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Note

Synthesis and characterization of the new peroxo complex aquaoxodiperoxoimidazolemolybdenum(VI)

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Abstract

A new peroxo complex of Mo(VI), $MoO(O_2)_2(Him)(H_2O)$ (Him = imidazole), has been prepared from octamolybdate of imidazole, $[H_2im]_4[Mo_8O_{26}(Him)_2]$, and H_2O_2. The crystal and molecular structure was determined by X-ray crystallography and showed that the molybdenum atom is seven-coordinated with the nitrogen atom of the imidazole and the four oxygen atoms of the two peroxo groups in the equatorial plane while the oxygen atom and one water molecule occupy the apical positions of a pentagonal bipyramid.

Keywords: Crystal structures; Molybdenum complexes; Peroxo complexes

1. Introduction

An important number of Mo(VI) peroxo complexes has been structurally characterized. Among them are mono-, di-, tetra- and heptanuclear compounds [1].

Mononuclear peroxo compounds with organic ligands bound to the metal are structurally known. These ligands are oxalate [2], glycine and proline [3], 2,2'-bipyridine [4] and tetra-*p*-tolylporphyrin [5]. Other mononuclear peroxo complexes with organic ligands have also been described [6,7].

The majority of mononuclear peroxo compounds described in the literature has been prepared from MoO_3, H_2O_2 and organic ligands. Nevertheless, the peroxo compound $[MoO(O_2)_2(H_2O)_2]$(18-crown-6)H_2O described in Ref. [8] was formed by oxygen uptake from the air involving MoO_3, THF and water. We report in this paper the synthesis and structure of the new peroxo complex $MoO(O_2)_2(Him)(H_2O)$ (Him-imidazole), prepared from octamolybdate of imidazole, $[H_2im]_4[Mo_8O_{26}(Him)_2]$ [9] and H_2O_2.

2. Experimental

2.1. Preparation of the complex

1 g (6.94 mmol) of octamolybdate of imidazole and 30 cm^3 of H_2O_2 (30%) were refluxed with stirring for several hours. Yellow dust appeared after several weeks, and was filtered off. Yellow crystals suitable for X-ray crystallography were obtained upon recrystallization in a mixture of water and acetone 1/1. The octamolybdate of imidazole $[H_2im]_4[Mo_8O_{26}(Him)_2]$ was prepared as described previously [9].

2.2. Physical measurements

IR spectra were recorded in the range 4000–250 cm^{-1} on a Nicolet 710 FT spectrophotometer using KBr pellets.

2.3. X-ray analysis

Crystal data are reported in Table 1. Intensity data were collected on an Enraf-Nonius CAD-4 diffracto-

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Table 1
Crystal data

Formula	$Mo(O)(O_2)_2(C_3H_4N_2)(H_2O)$
Formula weight	262.03
Temperature (K)	298
Crystal system	monoclinic
Crystal size (mm)	0.25 × 0.25 × 0.20
Space group	$P2_1/m$
a (Å)	7.317(2)
b (Å)	6.851(2)
c (Å)	8.570(2)
β (°)	114.32(2)
V (Å^3)	391.5(2)
Z	2
D_{calc} (g cm^{-3})	2.22
$F(000)$	252
Radiation, Mo Kα (Å)	0.71069
μ(Mo Kα) (mm^{-1})	1.67
ω–2θ Scan	$2\theta < 60°$
Range of hkl	$-10 \leq h \leq 9$; $0 \leq k \leq 9$; $0 \leq l \leq 12$
Reflections collected	1292
Reflections used $F > 4\sigma(F)$	1201
$R[\Sigma(\|F_o\| - \|F_c\|)\Sigma\|F_o\|]$	0.048
$R^2{}_w$	0.098
S	1.100
Max. shift/e.s.d.	<0.001
$\Delta\rho$ (e Å^{-3})	+1.48/−1.78

Units weights were adopted in the refinement procedure. $\omega = \sigma^2(F_o)^2 + (0.0698P)^2 + (0.398P)^{-1}$.

meter using graphite monochromated Mo Kα radiation. Lattice parameters were obtained from 25 reflections in the range $6 < 2\theta < 18°$. Lorentz and polarization corrections were applied. The structure was solved by the Patterson method SHELXS86 [10]; all non-H atoms were located on the E maps generated from molybdenum atom coordinates obtained from Patterson maps. All the atoms except the peroxo group are on a crystallographic mirror plane. The isotropic least-squares refinement SHELXL93 [11] converged to $R = 0.077$ and $S = 1.100$. Further anisotropic refinement for all non-H atoms, with H atoms positioned on calculated positions with isotropic thermal parameters, converged to final $R = 0.048$.

