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Group 6 Transition Metal Peroxo Complexes Stabilized by Polydentate Pyridinecarboxylate Ligands

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The solution and crystalline properties of hydrogen oxodiperoxo(pyridine-2-carboxylato)molybdate(VI) bis(pyridine-2-carboxylic acid) monohydrate, $H^+[Mo(O)(O_2)_2(C_5H_4NCO_2)]^-\cdot 2C_5H_4NCO_2H\cdot H_2O$ (**4**), and oxoperoxo(pyridine-2,6-dicarboxylato)aquomolybdenum(VI), $Mo(O)(O_2)[C_5H_3N(CO_2)_2](H_2O)$ (**5**), have been studied. The structures of the two complexes in the solid state have been determined by single-crystal X-ray diffraction methods. In **4**, the two peroxo bridges and the oxygen atom of the pyridine-2-carboxylato ligand lie approximately in the pentagonal plane. The nitrogen of the pyridine-2-carboxylato ligand and the oxo oxygen are located in the apical positions. The outer-sphere cationic moiety consists of a proton hydrogen bonded to several solvate molecules. Several similar complexes were synthesized and characterized with different solvates apparently hydrogen bonded to the proton. In complex **5**, the peroxo bridge and the two oxygen atoms as well as the nitrogen of the pyridine-2,6-dicarboxylato ligand occupy the pentagonal plane. The water molecule and the oxo group are located in the apical positions. Based on ^{13}C NMR, conductivity measurements, and alkalimetric titrations, it was concluded that the structures of complexes **4** and **5** in nonaqueous solvents correspond to that of the crystalline state. The tungsten complexes analogous to **4** and its derivatives exist in nonaqueous solution principally as nonionic species and exhibit greater ligand lability.

Very few Mo(VI) and W(VI) peroxo complexes have been isolated and well characterized. Single-crystal structures have been reported[1,2] only for $(C_5H_5NH)_2{}^+(Mo_2O_{11})^{-2}$ (**1**) and $Mo(O)(O_2)_2(HMPA)(L)^3$ (**2**, $L = H_2O$; **3**, $L = C_5H_5N$). Complex **1** contains no bound organic ligand and belongs to a class of binuclear peroxo anions where the pyridinium ion can be substituted by various cations. Complexes **2** and **3** are the first well-characterized covalent molybdenum peroxo complexes. They are stoichiometric reagents for epoxidation of olefins[4] and catalysts for epoxidation of allylic alcohols to the corresponding epoxy alcohols and derivatives.[5] These results suggest a relationship between the chemistry of group 6 metal peroxo complexes and organic peracids. We have been interested in the extension of this analogy for oxidation of substrates such as alcohols and ketones. Preliminary experiments using the known group 6 peroxo complexes as catalysts showed that complexes of increased stability are needed for the transformation. Molybdenum and tungsten peroxo complexes containing polydentate ligands based on pyridinecarboxylic acids have been chosen as candidates. Some of these complexes have been prepared previously.[6] However, their structures, which are essential for the understanding of the catalytic activity, have not been established. We have, therefore, undertaken an investigation of these complexes in the crystalline state and in solution. The results of this work are summarized in this paper. The catalytic properties of these complexes are the subjects of forthcoming publications.[7]

Results and Discussion

Preparation of Complexes. The general preparation of these complexes involved reaction of molybdenum trioxide or tungstic acid, 30% aqueous hydrogen peroxide, and the appropriate ligand. This method avoided the necessity of sulfuric acid as in previous attempts[6] and substantially increased the yields obtained for the molybdenum and tungsten derivatives.

Table I. Group 6 Transition Metal Complexes

1. $(C_5H_5NH)_2{}^+(Mo_2O_{11})^{2-}$
2. $Mo(O)(O_2)_2(HMPA)(H_2O)$
3. $Mo(O)(O_2)_2(HMPA)(C_5H_5N)$
4. $H^+[Mo(O)(O_2)_2(C_5H_4NCO_2)]^-\cdot 2C_5H_4NCO_2H\cdot H_2O$
5. $Mo(O)(O_2)[C_5H_3N(CO_2)_2](H_2O)$
6. $H^+[W(O)(O_2)_2(C_5H_4NCO_2)]^-\cdot 2C_5H_4NCO_2H$
7. $H^+[Mo(O)(O_2)_2(C_5H_4NCO_2)]^-\cdot H_2O$
8. $H^+[W(O)(O_2)_2(C_5H_4NCO_2)]^-\cdot H_2O$
9. $W(O)(O_2)[C_5H_3N(CO_2)_2](H_2O)\cdot H_2O$
10. $H^+[Mo(O)(O_2)_2(C_5H_4NCO_2)]^-\cdot C_5H_4NCO_2H\cdot H_2O$
11. $H^+[Mo(O)(O_2)_2(C_5H_4NCO_2)]^-\cdot C_5H_4NCO_2CH_3$
12. $Mo(O)(O_2)[C_5H_3N(CO_2)_2](HMPA)$
13. $W(O)(O_2)[C_5H_3N(CO_2)_2](HMPA)\cdot H_2O$

