinement of the structure using 4722 independent reflections with* $I \geqslant 3\sigma(I)$ *converged at* $R = 0.0345$ *and* $R_w = 0.0484$. *The crystal contains* $[Ph_4As]^+$ *cations and* $[MoOCl_2(SalphO)]^-$ *anions. The Mo atom in the anion is in a distorted octahedral coordination environment. A planar terdentate Schiff base ligand occupies meridional positions with the N atom* trans *to the terminal oxo group* (O_t). *Two Cl atoms are* cis *to the* O_t *atom. The Mo atom is displaced by 0.33 Å from the equatorial plane toward the* O_t *atom. The Mo–*O_t *distance is 1.673(3) Å. The Mo–N bond* trans *to the* O_t *atom is 2.298(4) Å. The two Mo–Cl bond lengths are 2.371(1) and 2.408(1) Å. The difference of 0.037 Å is significant (30 σ). Preparations of the title complex and the related complexes are also described.*

Introduction

One of the earliest spectral probes of molybdenum centers in enzymes such as xanthine oxidase, sulfite oxidase, and nitrate reductase was the technique of electron paramagnetic resonance (EPR) spectroscopy [1, 2]. Comparison of the EPR spectra of these enzymes with the solution EPR spectra of molybdenum complexes has strongly suggested that these enzymes contain a molybdenum(V) center ligated by one or more sulfur atoms. However, interpretation of the enzyme EPR spectra in terms of a specific coordination environment about molybdenum has been frustratingly slow because of the lack of definitive structural information on monomeric molybdenum(V) complexes [3–5]. Among the difficulties are the propensity of monomeric molybdenum(V) to form oxo- and sulfido-bridged binuclear diamagnetic compounds, and the general difficulty of growing single crystals of monomeric molybdenum(V) complexes for X-ray crystallographic structure determination. Therefore, we have been conducting single crystal X-ray structure determinations of a variety of monomeric molybdenum(V) complexes. Herein are described the preparation and structure of $[MoOCl_2(SalphO)]^-$ (*1*), a monomeric oxo-molybdenum(V) anion with a planar terdentate ligand (*2*). The EPR spectrum [6] and the electrochemistry [7] of *1* and the kinetics of the reaction [8] of *1* with nitrate have been previously described. The general stereochemistry of *1* has been noted [6], and a complete description of the structure determination is presented here.



2

Experimental

All the preparative manipulations were carried out in a dry nitrogen atmosphere, and all the solvents used for preparations of complexes were dried

---

[*] Author to whom correspondence should be addressed.

[‡] University of Arizona.

[§] Osaka University.

0020-1693/84/$3.00

TABLE I. Crystallographic Data at 25 °C.[a]

Formula	$[(C_6H_5)_4As][C_{13}H_9NO_3Cl_2Mo]$
Fwt	777.42
Space group	$P2_1/n$
Equivalent positions	1) x, y, z; 2) $\bar{x}, \bar{y}, \bar{z}$; 3) ½ + x, ½ − y, ½ + z; 4) ½ − x, ½ + y, ½ − z
Cell dimensions[b]	
a, Å	11.829(2)
b, Å	16.149(3)
c, Å	17.410(3)
β, deg	97.485(14)
V, Å^3	3297.4(10)
Z	4
d_{obsd}, g cm^{-3} [c]	1.573(10)
d_{calcd}, g cm^{-3}	1.566
crystal shape	Rod
crystal dimensions, mm	0.46 × 0.42 × 0.78
Radiation, Å	λ(MoKα) 0.71069
Monochrometer	Graphite crystal
Supplied power	40 KV, 15 ma
Data collection method	$\theta-2\theta$ scan
Scan speed, deg min^{-1}	Variable (2.0–29.3), determined as a function of peak intensity
Scan range (2θ), deg	MoKα_1 −0.8 to MoKα_2 + 0.8
Ratio of total background time to peak scan time	0.5
Std reflections	(1 4 −2), (0 3 7), (6 4 −3) after every 97 readings
Std dev of standards	<2%
2θ limit, deg	3.5–50
NO of unique data	5849
NO of data used in the calculations	4722, $I \geqq 3\sigma(I)$
Absorption coeff. (μ), cm^{-1}	16.44 (MoKα)
Range of empirical absorption correction[d]	1.00–1.19

[a]The standard deviation of the least significant figure is given in the parentheses in this table and in following tables. [b]Cell dimensions were obtained from a least-squares refinement of setting angles of 25 reflections in the 2θ range from 15 to 25 deg. [c]Density was determined by the flotation method using a solution of carbon tetrachloride and chloroform. [e]Empirical absorptin correction was applied using the program TAPER.

by the standard procedures and distilled before use. All the solid materials were stored over phosphorus pentoxide.

