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Monomeric Molybdenum(V) Complexes. 3. The Structure of 8-Hydroxyquinolinium Trichloro-(8-hydroxyquinolinato)oxomolybdate(V), $[C_9H_8NO][Mo(C_9H_6NO)Cl_3O]$

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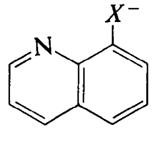
Abstract

The structure of $[oxH_2][MoCl_3O(ox)]$, where oxH_2 and ox are the cation and the anion of 8-hydroxyquinoline, respectively, has been determined by X-ray crystallography. The compound crystallizes in the orthorhombic space group *Pbca* with a = 7·366 (3), b = 16·301 (3), c = 32·122 (11) Å and Z = 8. The calculated and observed densities are 1·752 and 1·751 (10) Mg m^{-3} respectively. Full-matrix least-squares refinement of the structure using the 1525 data with $I > 3\sigma(I)$ gave R_1 = 0·044 and R_2 = 0·043. The crystal contains infinite chains of the $[oxH_2]^+$ cations and the $[MoCl_3O(ox)]^-$ anions joined by two kinds of hydrogen bonds. The Mo atom in the anion is in a distorted octahedral coordination environment. All three Cl atoms are *cis* to the terminal oxo group (O_t). The other equatorial position is occupied by a N atom from the ox ligand. The Mo atom is displaced by 0·20 (2) Å from the equatorial plane toward the O_t atom. The Mo—O_t distance is 1·673 (6) Å. An Mo—O distance of 2·039 (5) Å and an Mo—N distance of 2·198 (8) Å are found for the ox ligand. The unique Mo—Cl group, despite linkage by a hydrogen bond to the N—H group of an $[oxH_2]^+$ cation, has a significantly shorter Mo—Cl distance [2·358 (3) Å] than the Mo—Cl bonds *trans* to each other [2·389 (3) and 2·425 (3) Å]. The Cl atom in the longest Mo—Cl bond is also involved in hydrogen bonding to the O—H group of another $[oxH_2]^+$ cation.

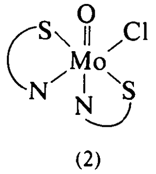
Introduction

There is considerable current interest in the reactions and properties of monomeric Mo^V complexes because the electron paramagnetic resonance (EPR) spectra of several Mo-containing enzymes show signals characteristic of Mo^V (Bray, 1975; Stiefel, 1977). In view of the complexity of the enzymes themselves a knowledge of the structures, reactions and properties of monomeric Mo^V complexes is important for interpreting the reactions of the enzymes. Of particular interest are complexes which mimic the chemical reactions and/or spectral properties of the enzymes.

Recently the kinetics of oxidation of several monomeric Mo^V complexes by nitrate ion (NO_3^-) have been investigated (Taylor, Todd, Chasteen & Spence, 1979). Two complexes of particular interest are $MoClO(ox)_2$ and $MoClO(tox)_2$, where ox is the anion of 8-hydroxyquinoline (1*a*), and tox is the anion of 8-mercaptoquinoline (1*b*). The rates of reaction with nitrate are very different for these two compounds with $MoClO(tox)_2$ reacting much more slowly (Taylor, Todd, Chasteen & Spence, 1979). The stereochemistry of $MoClO(tox)_2$ in the solid state has been established to be (2) by an X-ray structure determination (Yamanouchi & Enemark, 1979). The greater reactivity of $MoClO(ox)_2$ with nitrate and the general lack of definitive structural information for monomeric Mo^V compounds prompted us to investigate the structural chemistry of $MoClO(ox)_2$. However, recrystallization of $MoClO(ox)_2$ from dichloromethane/hexane resulted in an unexpected reaction to produce $[oxH_2]$-$[MoCl_3O(ox)]$, where $[oxH_2]^+$ is the 8-hydroxyquinolinium cation. Herein we describe the stoichiometry and stereochemistry of this unexpected product.