Crystal and Molecular Structures of $H^+[Mo(O)(O_2)_2(C_5H_4NCO_2)]^-\cdot 2C_5H_4NCO_2H\cdot H_2O$ (4) and $Mo(O)(O_2)[C_5H_3N(CO_2)_2](H_2O)$ (5).[8] The complexes hydrogen oxodiperoxo(pyridine-2-carboxylato)molybdate(VI) bis(pyridine-2-carboxylic acid) monohydrate, $H^+[Mo(O)(O_2)_2(C_5H_4NCO_2)]^-\cdot 2C_5H_4NCO_2H\cdot H_2O$ (**4**), and oxoperoxo(pyridine-2,6-dicarboxylato)aquomolybdenum(VI), $Mo(O)(O_2)(C_5H_4N(CO_2)_2](H_2O)$ (**5**), crystallize as stable yellow and yellow-orange prisms, respectively. The crystals of **4** are monoclinic, space group $P2_1/c$.[9] They contain four molecules of $MoC_{18}H_{16}N_3O_{12}$ per unit cell. The crystals of **5** are also monoclinic, space group *Cc*. They contain four molecules of $MoC_7H_5NO_8$ per unit cell. Hydrogen atoms in

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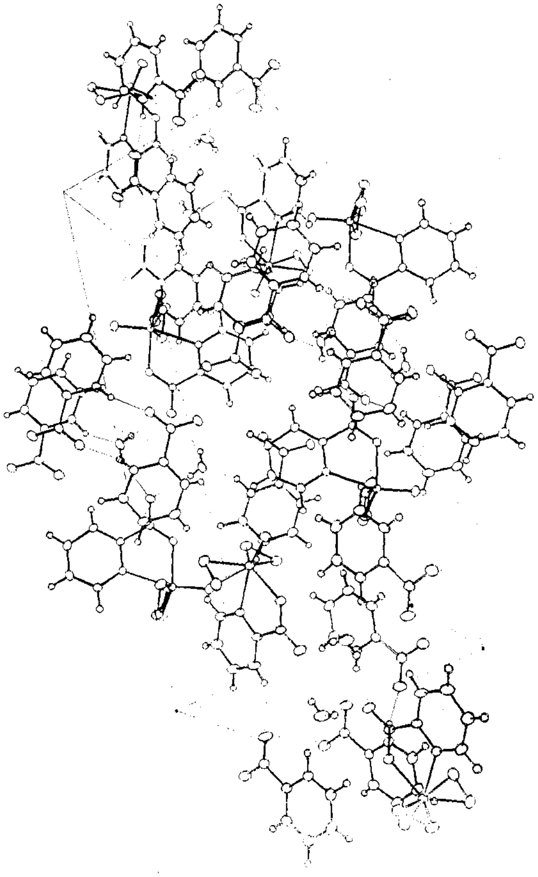


Figure 1. Stereoscopic diagram of the crystal packing of complex **4**.

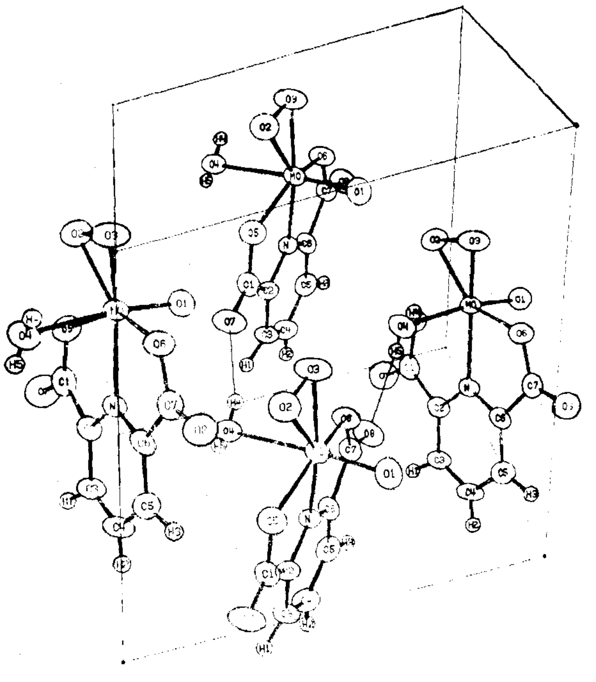


Figure 2. Stereoscopic diagram of the crystal packing of complex **5**.

both complexes have been located after anisotropic refinement of all nonhydrogen atoms.

The spacial arrangements of the molecules in the crystals and the molecular structures of **4** and **5** are represented in Figures 1–4. The bond distances and bond angles are summarized in Tables III and IV and Tables VI and VII.

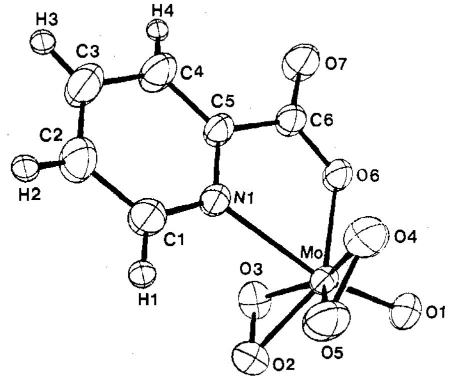


Figure 3. Molecular structure of complex **4**.

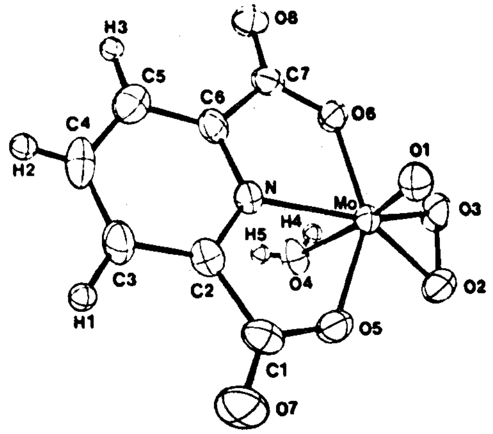


Figure 4. Molecular structure of complex **5**.

Both complexes can be described as slightly distorted pentagonal bipyramids. However, the arrangement of the ligands around the molybdenum atoms in complexes **4** and **5** differs.