3. Results and discussion

Atomic fractional coordinates are reported in Table 2 and a list of bond lengths and angles is given in Table 3. Fig. 1 shows a view of the molecular structure. Molybdenum is seven-coordinated with the nitrogen atom N1 of the imidazole and the four oxygen atoms of the two peroxo groups in the equatorial plane, while the oxygen atom O4 and the oxygen atom of the water molecule O3 occupy the apical positions of a pentagonal bipyramid of the kind hitherto found in most seven-coordinated transition metal diperoxo complexes. The imidazole group, the oxo group and the oxygen atom

Table 2
Fractional atomic coordinates and equivalent isotropic thermal parameters (Å^2)

Atom	x	y	z	B_{eq}
Mo	0.1961(4)	0.2500	0.2399(3)	2.03(1)
O1	0.2621(4)	−0.0272(4)	0.2626(3)	2.89(6)
O2	0.2230(4)	0.0485(4)	0.4062(3)	3.12(6)
O3	0.5439(5)	0.2500	0.3694(4)	2.94(8)
O4	−0.0489(5)	0.2500	0.1131(4)	2.99(8)
N1	0.2615(5)	0.2500	0.0169(4)	2.49(8)
C1	0.4323(7)	0.2500	−0.0046(7)	3.55(13)
C2	0.3893(9)	0.2500	−0.1777(7)	3.67(15)
C3	0.1856(9)	0.2500	−0.2591(6)	4.19(22)
N2	0.1138(6)	0.2500	−0.1409(5)	3.40(12)

Table 3
Selected bond lengths (Å) and angles (°)

Mo–O1	1.949(2)	N1–C1	1.337(7)
Mo–O2	1.935(2)	N1–N2	1.339(4)
Mo–O3	2.320(3)	C1–C2	1.384(9)
Mo–O4	1.670(3)	C2–C3	1.361(8)
Mo–N1	2.152(4)	C3–N2	1.320(8)
O4–Mo–N1	89.6(1)	O1–Mo–O2^a	132.5(1)
O3–Mo–N1	79.9(1)	Mo–N1–N2	121.0(3)
O3–Mo–O4	169.5(1)	Mo–N1–C1	133.2(3)
O2–Mo–N1	131.4(1)	C1–N1–N2	105.8(4)
O2–Mo–O4	103.6(1)	N1–C1–C2	109.6(5)
O2–Mo–O3	83.6(1)	C1–C2–C3	105.5(5)
O1–Mo–N1	87.3(1)	C2–C3–N2	107.7(5)
O1–Mo–O4	102.7(1)	N1–N2–C3	111.4(4)
O1–Mo–O3	76.9(1)	O2–Mo–O1^a	132.5(1)
O2–Mo–O2^a	91.0(1)	O1–Mo–O1^a	153.9(1)

$^a x, -y+\frac{1}{2}, z$.

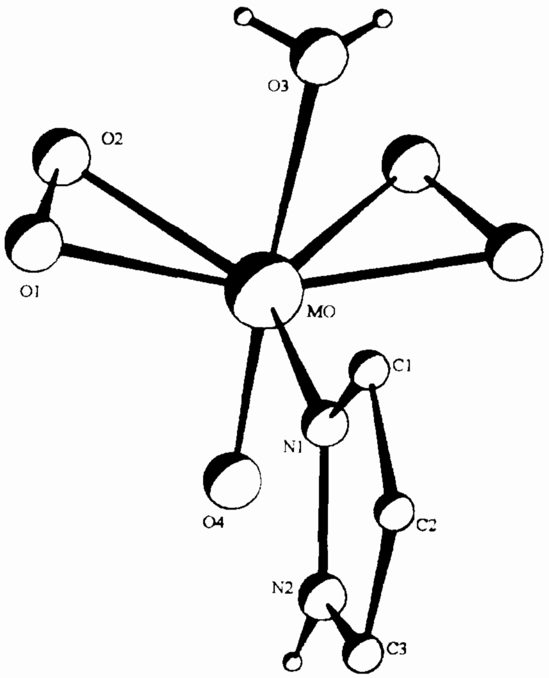

Fig. 1. Perspective view of the structure showing the atom numbering.

of the water molecule are in a crystallographic mirror plane perpendicular to the equatorial plane.