N-2-hydroxysalicylidenimine, (SalphO)H_2

Freshly distilled salicylaldehyde (20 mmol) in ethanol (30 ml) was added to a solution of 2-aminophenol (20 mmol), which had been recrystallized from ethanol, in 100 ml of ethanol. The mixture was heated with stirring under reflux for about 15 min. Orange crystals which formed in the cooled solution were filtered, washed with ethanol and diethylether, and dried *in vacuo*.

Pyridinium Oxodichloro(N-2-oxophenylsalicylideniminato)molybdate(V), [pyH][MoOCl$_2$*(SalphO)]*

Pyridinium oxopentachloromolybdate(V) (10 mmol) in methanol (40 ml) was added to a suspension of 2-hydroxyphenylsalicylidenimine (10 mmol) in methanol (50 ml) with stirring at 50 °C. After complete dissolution of 2-hydroxyphenylsalicylidenimine into the solution, pyridine (20 mmol) in 10 ml of methanol was slowly added to the solution to immediately give a precipitate of the desired compound. After the mixture was allowed to cool to room temperature, dark reddish brown microcrystals were collected by filtration, washed with a small amount of methanol and diethyl ether, and dried *in vacuo*. Recrystallization was performed as follows. The compound (5 mmol) was dissolved in hot methanol (or ethanol) and the resulting dark red solution was filtered. To the filtrate was added pyridinium chloride (15 mmol) in a minimal amount of methanol, and the solution was allowed to stand overnight at room temperature. The crystals which separated were filtered off, washed with a small amount of methanol and diethyl ether, and dried *in vacuo.*

Oxochloro(N-2-oxophenylsalicylideniminato)(methanol)molybdenum(V), MoOCl(SalphO)(MeOH)

Pyridinium oxodichloro(N-2-oxophenylsalicylideniminato)molybdate(V) (5 mmol) was dissolved in hot methanol. After filtration of the solution, the filtrate was allowed to stand at room temperature for a few days. The desired compound was obtained as bright red crystals. After filtration, the crystals were washed with methanol and dried *in vacuo.*

Other Oxodichloro(N-2-oxophenylsalicylideniminato)molybdate(V) Salts, M[MoOCl$_2$(SalphO)] (M = NEt$_4$, Ph$_4$As)

These salts were prepared by the following methods:

1) All the procedures were similar to those in the recrystallization of the pyridinium salt except that tetraethylammonium chloride or tetraphenylarsonium chloride was employed instead of pyridinium chloride. The tetraethylammonium salt was obtained as reddish brown microcrystals and the tetraphenylarsonium salt as dark reddish brown crystals.

2) Oxochloro(N-2-oxophenylsalicylideniminato)(methanol)molybdenum(V) (1 mmol) was dissolved in acetonitrile (30 ml) and the resulting dark red solution was filtered. The chloride salt of the desired cation (3 mmol) was added to the filtrate at room temperature. To this solution diethyl ether was gradually added, until the solution became turbid. The desired salt precipitated from the solution after standing at room temperature for a few days.

Crystal Structure Determination of [Ph$_4$As][MoOCl$_2$(SalphO)]

A dark reddish brown crystal suitable for X-ray data collection was cut from a crystal approximately twice as large, and attached to a glass fiber. Preliminary rotation photographs and preliminary data collection on a P2$_1$ four-circle diffractometer displayed 2/m Laue symmetry and systematic absences 0k0, k ≠ 2n, and h0l, h + l = 2n; consistent with space group C_{2h}^5-P2$_1$/n (alternative setting for P2$_1$/c being $\begin{pmatrix} 100 \\ 0\bar{1}0 \\ \bar{1}0\bar{1} \end{pmatrix}$). The refined cell constants and other information about the crystal are given in Table I.

Initially the structure was solved and refined using the data (2768 reflections having $3.5 \leqslant 2\theta \leqslant 40°$ and $I \geqslant 3\sigma(I)$) which had been collected with supplied power of 50 kv and 15 mA. In the course of refinements, however, it was noted that the low-angle data had a serious extinction problem. A new data set was obtained from the same crystal at reduced power and used in the subsequent refinements. Details of data collection for this set are shown in Table I.

The structure was solved by direct methods which revealed the coordinates of the molybdenum, arsenic and chlorine atoms. All other non-hydrogen atoms were located by additional least-squares and difference Fourier calculations. The atomic scattering factors and anomalous dispersion terms for the molybdenum, arsenic and chlorine atoms in all calculations were taken from the usual source [9].

During the refinements, it was found that the C(7)–N distance was less than 1.20 Å, much shorter than normal (1.27–1.30 Å). Examination of a difference Fourier map revealed two additional regions of electron density within 1 Å of the C(7) and N atoms. These two small peaks are roughly related to C(7) and N atoms by a C_2 rotation around Mo–O(1) vector. The subsequent least-squares refinements included this disorder. The occupancy (x) of the N atom was refined and occupancies of C(7), N′ and C(7′) were set to x, 1 – x and 1 – x, respectively.