(1*a*) X = S (tox)
(1*b*) X = O (ox)



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Experimental

Light-green crystals of $[oxH_2][MoCl_3O(ox)]$ were obtained by liquid diffusion of hexane into a dichloromethane solution of $MoClO(ox)_2$. An intense IR absorption due to the Mo=O stretch appears at 935 cm^{-1} for $MoClO(ox)_2$ and at 942 cm^{-1} for $[oxH_2][MoCl_3O(ox)]$. In addition to this band, $[oxH_2][MoCl_3O(ox)]$ exhibits characteristic bands at 3200 and 3300 cm^{-1} which are assigned to ν(NH) and ν(OH) respectively. The compound $[oxH_2][MoCl_3O(ox)]$ shows a broad EPR signal with g value of 1·952 in the solid state, while a much broader solid-state absorption (g = 1·960) is observed for $MoClO(ox)_2$. The features of the IR and EPR spectra of the title compound are similar to those for the product from the reaction of $Mo(CH_3CN)_2Cl_3O$ with 8-hydroxyquinoline (McAuliffe & Sayle, 1975).

Table 1. *Crystallographic data at* 297 K

The standard deviation of the least significant figure is given in parentheses in this table and in following tables.

Formula	$[C_9H_8NO][C_9H_6Cl_3MoNO_2]$
FW	508·62
Space group	*Pbca* (No. 61)
Cell dimensions*	
a (Å)	7·366 (3)
b (Å)	16·301 (5)
c (Å)	32·122 (11)
V ($Å^3$)	3857 (2)
Z	8
d_{obs} ($Mg\ m^{-3}$)†	1·751 (10)
d_{calc} ($Mg\ m^{-3}$)	1·752
Crystal shape	Plate
Crystal dimensions (mm)	0·06 × 0·18 × 0·37
Radiation (Å)	$\lambda(Mo\ K\alpha) = 0·71073$
Monochromator	Graphite crystal
Supplied power	50 kV, 30 mA
Data-collection method	θ–2θ scan
Scan speed (deg min^{-1})	Variable (2·0–29·3), determined as a function of peak intensity
Scan range (2θ) (°)	Mo $K\alpha_1 - 0·8$ to $K\alpha_2 + 0·8$
Ratio of total background time to peak scan time	0·5
Standard reflections	$0\bar{2}4$, $\bar{2}0\bar{6}$, $\bar{2}00$, every 97 readings
Standard deviation of standards	≤3%
2θ limit (°)	4·0–50
Number of unique data	3413
Number of data used in the calculation	1525, $I > 3\sigma(I)$
Absorption coefficient (μ) (mm^{-1})	1·104
Maximum absorption correction factor‡	1·230

* Cell dimensions were obtained from a least-squares refinement of setting angles of 25 reflections in the 2θ range from 5 to 21°.

† Density was determined by the flotation method using a solution of carbon tetrachloride and methylene iodide.

‡ Empirical absorption correction was applied using the program *TAPER*.

A single crystal was mounted on a Syntex $P2_1$ autodiffractometer equipped with a scintillation counter and a graphite monochromator. The unit-cell parameters which were refined by a least-squares routine (*Syntex $P2_1$ Fortran Operations Manual*, 1975) and other crystallographic data are given in Table 1. The conditions used for the data collection are also shown in Table 1. The data were reduced to F_o^2 and $\sigma(F_o^2)$ by the procedures previously described (Yamanouchi & Enemark, 1978). An empirical absorption correction was applied using the program *TAPER* (*Syntex $P2_1$ Fortran Operations Manual*, 1975). Nine strong reflections with χ values of *ca* 90° and 2θ in the range 5–45° were measured by the ψ-scan method to define the absorption curves.