In complex **4**, the apical positions are occupied by the oxo oxygen (O1) and the nitrogen of the pyridine-2-carboxylato ligand. The oxygens (O2–O5) of the peroxo groups and the oxygen (O6) of the pyridine-2-carboxylato ligand are located in the equatorial positions and form approximately a pentagonal plane (Table VIII, plane no. 4) which is perpendicular to the plane defined by the pyridine-2-carboxylato ligand, molybdenum atom, and the oxo group (O1).[10] The molybdenum atom is displaced from the pentagonal plane by 0.35 Å toward the oxo oxygen.

In complex **5** the oxo group (O1) and the water molecule (O4) are located in the apical positions. The pentagonal plane (Table IX) is formed by the tridentate pyridine-2,6-dicarboxylato ligand and the peroxo group. Again, the molybdenum atom is displaced by 0.28 Å from the pentagonal plane toward the oxo group. Similar displacements of the metal from the pentagonal plane have been observed in the molybdenum peroxo complexes **2** and **3** (0.40 Å),[2] in the vanadium peroxo complex $NH_4^+\{V(O)(O_2)[C_5H_3N(CO_2)_2]\}^-$ (0.25 Å),[11] and in the chromium peroxo complex $Cr(O)(O_2)_2(1,10\text{-phen})$ (0.25 Å).[12] This displacement is apparently a general phenomenon for peroxo complexes of group 5 and 6 metals.

It is of interest to note that in complexes **3**–**5** the bond length of the pyridine nitrogen to molybdenum steadily decreases from 2.45 Å in **3** to 2.11 Å in **5**. These data are reflected in the decreasing tendency of the pyridine type ligands of **3** and **5** toward dissociation. The pyridine molecule in **3** dissociates at room temperature even in nonpolar solvents,[13] while the pyridine-2,6-dicarboxylato ligand is not labile under similar conditions. This substantial change can be accounted for by two factors: (a) a change from the monodentate ligand in **3**