The final cycles of block-diagonal least-squares refinement included anisotropic temperature factors for all the atoms except the disordered atoms. One block (226 variables) contained the scale factor and parameters for all atoms in the cation, while the other block (189 variables) consisted of the scale factor and parameters for all atoms in the anion and the As atom. Hydrogen atoms were included as fixed contributors.

The final agreement indices and goodness of fit were $R = \Sigma \| F_o| - |F_c\| / \Sigma |F_o| = 0.0345$, $R_w = (\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^{\,2})^{1/2} = 0.0484$ and GOF = $[(\Sigma w |F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2} = 1.669$ (where NO = number of observations and NV = number of variables). Additional details concerning computer programs and techniques of structure solution and refinement can be found in a previous publication [10].

The final positional and thermal parameters for all atoms are given in Table II. Parameters for fixed hydrogen atoms appear in Table III (supplementary material). A structure factor calculation for all 5849 data gave $R = 0.0462$ and $R_w = 0.0513$. Tables of observed and calculated structure factors are also available as supplementary material (20 pp). Interatomic distances and angles for the [MoOCl$_2$(SalphO)]$^-$ anion are in Tables IV and V, and those for the Ph$_4$As$^+$ cation in Tables VI and VII (supplementary material).

Results and Discussion

The crystal structure consists of a discrete tetraphenylarsonium cation and an anion of [MoOCl$_2$(SalphO)]$^-$ (*1*) per asymmetric unit. A stereoview of