All computations were performed on the CDC CY-175 computer at the University of Arizona Computer Center. Details of the programs used in the course of the structure determination are described in a previous paper (Yamanouchi & Enemark, 1978). Neutral atomic scattering factors used for the nonhydrogen atoms and correction for the real and imaginary components of the anomalous dispersion made for the Mo and Cl atoms were obtained from *International Tables for X-ray Crystallography* (1974). The H-atom scattering factors were taken from the calculation of Stewart, Davidson & Simpson (1965).

The position of the Mo atom was determined by direct methods using the 400 reflections with the largest $|E|$ values. All the remaining non-hydrogen atoms were located by subsequent structure factor calculations and difference electron density maps.

The structure was refined by full-matrix least-squares techniques, minimizing the function $\sum w(|F_o| - |F_c|)^2$ with $w = 4F_o^2/[\sigma^2(F_o^2) + (pF_o^2)^2]$ where p was set equal to 0·03. Refinement of the model with anisotropic thermal parameters for all the nonhydrogen atoms resulted in $R_1 = \sum ||F_o| - |F_c||/\sum |F_o| = 0·052$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0·054$. A difference electron-density map calculated at this stage revealed the positions of all 14 H atoms. The 12 H atoms attached to the phenyl C atoms were included as fixed contributors in idealized positions (C–H = 0·95 Å) (Churchill, 1973) assuming trigonal geometry about the C atoms. Each H atom was assigned an isotropic thermal parameter 1 $Å^2$ greater than the value of its bonded C atom. The positional and isotropic thermal parameters of the H atoms involved in the O–H···Cl and N–H···Cl hydrogen bonds were allowed to vary in subsequent cycles of refinement. Two additional cycles of full-matrix least-squares refinement (252 variables) led to final convergence with $R_1 = 0·044$ and $R_2 = 0·043$. All parameter shifts during the final cycle of refinement were less than $0·5\sigma$ except for the temperature factor of one of the H atoms which shifted by $0·9\sigma$. The 'goodness of fit', defined by $[\sum w(|F_o| - |F_c|)^2/(n - m)]^{1/2}$ where n is the number of reflections used in the refinement and m is the number of refined parameters, was 1·284. The overdetermination ratio (n/m) was 6·1. An analysis of $w(\Delta F)^2$ showed no appreciable dependence either upon $\sin\theta/\lambda$ or $|F_o|$. No peak in the final electron density map was greater than 0·5 e Å^{-3}. A structure factor calculation for all 3413 unique data yielded $R_1 = 0{\cdot}145$ and $R_2 = 0{\cdot}058$.* The large values of the discrepancy indices resulted from the large number of unobserved reflections due to the small size of the crystal.

The final positional parameters for the refined atoms are listed in Table 2. The root-mean-square amplitudes of vibration for the anisotropic atoms are given in Table 3.* The fixed positional and thermal parameters for H atoms appear in Table 4.*