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations[a] for Complex 4

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo	0.29543 (4)	0.15956 (2)	0.70775 (1)	0.01756 (6)	0.00429 (2)	0.00073 (0)	−0.00210 (6)	0.00218 (2)	0.00014 (1)
O1	0.1831 (4)	0.0311 (2)	0.72525 (10)	0.0262 (6)	0.0053 (2)	0.00136 (4)	−0.0037 (6)	0.0039 (3)	0.0008 (2)
O2	0.1402 (4)	0.2939 (3)	0.72735 (10)	0.0239 (6)	0.0066 (2)	0.00131 (4)	0.0004 (7)	0.0034 (3)	−0.0009 (2)
O3	0.1007 (4)	0.2546 (2)	0.67658 (10)	0.0198 (5)	0.0064 (2)	0.00146 (4)	0.0001 (6)	0.0004 (3)	0.0001 (2)
O4	0.5425 (4)	0.1183 (3)	0.72956 (10)	0.0217 (6)	0.0092 (2)	0.00107 (4)	0.0030 (7)	0.0014 (2)	0.0009 (2)
O5	0.4457 (4)	0.2008 (3)	0.76352 (9)	0.0242 (6)	0.0097 (3)	0.00084 (3)	−0.0022 (7)	0.0009 (2)	−0.0001 (2)
O6	0.3527 (4)	0.0873 (2)	0.63784 (9)	0.0224 (5)	0.0041 (2)	0.00091 (3)	−0.0049 (5)	0.0025 (2)	−0.0005 (1)
O7	0.4814 (4)	0.1006 (2)	0.56389 (9)	0.0313 (7)	0.0068 (2)	0.00088 (3)	−0.0082 (7)	0.0035 (2)	−0.0015 (1)
O8	0.8535 (5)	0.5790 (3)	0.44653 (11)	0.0393 (8)	0.0061 (2)	0.00119 (4)	−0.0094 (7)	0.0030 (3)	−0.0005 (2)
O9	0.7309 (5)	0.4116 (3)	0.48142 (11)	0.0521 (10)	0.0082 (3)	0.00111 (4)	−0.0128 (9)	0.0070 (3)	−0.0007 (2)
O10	0.8199 (5)	−0.3100 (3)	0.52812 (11)	0.0451 (9)	0.0052 (2)	0.00132 (4)	−0.0103 (7)	0.0046 (3)	−0.0011 (2)
O11	0.9197 (5)	−0.1432 (3)	0.48845 (11)	0.0412 (9)	0.0068 (2)	0.00106 (4)	−0.0124 (7)	0.0035 (3)	−0.0007 (2)
O12	0.3600 (6)	−0.1282 (3)	0.53387 (12)	0.0585 (11)	0.0068 (2)	0.00135 (4)	−0.0214 (8)	0.0059 (4)	−0.0013 (2)
N1	0.4706 (4)	0.3057 (2)	0.6646 (1)	0.0169 (5)	0.0043 (2)	0.00077 (3)	−0.0029 (6)	0.0016 (2)	−0.0000 (1)
N2	0.7597 (4)	0.2834 (3)	0.3969 (1)	0.0205 (6)	0.0051 (2)	0.00100 (4)	−0.0027 (7)	0.0017 (3)	0.0002 (2)
N3	0.9100 (4)	−0.0099 (3)	0.5726 (1)	0.0200 (6)	0.0055 (2)	0.00100 (4)	−0.0050 (6)	0.0018 (3)	−0.0005 (2)
C1	0.5326 (5)	0.4138 (3)	0.6811 (1)	0.0222 (8)	0.0059 (3)	0.00088 (4)	−0.0054 (8)	0.0018 (3)	−0.0009 (2)
C2	0.6331 (6)	0.4920 (3)	0.6519 (1)	0.0264 (9)	0.0059 (3)	0.00126 (5)	−0.0100 (8)	0.0021 (4)	−0.0010 (2)
C3	0.6705 (6)	0.4588 (4)	0.6037 (2)	0.0277 (9)	0.0073 (3)	0.00126 (5)	−0.0111 (9)	0.0040 (4)	0.0003 (2)
C4	0.6108 (6)	0.3455 (3)	0.5866 (1)	0.0277 (9)	0.0068 (3)	0.00078 (4)	−0.0087 (9)	0.0032 (3)	−0.0003 (2)
C5	0.5109 (5)	0.2720 (3)	0.6181 (1)	0.0195 (7)	0.0048 (3)	0.00065 (4)	−0.0029 (7)	0.0016 (3)	0.0002 (2)
C6	0.4444 (5)	0.1455 (3)	0.6043 (1)	0.0194 (7)	0.0049 (3)	0.00071 (4)	−0.0027 (7)	0.0015 (3)	−0.0003 (2)
C7	0.7655 (5)	0.2139 (3)	0.3561 (1)	0.0197 (8)	0.0056 (3)	0.00128 (5)	−0.0015 (8)	0.0004 (3)	−0.0006 (2)
C8	0.8289 (6)	0.2640 (4)	0.3128 (1)	0.0207 (8)	0.0079 (3)	0.00114 (5)	0.0001 (9)	0.0008 (3)	−0.0017 (2)
C9	0.8809 (6)	0.3859 (4)	0.3119 (1)	0.0214 (8)	0.0084 (3)	0.00101 (5)	0.0005 (9)	0.0021 (3)	0.0005 (2)
C10	0.8741 (5)	0.4564 (3)	0.3548 (1)	0.0216 (8)	0.0054 (3)	0.00108 (5)	−0.0030 (8)	0.0011 (3)	0.0009 (2)
C11	0.8116 (5)	0.4028 (3)	0.3975 (1)	0.0178 (7)	0.0052 (3)	0.00095 (4)	−0.0015 (7)	0.0012 (3)	−0.0000 (2)
C12	0.7953 (6)	0.4662 (3)	0.4471 (1)	0.0255 (9)	0.0054 (3)	0.00102 (5)	−0.0025 (9)	0.0020 (3)	−0.0000 (2)
C13	0.9054 (6)	0.0657 (4)	0.6113 (1)	0.0206 (8)	0.0065 (3)	0.00127 (5)	−0.0030 (8)	0.0019 (3)	−0.0013 (2)
C14	0.8241 (6)	0.0267 (4)	0.6544 (1)	0.0204 (8)	0.0096 (4)	0.00102 (5)	0.0019 (10)	0.0011 (3)	−0.0016 (2)
C15	0.7502 (6)	−0.0891 (4)	0.6559 (2)	0.0232 (9)	0.0096 (4)	0.00116 (5)	0.0012 (10)	0.0034 (4)	0.0007 (2)
C16	0.7577 (6)	−0.1651 (3)	0.6152 (2)	0.0245 (9)	0.0063 (3)	0.00122 (5)	−0.0041 (9)	0.0019 (4)	0.0005 (2)
C17	0.8411 (5)	−0.1245 (3)	0.5724 (1)	0.0186 (7)	0.0050 (3)	0.00098 (5)	0.0001 (7)	0.0006 (3)	−0.0000 (2)
C18	0.8621 (6)	−0.1981 (3)	0.5249 (1)	0.0230 (8)	0.0051 (3)	0.00110 (5)	−0.0042 (8)	0.0016 (3)	−0.0004 (2)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
H1	0.496 (6)	0.440 (4)	0.714 (2)	5.4 (11)	H9	0.907 (4)	0.532 (3)	0.354 (1)	2.3 (7)
H2	0.689 (5)	0.563 (4)	0.665 (2)	4.2 (9)	H10	0.958 (5)	0.025 (4)	0.550 (2)	4.6 (10)
H3	0.742 (5)	0.503 (4)	0.583 (1)	4.1 (9)	H11	0.961 (6)	0.145 (4)	0.606 (2)	4.5 (11)
H4	0.633 (5)	0.329 (3)	0.556 (1)	3.0 (8)	H12	0.812 (5)	0.078 (4)	0.681 (2)	4.8 (10)
H5	0.717 (6)	0.249 (4)	0.427 (2)	4.6 (10)	H13	0.689 (6)	−0.105 (4)	0.680 (2)	4.8 (10)
H6	0.714 (5)	0.124 (4)	0.359 (1)	2.8 (9)	H14	0.718 (5)	−0.225 (3)	0.618 (1)	3.0 (8)
H7	0.837 (6)	0.208 (4)	0.289 (2)	4.6 (10)	H15	0.378 (6)	−0.073 (4)	0.542 (2)	4.7 (10)
H8	0.927 (7)	0.429 (5)	0.283 (2)	6.2 (12)	H16	0.383 (8)	−0.146 (5)	0.508 (2)	8.6 (17)

[a] The form of the anisotropic thermal parameter is $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$.