Atom	x	y	z	β_{11}[a] or B, Å^2	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	A_1[b]	A_2	A_3
Mo	0.622470(24)	0.677545(22)	0.143514(17)	49.40(25)	46.72(17)	28.87(12)	3.05(15)	3.90(12)	−6.29(10)	0.185(1)	0.197(1)	0.256(1)
Cl(1)	0.62167(9)	0.80359(7)	0.07356(7)	91.5(9)	51.5(5)	50.5(5)	7.1(5)	19.2(5)	6.1(4)	0.236(1)	0.250(1)	0.295(1)
Cl(2)	0.60453(9)	0.53723(6)	0.18717(6)	89.6(9)	49.5(5)	39.3(4)	−0.7(5)	4.0(4)	2.2(3)	0.238(1)	0.252(1)	0.261(1)
O(1)	0.67773(23)	0.71624(18)	0.22942(15)	95.8(26)	53.3(14)	32.9(10)	−3.5(15)	−4.4(13)	−8.8(10)	0.200(4)	0.268(4)	0.280(4)
O(2)	0.45752(21)	0.68944(18)	0.14276(16)	54.2(20)	65.4(16)	48.5(12)	5.5(14)	9.1(13)	4.6(11)	0.192(4)	0.266(4)	0.299(4)
O(3)	0.76441(22)	0.64528(18)	0.10305(17)	72.5(23)	50.7(14)	47.6(12)	10.7(14)	20.4(13)	−0.7(11)	0.197(4)	0.264(4)	0.279(4)
C(1)	0.3677(3)	0.68242(23)	0.08860(26)	46.1(26)	35.8(17)	56.0(19)	5.3(17)	5.0(18)	5.9(14)	0.175(5)	0.218(5)	0.295(5)
C(2)	0.2616(3)	0.70620(26)	0.10793(28)	62.0(3)	40.4(18)	66.8(22)	4.1(19)	19.6(21)	−7.9(17)	0.191(5)	0.233(5)	0.322(5)
C(3)	0.1675(4)	0.7009(3)	0.0539(4)	48.0(3)	67.0(28)	96.0(3)	12.9(24)	9.5(27)	−14.2(25)	0.172(6)	0.291(6)	0.391(7)
C(4)	0.1749(4)	0.6717(4)	−0.0186(4)	78.0(5)	97.0(4)	91.0(4)	7.0(3)	−18.0(3)	−5.0(3)	0.217(7)	0.353(8)	0.395(8)
C(5)	0.2773(5)	0.6470(4)	−0.0386(3)	110.0(5)	80.0(3)	53.8(23)	−1.0(3)	0.5(27)	−11.4(22)	0.259(6)	0.291(6)	0.339(7)
C(6)	0.3758(3)	0.65174(26)	0.01410(27)	69.0(3)	40.5(18)	55.0(20)	8.8(20)	21.3(21)	3.0(16)	0.197(5)	0.235(5)	0.295(5)
C(8)	0.6684(3)	0.58607(25)	−0.0144(23)	64.0(3)	44.3(18)	41.5(16)	14.9(19)	20.8(18)	14.6(14)	0.184(5)	0.200(5)	0.297(5)
C(9)	0.6730(4)	0.5426(3)	−0.07952(26)	90.0(4)	60.8(25)	43.6(19)	2.3(24)	3.6(22)	14.6(17)	0.224(6)	0.254(6)	0.309(6)
C(10)	0.7766(5)	0.52020(29)	−0.10099(27)	144.0(6)	52.8(24)	37.0(17)	21.0(28)	22.7(25)	7.2(16)	0.222(6)	0.246(6)	0.336(6)
C(11)	0.8771(4)	0.54273(28)	−0.05485(27)	94.0(4)	53.9(22)	49.1(20)	32.1(24)	37.9(24)	19.1(17)	0.183(6)	0.214(5)	0.352(6)
C(12)	0.8734(3)	0.58446(26)	0.01260(24)	60.0(3)	48.1(19)	45.7(17)	18.4(19)	17.9(18)	13.7(15)	0.177(5)	0.220(5)	0.302(5)
C(13)	0.7683(3)	0.60539(23)	0.03642(23)	60.6(29)	36.5(16)	43.6(16)	14.1(17)	18.4(17)	11.0(14)	0.177(5)	0.204(5)	0.283(5)
N	0.5722(4)	0.62002(23)	0.02319(22)	3.41(11)								
C(7)	0.4744(5)	0.6195(3)	−0.0171(3)	4.16(13)								
N′[c]	0.5063(13)	0.6346(9)	0.0331(9)	2.9(4)								
C(7′)[c]	0.5469(13)	0.5894(10)	−0.0233(9)	2.5(4)								
As	0.235442(29)	0.965923(23)	0.131453(20)	54.00(28)	35.19(16)	27.29(13)	−1.35(16)	4.56(14)	−0.27(11)	0.194(1)	0.203(1)	0.216(1)
R1C1	0.17577(28)	1.07554(23)	0.12298(20)	50.5(26)	38.0(16)	31.4(13)	0.4(16)	3.8(15)	0.9(12)	0.187(5)	0.218(5)	0.225(5)
R1C2	0.2055(4)	1.12653(27)	0.06625(26)	108.0(4)	45.0(21)	49.1(19)	7.9(23)	35.8(23)	10.1(16)	0.204(6)	0.238(6)	0.322(6)
R1C3	0.1731(4)	1.2079(3)	0.0637(3)	128.0(5)	44.2(21)	60.9(23)	8.0(27)	35.0(28)	18.7(18)	0.205(6)	0.265(6)	0.348(6)
R1C4	0.1092(4)	1.23859(27)	0.11754(28)	95.0(4)	38.1(19)	55.5(21)	9.4(22)	6.9(22)	−0.6(17)	0.215(6)	0.264(5)	0.291(6)
R1C5	0.0793(4)	1.18812(29)	0.17374(27)	111.0(4)	53.4(24)	43.5(19)	26.8(26)	20.9(23)	1.1(17)	0.209(6)	0.256(6)	0.318(6)
R1C6	0.1102(4)	1.10498(27)	0.17712(23)	97.0(4)	47.6(20)	36.2(15)	13.5(22)	24.0(19)	6.0(14)	0.202(5)	0.232(5)	0.294(5)
R2C1	0.12687(29)	0.89714(23)	0.17326(22)	59.0(28)	33.6(16)	38.8(15)	−5.0(17)	8.4(16)	−3.5(13)	0.194(5)	0.213(5)	0.246(5)
R2C2	0.1556(3)	0.85418(26)	0.24105(23)	81.0(3)	42.8(18)	38.6(16)	−5.7(20)	10.9(19)	1.7(14)	0.220(5)	0.245(5)	0.249(5)
R2C3	0.0729(5)	0.80718(29)	0.27095(28)	126.0(5)	51.3(23)	49.5(20)	−17.7(27)	23.5(26)	8.0(17)	0.213(6)	0.288(6)	0.314(6)
R2C4	−0.0365(4)	0.8040(3)	0.2324(4)	101.0(5)	51.1(24)	79.0(3)	−22.9(27)	33.0(3)	0.5(21)	0.203(6)	0.291(6)	0.355(7)
R2C5	−0.0633(4)	0.8455(4)	0.1671(4)	80.0(4)	91.0(4)	87.0(3)	−35.0(3)	3.0(3)	12.0(3)	0.203(7)	0.337(7)	0.396(7)
R2C6	0.0165(4)	0.8938(4)	0.1366(3)	78.0(4)	90.0(3)	65.5(26)	−27.0(3)	−10.7(25)	21.1(25)	0.212(6)	0.278(6)	0.394(7)
R3C1	0.37704(28)	0.97093(22)	0.19802(19)	51.1(26)	39.8(16)	24.1(12)	−4.9(16)	5.8(14)	−1.2(11)	0.184(5)	0.191(5)	0.232(5)
R3C2	0.4452(3)	0.90093(22)	0.21102(22)	73.0(3)	37.3(17)	38.4(15)	0.4(19)	3.4(17)	−5.6(13)	0.211(5)	0.225(5)	0.253(5)
R3C3	0.5495(3)	0.90695(28)	0.25646(24)	71.0(3)	53.3(22)	41.6(17)	8.9(22)	−1.9(19)	−4.7(16)	0.212(5)	0.245(5)	0.284(5)
R3C4	0.5863(3)	0.9818(3)	0.28804(24)	62.0(3)	63.2(25)	37.5(16)	−10.3(22)	−3.3(18)	0.7(16)	0.194(5)	0.249(5)	0.294(6)
R3C5	0.5187(4)	1.05106(26)	0.27533(23)	86.0(4)	44.2(20)	35.7(16)	−21.2(21)	2.9(18)	−3.2(14)	0.193(5)	0.237(5)	0.282(5)
R3C6	0.4144(3)	1.04597(23)	0.23018(21)	72.0(3)	35.4(16)	32.5(14)	−4.9(18)	6.1(16)	1.4(12)	0.207(5)	0.222(5)	0.232(5)