Table 2. *Atomic parameters for* $[C_9H_8NO]^+[Mo(C_9H_6NO)Cl_3O]^-$

	x	y	z
Mo	0·07378 (12)	0·80518 (4)	0·604747 (25)
Cl(1)	−0·1829 (4)	0·81016 (16)	0·65197 (8)
Cl(2)	0·2593 (4)	0·76234 (15)	0·66049 (8)
Cl(3)	0·3334 (4)	0·82106 (15)	0·56090 (8)
O(1)	0·0019 (9)	0·7188 (3)	0·58201 (19)
O(2)	0·1020 (9)	0·9271 (3)	0·61724 (17)
N(1)	−0·0901 (11)	0·8686 (4)	0·55751 (22)
C(1)	−0·1817 (15)	0·8360 (6)	0·5262 (3)
C(2)	−0·2782 (15)	0·8840 (7)	0·4979 (3)
C(3)	−0·2774 (14)	0·9673 (7)	0·5012 (3)
C(4)	−0·1835 (13)	1·0048 (6)	0·5336 (3)
C(5)	−0·1732 (16)	1·0908 (6)	0·5413 (3)
C(6)	−0·0703 (17)	1·1193 (5)	0·5729 (4)
C(7)	0·0287 (15)	1·0674 (5)	0·5999 (3)
C(8)	0·0190 (13)	0·9835 (5)	0·59410 (27)
C(9)	−0·0873 (14)	0·9522 (5)	0·56139 (27)
O(3)	−0·0712 (13)	0·8703 (4)	0·74361 (23)
N(2)	−0·0274 (11)	0·9328 (5)	0·81951 (29)
C(10)	−0·0069 (15)	0·9582 (8)	0·8582 (3)
C(11)	0·0458 (16)	1·0384 (7)	0·8655 (4)
C(12)	0·0782 (17)	1·0910 (6)	0·8338 (4)
C(13)	0·0521 (15)	1·0644 (6)	0·7925 (3)
C(14)	0·0829 (18)	1·1138 (6)	0·7576 (4)
C(15)	0·0587 (18)	1·0824 (7)	0·7185 (4)
C(16)	0·0087 (15)	1·0006 (7)	0·7119 (3)
C(17)	−0·0195 (17)	0·9503 (6)	0·7457 (4)
C(18)	0·0014 (13)	0·9819 (6)	0·7857 (3)
H(O3)*	−0·101 (13)	0·855 (5)	0·7193 (28)
H(N2)	−0·068 (14)	0·874 (6)	0·8115 (29)

* Symbols in parentheses refer to atoms to which the H atoms are bonded.

Description and discussion of the structures

Fig. 1 is a stereodiagram showing that the crystal structure consists of the $[oxH_2]^+$ cations and the $[MoCl_3O(ox)]^-$ anions, linked through O–H···Cl and N–H···Cl hydrogen bonds. Interatomic distances and angles are given in Tables 5 and 6.

In the $[MoCl_3O(ox)]^-$ anion the Mo atom is ligated by an oxo ligand, three Cl atoms and a bidentate ox ligand in a distorted octahedral coordination environment. All three Cl atoms are *cis* to the terminal oxo group. The remaining equatorial position is occupied by a N atom from the ox ligand. In all monomeric chlorooxomolybdenum(V) compounds structurally characterized to date, the $MoCl_nO$ (n = 1–4) group has all Cl atoms *cis* to the oxo group (Yamanouchi & Enemark, 1979).

The Mo atom is displaced by 0·20 (2) Å from the equatorial plane toward the oxo group as is commonly observed in oxomolybdenum complexes. The short Mo–O(1) bond length of 1·673 (3) Å is in good agreement with previously reported Mo–O_t distances (1·65–

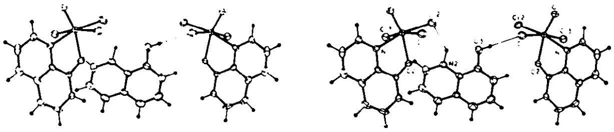

Fig. 1. Stereoview of the packing showing the hydrogen bonding. The *bc* plane is parallel to the paper. Parameters for O(3)–H(O3)···Cl(1): O(3)–H(O3) = 0·85 (9), Cl(1)···H(O3) = 2·36 (9), O(3)···Cl(1) = 3·210 (8) Å, O(3)–H(O3)–Cl(1) = 178 (8)°. Parameters for N(2)–H(N2)···Cl(3): N(2)–H(N2) = 1·04 (9), Cl(3)···H(N2) = 2·39 (10), N(2)···Cl(3) = 3·257 (9) Å, N(2)–H(N2)–Cl(3) = 140 (7)°.