to di- and tridentate ligands in **4** and **5**, respectively; (b) the absence of the labilizing effect of the trans oxo group in **5**. The effect of the change from a monodentate to a bidentate ligand (both trans to the oxo group) is clearly evident from comparison of the Mo–N bond length in **3** (2.45 Å) and **4** (2.35 Å). The latter Mo–N distance is in good agreement with the bond length of 2.33 Å in Mo(VI) oxo complexes containing polydentate nitrogen ligands located trans to the oxo group.[14] The labilizing effect of the trans oxo group on the M–N bond in high-valent group 6 metal complexes has been clearly documented in the cases of Cr(O)(O$_2$)$_2$(2,2′-bpy)[15] and Cr(O)(O$_2$)$_2$(1,10-phen)[12] where the apical (trans to the oxo group) Cr–N bond distance is longer (2.26 and 2.23 Å, respectively) than the equatorial (cis to the oxo group) Cr–N bond distance (2.11 Å for both complexes). It is, therefore, suggested that the decrease in the Mo–N bond distance in **5** as compared to **4** is attributable to the absence of the trans oxo group and to the substitution of a bidentate pyridine-2-carboxylato ligand in **4** for the tridentate pyridine-2,6-dicarboxylato ligand in **5**. The fact that the pyridine-2,6-dicarboxylato ligand is tridentate is also supported by the shortening of the carboxylato Mo–O6 or Mo–O5 distances in **5** by about 0.04–0.06 Å, when compared with the Mo–O6 distance in **4**. In both complexes the corresponding Mo–O bonds are cis to the oxo group and, therefore, directly comparable.

The O–O and Mo–O bond distances of the peroxo moiety as well as the Mo–O bond distance[1,2] of the oxo group in **4** and **5** (Tables III and VI) are very close to the analogous bond distances in the known molybdenum peroxo complexes. The insensitivity of the O–O distance of the peroxo bridge to the change of ligands is not at all surprising in view of the finding that even low-valent metal peroxo complexes based on Rh and Ir have similar O–O bond distances (1.45–1.52 Å).[16] These O–O distances are practically invariant to the metal and the ligand.

The coordinated water molecules in crystals of **2** and **5** also exhibit different labilities. The water in **2** is easily removed under vacuum; it is not labile in **5**. This phenomenon may be caused by the stronger Mo–O4 bond in **5** when compared to the same bond in **2**. This is indicated by the slightly shorter Mo–OH$_2$ bond distance (0.06 Å) in **5**. However, the intramolecular network of hydrogen bonding may play an even more important role. Each hydrogen of the water molecule is bonded to one carboxyl group of the pyridine-2,6-dicarboxylato ligand (e.g., O4–H5···O8 in Figure 2 and Table X).

The outer sphere of complex **4** is an interesting array of two molecules of pyridine-2-carboxylic acid and one molecule of water held together by hydrogen bonding (Figure 1). The oxygen of the water molecule (O12) is bonded to one N–H proton of one of the free pyridine-2-carboxylic acids (N2–H5)

Table III. Bond Distances (Å) for Complex **4**

Mo-O1	1.685 (2)	C1-H1	0.97 (4)
Mo-O2	1.923 (2)	C2-C3	1.379 (4)
Mo-O3	1.948 (2)	C2-H2	0.94 (3)
Mo-O4	1.954 (2)	C3-C4	1.380 (4)
Mo-O5	1.914 (2)	C3-H3	0.91 (3)
Mo-O6	2.088 (2)	C4-C5	1.378 (3)
Mo-N1	2.351 (2)	C4-H4	0.87 (3)
O2-O3	1.462 (3)	C5-C6	1.499 (3)
O4-O5	1.467 (3)	C7-C8	1.372 (4)
O6-C6	1.295 (3)	C7-H6	1.05 (3)
O7-C6	1.226 (3)	C8-C9	1.373 (5)
O8-C12	1.292 (3)	C8-H7	0.89 (4)
O9-C12	1.198 (3)	C9-C10	1.388 (4)
O10-C18	1.252 (3)	C9-H8	0.96 (4)
O11-C18	1.227 (4)	C10-C11	1.370 (4)
O12-H15	0.66 (4)	C10-H9	0.85 (3)
O12-H16	0.76 (6)	C11-C12	1.511 (4)
N1-C1	1.330 (3)	C13-C14	1.377 (4)
N1-C5	1.341 (3)	C13-H11	0.96 (4)
N2-C7	1.334 (4)	C14-C15	1.366 (5)
N2-C11	1.347 (3)	C14-H12	0.91 (4)
N2-H5	0.96 (4)	C15-C16	1.373 (5)
N3-C13	1.329 (4)	C15-H13	0.80 (4)
N3-C17	1.338 (3)	C16-C17	1.382 (4)
N3-H10	0.79 (4)	C16-H14	0.72 (3)
C1-C2	1.374 (4)	C17-C18	1.518 (4)