R4C1	0.2635(3)	0.93205(24)	0.03046(20)	65.0(3)	40.6(17)	27.5(13)	0.0(18)	5.3(15)	−2.0(12)	0.202(5)	0.213(5)	0.233(5)
R4C2	0.1770(4)	0.9226(6)	−0.0265(3)	85.0(4)	202.0(7)	43.3(22)	0.0(5)	2.8(25)	−39.0(3)	0.224(7)	0.248(6)	0.530(9)
R4C3	0.1980(5)	0.9037(6)	−0.1009(3)	129.0(6)	192.0(7)	39.6(22)	−33.0(5)	−2.0(29)	−34.0(3)	0.209(7)	0.309(7)	0.518(10)
R4C4	0.3032(5)	0.8957(4)	−0.11775(26)	135.0(6)	94.0(4)	31.5(18)	−12.0(4)	19.1(25)	−11.4(20)	0.204(6)	0.301(6)	0.363(7)
R4C5	0.3864(5)	0.9010(7)	−0.0615(3)	98.0(5)	237.0(9)	44.1(23)	21.0(5)	19.8(28)	−28.0(4)	0.215(7)	0.278(7)	0.568(11)
R4C6	0.3668(4)	0.9166(6)	0.01486(29)	83.0(4)	210.0(7)	34.5(19)	25.0(5)	1.8(23)	−25.0(3)	0.216(6)	0.236(7)	0.535(9)

[a] The form of the anisotropic thermal ellipsoid is exp[$-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})$]. The quantities given in the table are the thermal coefficients × 10^4. [b] A_1, A_2 and A_3 designate the minimum, intermediate and maximum values (Å) of the root-mean-square amplitudes of vibration for the anisotropically refined atoms. [c] N′ and C(7′) are the alternate atoms of N and C(7). The refined occupancy factor for the N atom is 0.80(1) (see text).

TABLE IV. Interatomic Distances (Å) for the [$MoOCl_2$(SalphO)]$^-$ Anion.

Atoms	Distance	Atoms	Distance
Mo–Cl(1)	2.371(1)	C(6)–C(7)	1.446(6)
Mo–Cl(2)	2.408(1)	C(7)–N	1.273(8)
Mo–O(1)	1.673(3)	N–C(8)	1.462(5)
Mo–O(2)	1.959(3)	C(8)–C(9)	1.385(6)
Mo–O(3)	1.974(3)	C(9)–C(10)	1.375(6)
Mo–N	2.298(4)	C(10)–C(11)	1.393(7)
O(2)–C(1)	1.330(4)	C(11)–C(12)	1.360(6)
C(1)–C(2)	1.396(5)	C(12)–C(13)	1.401(5)
C(2)–C(3)	1.364(6)	C(13)–C(8)	1.390(5)
C(3)–C(4)	1.360(8)	O(3)–C(13)	1.333(5)
C(4)–C(5)	1.363(7)		
C(5)–C(6)	1.389(6)	Mo–N′	2.319(14)
C(6)–C(1)	1.403(6)	C(7′)–N′	1.36(3)
O(1)–O(2)	2.868(4)	N–Cl(1)	3.125(4)
O(1)–O(3)	2.792(4)	N–Cl(2)	3.131(4)
O(1)–Cl(1)	3.054(3)	O(2)–Cl(1)	3.038(3)
O(1)–Cl(2)	3.079(3)	O(2)–Cl(2)	3.052(3)
N–O(2)	2.858(5)	O(3)–Cl(1)	3.070(3)
N–O(3)	2.596(6)	O(3)–Cl(2)	3.080(3)

the anion is shown in Fig. 1. The approximate point group of *1* is C_s, although no symmetry is required by the space group. The approximate stereochemistry about the Mo atom is a distorted octahedron. The oxo group and two Cl atoms occupy meridional positions. The Cl atoms are *trans* to each other. Other meridional positions are occupied by a terdentate Schiff base ligand with the N atom *trans* to the oxo group.