Table 5. *Selected interatomic distances* (Å) *and angles* (°) *for the* $[Mo(C_9H_6NO)Cl_3O]^-$ *anion*

Mo–O(1)	1·673 (6)	Mo–Cl(1)	2·425 (3)	O(1)–Mo–N(1)	85·5 (3)	O(2)–Mo–N(1)	74·5 (2)
Mo–O(2)	2·039 (5)	Mo–Cl(2)	2·358 (3)	O(1)–Mo–Cl(1)	93·1 (2)	O(2)–Mo–Cl(1)	85·6 (2)
Mo–N(1)	2·198 (8)	Mo–Cl(3)	2·389 (3)	O(1)–Mo–Cl(2)	105·4 (2)	O(2)–Mo–Cl(2)	94·6 (2)
				O(1)–Mo–Cl(3)	95·0 (2)	O(2)–Mo–Cl(3)	85·9 (2)
O(1)···N(1)	2·654 (9)	O(2)···N(1)	2·568 (10)	Cl(2)–Mo–Cl(1)	89·2 (1)	N(1)–Mo–Cl(1)	89·3 (2)
O(1)···Cl(1)	3·020 (6)	O(2)···Cl(1)	3·047 (6)	Cl(2)–Mo–Cl(3)	90·9 (1)	N(1)–Mo–Cl(3)	88·9 (2)
O(1)···Cl(2)	3·234 (7)	O(2)···Cl(2)	3·239 (6)	Cl(1)–Mo–Cl(3)	171·5 (1)	N(1)–Mo–Cl(2)	169·1 (2)
O(1)···Cl(3)	3·034 (7)	O(3)···Cl(3)	3·028 (6)	O(1)–Mo–O(2)	159·9 (3)		
Cl(2)···Cl(1)	3·360 (4)	N(1)···Cl(1)	3·253 (8)			Mo–O(2)–C(8)	121·1 (5)
Cl(2)···Cl(3)	3·384 (4)	N(1)···Cl(3)	3·216 (9)	Mo–N(1)–C(1)	128·0 (6)	Mo–N(1)–C(9)	113·4 (6)

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* Lists of structure factors and thermal parameters, and Tables 3 and 4 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34533 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* See previous footnote.

Table 6. *Interatomic distances* (Å) *and angles* (°) *for the* 8-*hydroxyquinolinate ligand and the* 8-*hydroxyquinolinium cation*

8-Hydroxyquinolinate ligand				8-Hydroxyquinolinium cation			
O(2)–C(8)	1·330 (10)	C(9)–N(1)–C(1)	118·5 (8)	O(3)–C(17)	1·360 (11)	C(18)–N(2)–C(10)	123·2 (10)
N(1)–C(9)	1·369 (10)	N(1)–C(1)–C(2)	122·0 (9)	N(2)–C(18)	1·365 (12)	N(2)–C(10)–C(11)	119·2 (11)
N(1)–C(1)	1·323 (11)	C(1)–C(2)–C(3)	120·4 (10)	N(2)–C(10)	1·319 (11)	C(10)–C(11)–C(12)	121·4 (11)
C(1)–C(2)	1·394 (13)	C(2)–C(3)–C(4)	119·9 (10)	C(10)–C(11)	1·384 (14)	C(11)–C(12)–C(13)	119·4 (10)
C(2)–C(3)	1·362 (14)	C(3)–C(4)–C(5)	126·0 (10)	C(11)–C(12)	1·351 (14)	C(12)–C(13)–C(14)	123·8 (10)
C(3)–C(4)	1·392 (13)	C(3)–C(4)–C(9)	116·8 (9)	C(12)–C(13)	1·408 (13)	C(12)–C(13)–C(18)	118·3 (10)
C(4)–C(5)	1·426 (13)	C(9)–C(4)–C(5)	117·2 (9)	C(13)–C(14)	1·398 (14)	C(18)–C(13)–C(14)	117·8 (10)
C(5)–C(6)	1·349 (14)	C(4)–C(5)–C(6)	119·9 (9)	C(14)–C(15)	1·370 (15)	C(13)–C(14)–C(15)	120·0 (10)
C(6)–C(7)	1·414 (13)	C(5)–C(6)–C(7)	122·9 (8)	C(15)–C(16)	1·398 (15)	C(14)–C(15)–C(16)	121·8 (10)
C(7)–C(8)	1·382 (12)	C(6)–C(7)–C(8)	119·0 (10)	C(16)–C(17)	1·376 (14)	C(15)–C(16)–C(17)	119·3 (10)
C(8)–C(9)	1·406 (12)	C(7)–C(8)–C(9)	119·2 (9)	C(17)–C(18)	1·393 (13)	C(16)–C(17)–C(18)	119·3 (11)
C(9)–C(4)	1·424 (12)	O(2)–C(8)–C(7)	125·8 (9)	C(18)–C(13)	1·413 (12)	O(3)–C(17)–C(16)	125·1 (11)
		O(2)–C(8)–C(9)	115·0 (8)			O(3)–C(17)–C(18)	115·6 (10)
O(2)···N(1)	2·568 (10)	N(1)–C(9)–C(8)	115·9 (8)	O(3)···N(2)	2·662 (12)	N(2)–C(18)–C(17)	120·0 (10)
		N(1)–C(9)–C(4)	122·3 (9)	O(3)–H(O3)	0·85 (9)	N(2)–C(18)–C(13)	118·4 (10)
		C(4)–C(9)–C(8)	121·8 (8)	N(2)–H(N2)	1·04 (9)	C(13)–C(18)–C(17)	121·6 (10)