Table IV. Bond Angles for Complex **4** in Degrees

H15-O12-H16	121 (5)	Mo-N1-C1	127.7 (2)
C1-N1-C5	118.4 (2)	O8-C12-C11	112.9 (2)
C7-N2-C11	122.7 (2)	O9-C12-C11	119.7 (3)
C7-N2-H5	120 (2)	N3-C13-C14	119.3 (3)
C11-N2-H5	117 (2)	N3-C13-H11	115 (2)
C13-N3-C17	124.1 (3)	C14-C13-H11	125 (2)
C13-N3-H10	108 (3)	C13-C14-C15	118.7 (3)
C17-N3-H10	128 (3)	C13-C14-H12	122 (2)
N1-C1-C2	122.1 (3)	C15-C14-H12	120 (2)
N1-C1-H1	118 (2)	C14-C15-C16	120.5 (3)
C2-C1-H1	120 (2)	C14-C15-H13	116 (3)
C1-C2-C3	119.5 (3)	C16-C15-H13	122 (3)
C1-C2-H2	122 (2)	C15-C16-C17	119.9 (3)
C3-C2-H2	118 (2)	C15-C16-H14	115 (3)
C2-C3-C4	118.8 (3)	C17-C16-H14	125 (3)
C2-C3-H3	125 (2)	N3-C17-C16	117.5 (3)
C4-C3-H3	116 (2)	N3-C17-C18	116.6 (2)
C3-C4-C5	118.3 (3)	C16-C17-C18	125.9 (3)
C3-C4-H4	116 (2)	O10-C18-O11	127.5 (3)
C5-C4-H4	126 (2)	O10-C18-C17	115.0 (3)
N1-C5-C4	122.8 (2)	O11-C18-C17	117.5 (2)
Mo-O3-O2	66.9 (1)	Mo-O2-O3	68.7 (1)
Mo-O6-C6	124.0 (2)	Mo-O5-O4	69.2 (1)
N1-C5-C6	114.1 (2)	Mo-N1-C5	113.9 (2)
C4-C5-C6	123.1 (2)	O1-Mo-O2	104.8 (1)
O6-C6-O7	123.3 (2)	O1-Mo-O3	101.4 (1)
O6-C6-C5	116.0 (2)	O1-Mo-O4	100.5 (1)
O7-C6-C5	120.6 (2)	O1-Mo-O5	104.6 (1)
N2-C7-C8	119.5 (3)	O1-Mo-O6	92.66 (8)
N2-C7-H6	117 (2)	O1-Mo-N1	164.48 (9)
C8-C7-H6	123 (2)	O2-Mo-O3	44.40 (9)
C7-C8-C9	119.3 (3)	O2-Mo-O4	129.8 (1)
C7-C8-H7	112 (2)	O2-Mo-O5	86.9 (1)
C9-C8-H7	128 (2)	O2-Mo-O6	130.88 (9)
C8-C9-C10	120.1 (3)	O2-Mo-N1	87.40 (8)
C8-C9-H8	125 (3)	O3-Mo-O4	158.05 (9)
C10-C9-H8	115 (3)	O3-Mo-O5	129.38 (9)
C9-C10-C11	118.9 (3)	O3-Mo-O6	87.60 (9)
C9-C10-H9	120 (2)	O3-Mo-N1	80.36 (8)
C11-C10-H9	122 (2)	O4-Mo-O5	44.54 (9)
N2-C11-C10	119.4 (3)	O4-Mo-O6	89.74 (8)
N2-C11-C12	115.0 (2)	O4-Mo-N1	78.11 (8)
C10-C11-C12	125.6 (3)	O5-Mo-O6	132.89 (9)
O8-C12-O9	127.3 (3)	O5-Mo-N1	85.36 (8)
Mo-O4-O5	66.3 (1)	O6-Mo-N1	71.94 (7)

which in the crystal exists in the form of an internal salt (Figure 1). Each hydrogen of the water molecule is in turn bonded to one carboxyl group of the pyridine-2-carboxylato ligand (O7···H15-O12-H16, Table X) and to one carboxyl of the free pyridine-2-carboxylic acid (Figure 1). Certain O···H distances (e.g., O7···H15, 2.10 Å, Table X), although longer than the average O···H bonds (1.7 Å) determined by neutron diffraction, are still significantly shorter than the van der Waals contact distance (2.6 Å)[17] and therefore considered to indicate hydrogen bonding. The proton needed to balance the monoanionic peroxomolybdenum moiety $[Mo(O)(O_2)_2(C_5H_4NCO_2)]^-$ has not been located.[18] However, the proton was detected by alkalimetric titration and by conductivity measurements as discussed below.

In conclusion, we would like to stress that complex **4** is one of the first well-characterized anionic molybdenum peroxo complexes with organic ligands covalently bonded to the metal.[19] Complex **5** is the first covalent peroxo molybdenum species containing only one peroxo bridge per molybdenum and a tridentate ligand.[20]

Spectral and Physical Properties of $H^+[Mo(O)(O_2)_2(C_5H_4NCO_2)]^-\cdot 2C_5H_4NCO_2H\cdot H_2O$ (4) and the Tungsten Analogue (6). The elemental analyses suggest that complexes **4** and hydrogen oxodiperoxo(pyridine-2-carboxylato)tungstate(VI) bis(pyridine-2-carboxylic acid), $H^+[W(O)(O_2)_2(C_5H_4NCO_2)]^-\cdot 2C_5H_4NCO_2H$ (**6**), are very similar in structure. In agreement with the single-crystal structure, the IR spectrum of **4** (Table XI) shows bands at 3530 and 3340 cm^{-1} which may be assigned to the outer-sphere water molecule. These bands are absent in the IR spectrum of **6**. Complex **4** shows three very closely spaced $\nu(C{=}O)_{as}$ modes at frequencies lower than expected for a free pyridine-2-carboxylic acid. The shift in the frequency may be attributed to the extensive hydrogen bonding (Figure 1). On the other hand, the tungsten analogue displays only two, well-separated $\nu(C{=}O)$ frequencies: the one at 1735 cm^{-1} is close to the free pyridine-2-carboxylic acid and the other one at 1690 cm^{-1} is close to that expected for the metal bonded pyridine-2-carboxylato ligand. Unlike complex **4** which shows only one $\nu(O{-}O)$ of equal intensity with the Mo=O band, complex 6 displays several modes in the peroxo region, each of lower intensity than the W=O band.

In order to obtain additional structural information, ^{13}C NMR, alkalimetric titration, and conductivity measurements in organic solvents were employed. The ^{13}C NMR spectrum of **4** in methanol clearly shows the presence of two types of pyridine-2-carboxylato ligands (Table XII) in the ratio of about 1:2 as required by the crystal structure.[21]

On complexation to molybdenum, the chemical shifts of the carbons in pyridine-2-carboxylic acid change substantially (Table XII). The signals assigned to the carbons in positions 2 and 6 are shifted upfield by ~7 and ~3 ppm, respectively, while the signals of the carbon in position 4 and the carboxylic carbon are shifted downfield ~6 and ~3 ppm, respectively. With the exception of the carboxylic carbon, similar changes are observed in the case of the outer-sphere pyridine-2-carboxylic acid in **4**. The direction of the changes is analogous to those observed on protonation of pyridine,[22] suggesting that Mo(VI) behaves as a strong Lewis acid.