As pointed out in earlier papers [11, 12], the $MoOCl_n$ (n = 1, 3, 4) groups in structurely characterized monomeric oxomolybdenum(V) compounds have all Cl atoms *cis* to the oxo group. For n = 2, two types of complexes with terdentate ligands are known. In $MoOCl_2[HB(3,5\text{-}Me_2pz)_3]$ [13, 14] the terdentate ligand restricts the O atom and the two Cl atoms to *fac* or *cis–cis* stereochemistry. On the other hand, the terdentate ligand, *2*, in the present structure restricts the O and Cl atoms to *mer* stereochemistry. This stereochemistry can be achieved by: (1) having one Cl atom *trans* and one *cis* to the terminal oxo group; (2) having both Cl atoms *cis* to the terminal oxo group. As can be seen in Fig. 1, arrangement (2) occurs here in line with the trends observed for other $MoOCl_n$ compounds.

The disorder of the anion is illustrated in Fig. 2, which depicts a C_2 rotation around the approximate Mo–O(1) vector. Such rotational disorder results in near coincidence of all ligand atoms except C(7) and N. The disorder may cause some minor discrepancies in the bond distances within the ligand, however, no systematic trends are apparent in Table IV.

TABLE V. Interatomic Angles (deg) for the $[MoOCl_2(salphO)]^-$ Anion.

Atoms	Angle	Atoms	Angle
O(1)–Mo–N	172.04(15)	C(3)–C(4)–C(5)	120.4(5)
O(2)–Mo–O(3)	156.41(12)	C(4)–C(5)–C(6)	120.8(5)
Cl(1)–Mo–Cl(2)	167.20(4)	C(5)–C(6)–C(1)	118.6(4)
O(1)–Mo–Cl(1)	96.52(11)	C(1)–C(6)–C(7)	129.0(4)
O(1)–Mo–Cl(2)	96.28(11)	C(5)–C(6)–C(7)	112.3(4)
O(1)–Mo–O(2)	104.01(13)	C(6)–C(7)–N	120.7(5)
O(1)–Mo–O(3)	99.57(13)	C(7)–N–C(8)	118.1(4)
O(2)–Mo–Cl(1)	88.57(9)	Mo–N–C(7)	127.9(4)
O(2)–Mo–Cl(2)	88.04(9)	Mo–N–C(8)	113.9(3)
O(2)–Mo–N	83.93(14)	N–C(8)–C(9)	131.5(4)
O(3)–Mo–Cl(1)	89.43(9)	N–C(8)–C(13)	108.4(4)
O(3)–Mo–Cl(2)	88.76(9)	C(9)–C(8)–C(13)	120.1(4)
O(3)–Mo–N	72.48(14)	C(8)–C(9)–C(10)	120.1(4)
N–Mo–Cl(1)	84.01(9)	C(9)–C(10)–C(11)	119.8(4)
N–Mo–Cl(2)	83.36(9)	C(10)–C(11)–C(12)	120.4(4)
Mo–O(2)–C(1)	134.3(3)	C(11)–C(12)–C(13)	120.3(4)
Mo–O(3)–C(13)	124.5(2)	C(12)–C(13)–C(8)	119.1(4)
O(2)–C(1)–C(2)	117.8(4)	O(3)–C(13)–C(8)	120.5(4)
O(2)–C(1)–C(6)	122.8(3)		
C(2)–C(1)–C(6)	119.5(4)	O(3)–C(13)–C(12)	120.5(3)
C(1)–C(2)–C(3)	119.7(4)	Mo–N′–C(7′)	122(1)
C(2)–C(3)–C(4)	121.1(4)		

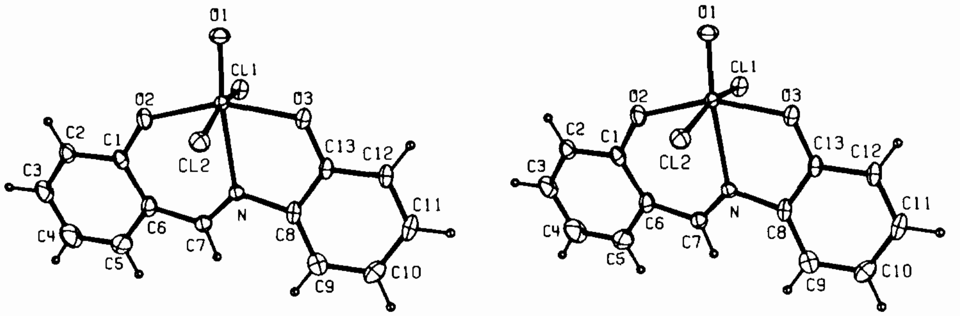


Fig. 1. Stereoview of the $[MoOCl_2(SalphO)]^-$ anion. The hydrogen atoms have been assigned arbitrarily small thermal parameters for clarity. Thermal ellipsoids are drawn to enclose 30% of the probability distribution.