1·72 Å) for six-coordinated oxomolybdenum compounds (Stiefel, 1977; Spivack & Dori, 1975).

The Mo–N(1) distance of 2·198 (8) Å is similar to the Mo–N distances of 2·205 (10) Å (average) for the ox ligands in the triply bridged dimer $Mo_2O_3(ox)_2$-(SCH_2CH_2O) (Gelder, Enemark, Wolterman, Boston & Haight, 1975) and 2·210 (6) Å for the 8-mercaptoquinolinate (tox) ligand in *cis*-$MoClO(tox)_2$. These Mo–N bonds are *cis* to the terminal oxo group. The Mo–N bonds for the same ligands which are *trans* to the oxo group, however, are significantly longer than the above values, *i.e.* 2·32 (2) Å in $MoO_2(ox)_2$ (Atovmyan & Sokolova, 1971), 2·408 (6) Å in $MoClO(tox)_2$ and 2·378 (6) Å (average) in $MoO_2(tox)_2$ (Yamanouchi & Enemark, 1979). On the other hand, the Mo–O(2) bond [2·039 (5) Å] of the ox ligand is *trans* to the terminal oxo group but only slightly longer than the Mo–O bonds for the same ligand in a *cis* position to the oxo group [2·030 (4) Å in $Mo_2O_3(ox)_2$-(SCH_2CH_2O) and 1·98 (2) Å in $MoO_2(ox)_2$].

Slight but significant deviations are observed among the three Mo–Cl bond lengths. As pointed out elsewhere (Yamanouchi & Enemark, 1979) in six-coordinate oxomolybdenum(V) compounds relatively longer Mo–Cl distances (2·38–2·42 Å) are found for Mo–Cl bonds *trans* to each other in the $MoCl_3O$ and $MoCl_2O^+$ groups while relatively shorter Mo–Cl distances (2·34–2·37 Å) are found for the unique Mo–Cl bond in the $MoCl_3O$ and $MoClO^{2+}$ groups. The present compound also has the unique Mo–Cl(2) bond shorter than the other Mo–Cl bonds (Table 5) even though Cl(2) is involved in hydrogen bonding. The difference between the Mo–Cl(1) and Mo–Cl(3) distances is probably due to the involvement of Cl(1) in the hydrogen-bonding scheme (see below).