The results of alkalimetric titrations are summarized in Table XIII.[23] Complexes **4** and **6** show three inflection points. In the case of **4** the inflection at pH 3.6 requires 1 equiv of base/mol of **4**. It is attributed to the neutralization of the outer-sphere proton (eq 1), the presence of which is suggested

$$H^+[Mo(O)(O_2)_2(C_5H_4NCO_2)]^-\cdot 2C_5H_4NCO_2H\cdot H_2O + NaOH \rightarrow Na^+[Mo(O)(O_2)_2(C_5H_4NCO_2)]^- + 2C_5H_4NCO_2H + 2H_2O \quad (1)$$

by the crystal structure. This assignment is supported (a) by ^{13}C NMR data suggesting that the pyridine-2-carboxylato ligand of the molybdenum anionic moiety does not dissociate

Table V. Positional and Thermal Parameters and Their Estimated Standard Deviations[a] for Complex **5**

atom	x	y	z	B_{11} or B (Å^2)	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo	0.2500 (0)	0.24950 (3)	0.0000 (0)	0.00546 (3)	0.00372 (2)	0.00754 (3)	0.00107 (5)	0.00525 (5)	0.00101 (6)
O1	0.3106 (4)	0.3200 (3)	0.1634 (4)	0.0098 (4)	0.0059 (3)	0.0087 (4)	0.0032 (6)	0.0054 (7)	−0.0004 (6)
O2	0.0675 (4)	0.3199 (3)	−0.0929 (4)	0.0087 (4)	0.0057 (3)	0.0119 (5)	0.0036 (6)	0.0050 (7)	0.0033 (6)
O3	0.0503 (4)	0.2169 (4)	−0.0101 (5)	0.0067 (4)	0.0067 (3)	0.0168 (6)	0.0007 (7)	0.0106 (7)	0.0025 (8)
O4	0.1982 (4)	0.1395 (3)	−0.2148 (4)	0.0077 (4)	0.0051 (2)	0.0106 (4)	−0.0033 (6)	0.0082 (6)	−0.0030 (6)
O5	0.3206 (4)	0.3688 (3)	−0.1265 (4)	0.0080 (3)	0.0041 (2)	0.0102 (4)	0.0016 (6)	0.0045 (7)	0.0031 (6)
O6	0.2798 (3)	0.0896 (3)	0.0988 (4)	0.0066 (3)	0.0044 (2)	0.0105 (4)	0.0009 (5)	0.0072 (6)	0.0030 (6)
O7	0.5076 (4)	0.4487 (3)	−0.1956 (5)	0.0116 (4)	0.0058 (3)	0.0160 (5)	−0.0049 (6)	0.0101 (8)	0.0054 (7)
O8	0.4301 (4)	−0.0551 (3)	0.1868 (4)	0.0111 (4)	0.0050 (3)	0.0127 (5)	0.0025 (6)	0.0102 (7)	0.0070 (6)
N	0.4611 (4)	0.1960 (3)	−0.0073 (4)	0.0054 (4)	0.0029 (2)	0.0068 (4)	−0.0008 (6)	0.0046 (6)	−0.0013 (6)
C1	0.4573 (6)	0.3716 (5)	−0.1371 (5)	0.0100 (6)	0.0042 (3)	0.0074 (6)	−0.0028 (8)	0.0057 (9)	0.0004 (8)
C2	0.5405 (6)	0.2665 (4)	−0.0719 (6)	0.0063 (5)	0.0039 (3)	0.0078 (6)	−0.0028 (7)	0.0049 (9)	−0.0023 (7)
C3	0.6826 (6)	0.2365 (4)	−0.0705 (7)	0.0049 (5)	0.0058 (4)	0.0105 (7)	−0.0004 (7)	0.0071 (9)	−0.0002 (8)
C4	0.7369 (5)	0.1348 (4)	−0.0048 (7)	0.0049 (5)	0.0071 (4)	0.0118 (5)	0.0006 (9)	0.0064 (8)	−0.0051 (11)
C5	0.6552 (5)	0.0639 (4)	0.0641 (6)	0.0077 (6)	0.0051 (4)	0.0086 (6)	0.0013 (8)	0.0021 (10)	−0.0022 (8)
C6	0.5153 (5)	0.0984 (4)	0.0587 (5)	0.0082 (5)	0.0036 (3)	0.0069 (5)	−0.0000 (7)	0.0071 (8)	−0.0018 (7)
C7	0.4053 (6)	0.0361 (4)	0.1220 (5)	0.0086 (5)	0.0045 (3)	0.0069 (5)	−0.0003 (8)	0.0051 (9)	0.0018 (8)
H1	0.729 (5)	0.286 (4)	−0.133 (5)	1.1 (8)					
H2	0.823 (5)	0.114 (4)	0.003 (6)	2.6 (11)					
H3	0.696 (5)	0.002 (4)	0.126 (6)	2.6 (10)					
H4	0.146 (8)	0.102 (8)	−0.193 (10)	8.1 (22)					
H5	0.248 (5)	0.113 (4)	−0.235 (5)	2.2 (10)					

[a] The form of the anisotropic thermal parameter is $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$.