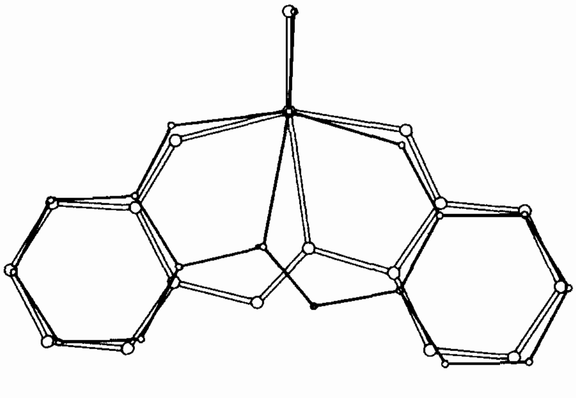


Fig. 2. Model for the disorder of the anion. For details refer to the text.

The Mo atom is displaced by 0.33 Å from equatorial plane (Cl_2O_2) toward the oxo group. This value is nearly identical to the displacements in $MoOCl(tox)_2$ [11] and $[MoO(Salen)(MeOH)]^+$ [15], but somewhat longer than the value in $[MoOCl_3(ox)]^-$ [12].

The Mo–O distance of 1.673(3) Å for the oxo group falls within the range, 1.65–1.72 Å, previously found in six-coordinate oxo-molybdenum(V) compounds [3]. The Mo–O(phenol) bond lengths *cis* to oxo group (1.967 Å (mean)) are similar to those observed in the structures of the related Schiff base complexes; 1.965 Å (mean) in $MoO_2(Salme)_2$ [16], 1.939(5) Å in $MoO_2(Saltn)$ [17], 1.962 Å (mean) in $[MoO(Salen)(MeOH)]^+$ cation [15] and 1.953(6) Å in $MoCl_2(Salen)$ [18].

A significant difference (0.037 Å, 30σ) is found between the two Mo–Cl distances. This difference may relate to the easy dissociation of one Cl atom from *1* to form MoOCl(SalphO)(MeOH) in methanol solution. Interestingly, relatively shorter Mo–Cl distances (2.34–2.37 Å) are observed for the unique Mo–Cl bond in the $MoOCl^{2+}$ and $MoOCl_3$ groups [11, 12]. The other two Mo–Cl bonds in the $MoOCl_3$ group are relatively longer (2.39–2.42 Å).

The Mo–N bond length of 2.298(4) Å *trans* to the oxo group is considerably longer than Mo–N distances *cis* to an oxo group, as expected. *Cis* Mo–N distances are 2.135(5) Å in MoO_2(Saltn) [17], 2.198(8) in $[MoOCl_3(ox)]^-$ [12], 2.112 Å (mean) in $[MoO(Salen)(MeOH)]^+$ [15], 2.210(6) Å in $MoOCl(tox)_2$ [11], 2.109(6) Å in $MoO(NCS)_2[HB(3,5\text{-}Me_2pz)_3]$ [19] and 2.186 Å (mean) in $MoO(SPh)_2[HB(3,5\text{-}Me_2pz)_3$ [20]. An Mo–N bond of 2.137(8) Å was found in *trans*-$MoCl_2(Salme)_2$ [18]. A careful comparison of Mo–N distances *trans* to an oxo group reveals that the distance in *1* is slightly but significantly shorter than the corresponding distances in other oxo-molybdenum compounds. Other *trans* Mo–N distances are 2.341 Å (mean) in $MoO_2(Salme)_2$ [16], 2.378 Å (mean) in $MoO_2(tox)_2$ [11], 2.408(6) Å, in $MoOCl(tox)_2$ [11], 2.347(8) Å in $MoO(NCS)_2[HB(3,5\text{-}Me_2pz)_3]$ [19] and 2.360(6) Å in $MoO(SPh)_2[HB(3,5\text{-}Me_2pz)_3]$ [20]. A similar length of 2.313(4) Å is found in MoO_2(Saltn) [17], where the tetradentate ligand, Saltn, adopts a non-planar conformation. Thus, somewhat shorter *trans* Mo–N distances occur when the N atom is constrained by two chelate rings. The dihedral angle between the two chelate rings is 11.6°.