The distances between the molybdenum atom and the two oxygen atoms of the peroxo group are 1.949(2) and 1.935(2) Å. These values are similar to those described in the literature for other peroxo molybdates [1,2]. The value 1.670(3) Å for the distance between the molybdenum atom and the double-bonded oxygen atom O4 does not differ significantly from the corresponding values found in other peroxo compounds of molybdenum(VI) [1,2].

The distance between the molybdenum atom and the equatorial nitrogen atom, which belongs to the imidazole group, is 2.152(4) Å, being of the same order found in octamolybdate of imidazole for the Mo–N distance [9].

The bond length between the water oxygen atom and molybdenum atom is 2.320(3) Å. This value is similar to that found in the $[MoO(O_2)_2(H_2O)_2](18\text{-crown-}6)H_2O$ complex [8] for the same distance, Mo–Ow (2.325 Å), and indicates that the water oxygen atom is weakly bonded to the molybdenum atom. This water molecule is in *trans* position with respect to the oxo group in both compounds. It is interesting to note that *trans* atoms to the terminal oxo group present bond distances to molybdenum greater than in the *cis* position [4,8]. This feature indicates that the oxo ligands have an appreciable *trans* effect.

The O–O distance of the peroxo groups is 1.468(4) Å, which falls in the range of values found in other peroxo complexes of molybdenum(VI) [1,2,12].

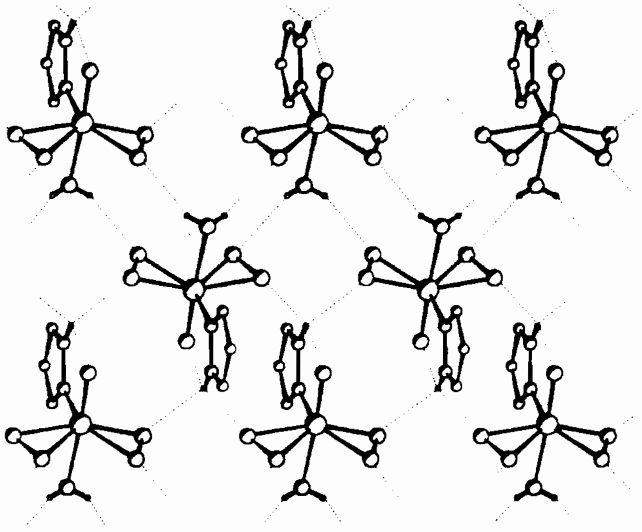

Fig. 2. A view of the crystal showing the hydrogen bonds.

The $MoO(O_2)_2(Him)(H_2O)$ molecules are hydrogen bonded in the crystal, as observed in Fig. 2. There is a hydrogen bond between the N–H of the imidazole and the O oxo group, N2–H···O4 2.879(7) Å (intramolecular), and N2–H···O1 2.937(4) Å ($-x$, $-y$, $-z$). The hydrogen atoms of the water molecules are also bonded to O atoms of the peroxo groups by a hydrogen bond: O3–H···O2 2.844(3) Å ($-x+1$, $+y$, $-z+1$). The IR spectrum shows bands at 961 and 912 cm^{-1} corresponding to $Mo=O_t$ stretching vibrations and in the 887–852 cm^{-1} region the O–O stretching vibrations appear, such as are found in other mononuclear peroxo complexes of molybdenum [1].

Finally, the synthesis of the compound from the octamolybdate of imidazole involves depolymerization by H_2O_2 of the polynuclear anion to a mononuclear peroxo complex, maintaining an imidazole group and a terminal oxygen of the initial octamolybdate of imidazole.

4. Supplementary material

Lists of observed and calculated structure factors, complete bond distances and angles, anisotropic thermal parameters for non-hydrogen atoms, and hydrogen atoms parameters are available from the authors on request.

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