The nonbonded contacts among the donor atoms of the ligands (Table 5) provide important insight into the nature of the *trans* effect in oxomolybdenum(V) complexes. The contacts of the terminal oxo ligand O(1) with the Cl atoms in the equatorial plane are essentially identical to the corresponding contacts involving the O atom of the ox ligand, O(2). Even the O(1)···N(1) edge [2·654 (9) Å] is similar to the O(2)···N(1) chelate bite distance [2·568 (10) Å]. Thus, ligand–ligand repulsions appear to be a major factor in determining the shape of the coordination polyhedron. On the other hand, the short Mo–O(1) distance requires that the Mo atom be displaced from the centroid of the polyhedron toward the terminal ox group and away from the *trans* ligand. A similar conclusion has been drawn from inspection of the intramolecular contacts in the $[MoCl_4O(OH_2)]^-$ anion (Garner, Hill, Mabbs, McFadden & McPhail, 1977).

It has previously been noted (Yamanouchi & Enemark, 1979) that oxomolybdenum complexes containing chelating ligands exhibit irregular stereochemistries about the Mo atom due to anisotropic repulsions between the oxo group and the spatially localized electron density on the chelate donor atom. Such repulsions are weak when the oxo group and the atoms of the chelating ligands are approximately coplanar. This arrangement occurs in the present structure and the O(1)···N(1) distance [2·654 (9) Å] is significantly shorter than the sum of the van der Waals radii (2·90 Å). Moreover, the O(1)–Mo–N(1) angle is acute [85·6 (2)°], even though the Mo atom is displaced toward O(1). In contrast the nonbonded interaction between O(1) and the unidentate donor Cl(2) [3·234 (7) Å] is similar to the expected van der Waals contact (3·20 Å), and the O(1)–Mo–Cl(2) angle is 105·4 (2)°.

The details of the two hydrogen-bonding interactions which connect the $[oxH_2]^+$ cations and the $[MoCl_3O(ox)]^-$ anions into chains approximately parallel to the *a* axis are shown in Fig. 1. One of the hydrogen bonds occurs between the O(3) atom of a cation and the Cl(1) atom of an adjacent anion. The O(3)···Cl(1) distance is 3·210 (8) Å and the O(3)—H(O3)—Cl(1) angle is 178 (8)°. Another hydrogen bond involves the N(2) atom in the cation and Cl(2) atom in another neighboring anion. The N(2)···Cl(2) distance is 3·257 (9) Å, but the N(2)—H(N2)—Cl(2) angle is 140 (7)°, indicating that this hydrogen bond is relatively weak.

Interatomic distances and angles for the oxH_2 cation and the ox ligand are listed in Table 6. The chemically equivalent parameters of the cation and the ligand are very similar. A slight deviation is found for the O—C distance: 1·360 (11) Å in the cation and 1·330 (10) Å in the ligand. One of the two N—C distances is consistently shorter than the other in both the cation and the ligand; the average distance* is 1·321 (3) Å for the shorter and 1·367 (3) Å for the longer. The mean C—C distance is 1·388 (19) Å for the cation and 1·394 (25) Å for the ligand. These parameters are typical of those found for the 8-hydroxyquinolinate ligand and for the 8-hydroxyquinolinium cation in other compounds (Gelder, Enemark, Wolterman, Boston & Haight, 1975; Atovmayan & Stokolova, 1971; Ružić-Toroš, Kojić-Prodić, Gabela & Šljukić, 1977).

Finally, this work re-emphasizes the complexities of the chemistry of oxomolybdenum compounds. The existence of $MoClO(ox)_2$ has been well established by analytical and spectroscopic data. The stereochemistry of $MoClO(ox)_2$ remains unknown because attempts to grow suitable crystals have produced $[oxH_2][MoCl_3O(ox)]$, described in this paper. It seems likely that the compound previously formulated as $MoCl_3O(oxH)_2$ (McAuliffe & Sayle, 1975) is also $[oxH_2][MoCl_3O(ox)]$ in view of the similarities of their EPR and IR spectra.

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* For mean distances the r.m.s. deviation from the mean is given in parentheses.