The C(7)–N length of 1.273(8) Å is normal. The C=N bond lengths range from 1.27 Å to 1.30 Å in the Schiff base complexes cited above [15–18].

The distances and angles found in the Ph_4As^+ cation are typical for this cation [21]. Geometry about the As atom is tetrahedral. The average As–C bond distance is 1.909(4) Å. The average C–As–C angle is 109(2)°.

Acknowledgement

We thank the National Institutes of Environmental Health Sciences (Grant No. ES00966) and the Ministry of Education of Japan for support. We also thank the University of Arizona Computer Center for a generous allocation of computer time.

Supplementary Material

Table III, parameters for fixed hydrogen atoms, Table VI and VII, interatomic distances and angles for the Ph_4As^+ cation, and listings of the observed and calculated structure factor amplitudes (20 pages) (deposited with the editors).

References

1 R. C. Bray, In 'Biological Magnetic Resonance', Vol 2, L. J. Berliner and J. Reuben, Eds., Plenum Press, New York, pp. 45 (1980).

2 R. C. Bray, *Adv. Enzymol. Relat. Areas Mol. Biol., 51,* 107 (1980).

3 E. I. Stiefel, *Prog. Inorg. Chem., 22,* 1 (1977);
E. I. Stiefel, in 'Molybdenum and Molybdenum-containing Enzymes', M. P. Coughlan Ed., Pergamon Press, New York, pp. 41 (1980).

4 K. Yamanouchi, J. T. Huneke and J. H. Enemark, in 'Molybdenum Chemistry of Biological Significance', W. E. Newton and S. Otsuka Eds., Plenum Press, New York pp. 309 (1980).

5 J. T. Spence, *Coordin. Chem. Rev., 48,* 59 (1983).

6 M. I. Scullane, R. D. Taylor, M. Minelli, J.T. Spence, K. Yamanouchi, J. H. Enemark and N. D. Chasteen, *Inorg. Chem., 18,* 3213 (1979).

7 J. T. Spence, M. Minelli, C. A. Rice, N. D. Chasteen and M. I. Scullane, In 'Molybdenum Chemistry of Biological Significance', W. E. Newton and S. Otsuka, Eds., Plenum Press, New York, pp. 263 (1980).

8 R. D. Taylor, P. G. Todd, N. D. Chasteen and J. T. Spence, *Inorg. Chem., 18,* 44 (1979).

9 D. T. Cromer and J. T. Waber, In 'International Tables for X-ray Crystallography', Vol. IV, J. A. Ibers and W. C. Hamilton Eds., Kynoch Press, Birmingham, England, Table 2.2A, P149 (1974);
D. T. Cromer, *ibid.,* Table 2.3.1, P72.

10 K. Yamanouchi and J. H. Enemark, *Inorg. Chem., 17,* 1981 (1978).

11 K. Yamanouchi and J. H. Enemark, *Inorg. Chem., 18,* 1626 (1979).

12 K. Yamanouchi, J. T. Huneke, J. H. Enemark, R. D. Taylor and J. T. Spence, *Acta Cryst., B35,* 2326 (1979).

13 Abbreviations of ligands in the text: $HB(3,5\text{-}Me_2pz)_3^-$, hydrotris(3,5-dimethylpyrazolyl)borate anion; Salen, N,N'-ethylenebis(salicylideniminate)dianion; Saltn, N,N'-trimethylenebis(salicylideniminate) dianion; Salme, N-methylsalicylideniminate anion; ox, 8-oxoquinolinate anion; tox, 8-mercaptoquinolinate anion.

14 G. Ferguson, B. Kaitner, F. J. Lalor and G. Roberts, *J. Chem. Research(s),* 6 (1982).

15 S. F. Gheller, J. R. Bradbury, M. F. Mackay and A. G. Wedd, *Inorg. Chem., 20,* 3899 (1981).

16 K. Tsukuma, T. Kawaguchi and T. Watanabe, *Acta Cryst., B31,* 2165 (1975).

17 A. C. Villa, L. Coghi, A. G. Manfredotti and C. Guastini, *Cryst. Structure Commun., 3 (3),* 551 (1974).

18 J. E. Davies and B. M. Gatehouse, *J. Chem. Soc., Dalton Trans.,* 184 (1974).

19 K. Yamanouchi, R. B. Ortega and J. H. Enemark, to be submitted for publication.

20 K. Yamanouchi, K. M. Barnhart, R. B. Ortega, J. H. Enemark, D. Collison and F. E. Mabbs, submitted for publication.

21 J. R. Bradbury, M. F. Mackay and A. G. Wedd, *Aust. J. Chem., 31,* 2423 (1978).