Table VI. Bond Distances (Å) for Complex **5**

Mo-O1	1.670 (5)	O7-C1	1.202 (8)
Mo-O2	1.907 (5)	O8-C7	1.206 (8)
Mo-O3	1.912 (6)	N-C2	1.347 (9)
Mo-O4	2.287 (6)	N-C6	1.324 (9)
Mo-O5	2.026 (5)	C1-C2	1.492 (10)
Mo-O6	2.052 (4)	C2-C3	1.390 (10)
Mo-N	2.116 (6)	C3-C4	1.365 (10)
O2-O3	1.447 (8)	C3-H1	0.99 (7)
O4-H4	0.72 (13)	C4-C5	1.389 (11)
O4-H5	0.63 (8)	C4-H2	0.84 (7)
O5-C1	1.327 (8)	C5-C6	1.376 (9)
O6-C7	1.311 (8)	C5-H3	0.93 (7)
		C6-C7	1.504 (9)

Table VII. Bond Angles for Complex **5** in Degrees

Mo-O2-O3	67.9 (3)	H1-C4-H2	101 (5)
Mo-O3-O2	67.5 (3)	H1-C4-H3	166 (3)
Mo-O4-H4	97 (11)	H2-C4-H3	94 (5)
Mo-O4-H5	121 (8)	C4-C5-C6	117.3 (6)
H4-O4-H5	114 (13)	C4-C5-H2	23 (2)
Mo-O5-O7	148.1 (3)	C4-C5-H3	123 (5)
Mo-O5-C1	122.1 (4)	C6-C5-H2	141 (2)
O7-O5-C1	26.5 (4)	C6-C5-H3	119 (5)
Mo-O6-O8	148.0 (3)	H2-C5-H3	99 (5)
Mo-O6-C7	121.1 (4)	N-C6-C5	121.6 (6)
O8-O6-C7	27.0 (3)	N-C6-C7	111.1 (6)
O5-O7-C1	29.5 (4)	N-C6-H3	145 (2)
O6-O8-C7	29.6 (4)	C5-C6-C7	127.3 (6)
Mo-N-C2	118.5 (5)	C5-C6-H3	24 (2)
Mo-N-C6	119.8 (5)	C7-C6-H3	104 (2)
C2-N-C6	121.6 (6)	O6-C7-O8	123.3 (6)
O5-C1-O7	123.9 (7)	O6-C7-C6	113.7 (5)
O5-C1-C2	112.2 (6)	O8-C7-C6	123.0 (6)
O7-C1-C2	123.8 (7)	O1-Mo-O2	104.7 (2)
N-C2-C1	111.9 (6)	O1-Mo-O3	104.4 (3)
N-C2-C3	119.7 (6)	O1-Mo-O4	171.8 (3)
N-C2-H1	145 (2)	O1-Mo-O5	95.0 (2)
C1-C2-C3	128.4 (6)	O1-Mo-O6	94.2 (2)
C1-C2-H1	102 (2)	O1-Mo-N	93.5 (2)
C3-C2-H1	26 (2)	O2-Mo-O3	44.5 (3)
C2-C3-C4	118.5 (7)	O2-Mo-O4	83.5 (2)
C2-C3-H1	115 (4)	O2-Mo-O5	81.3 (2)
C2-C3-H2	140 (2)	O2-Mo-O6	126.2 (2)
C4-C3-H1	126 (4)	O2-Mo-N	150.6 (2)
C4-C3-H2	21 (2)	O3-Mo-O4	81.7 (3)
H1-C3-H2	105 (4)	O3-Mo-O5	125.3 (3)
C3-C4-C5	121.3 (7)	O3-Mo-O6	82.2 (2)
C3-C4-H1	23 (2)	O3-Mo-N	151.2 (2)
C3-C4-H2	123 (5)	O4-Mo-O5	85.5 (2)
C3-C4-H3	143 (2)	O4-Mo-O6	81.3 (2)
C5-C4-H1	143 (2)	O4-Mo-N	78.8 (2)
C5-C4-H2	116 (5)	O5-Mo-O6	147.3 (2)
C5-C4-H3	23 (2)	O5-Mo-N	74.2 (2)
		O6-Mo-N	74.0 (2)

at room temperature and (b) by the analogy of the suggested sodium salt of the molybdenum anion to the known vanadium complex[11] $NH_4^+\{V(O)(O_2)[C_5H_3N(CO_2)_2]\}^-$ and the molybdenum complex[24] $K^+_2[MoO(O_2)_2(C_2O_4)]^{2-}$.

The second inflection (pH 7.4) corresponds to the neutralization of the outer-sphere pyridine-2-carboxylic acid. This assignment is unequivocally established by (a) the absence of this inflection in the case of complexes **5** and **7** and (b) the effect of the addition of 2 equiv of pyridine-2-carboxylic acid/mol of complex **4** on the titration curve. In this latter case, the titration is identical with the exception that two additional equivalents of the base are needed to reach the inflection at pH 7.4.

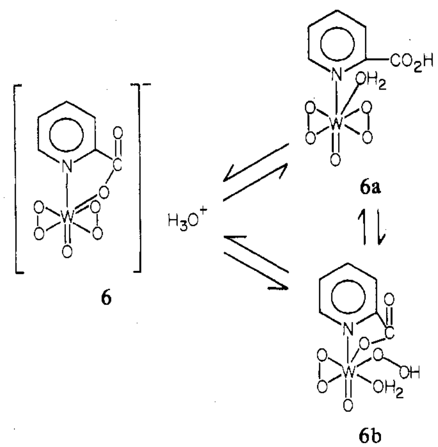
The third inflection requiring 1 equiv of base/mol of **4** may be expressed by eq 2.[25]

$$2Na^+[Mo(O)(O_2)_2(C_5H_4NCO_2)]^- + 2NaOH \rightarrow Na^+_2[Mo_2O_{11}]^{2-} + H_2O + 2C_5H_4NCO_2^-Na^+ \quad (2)$$

In contrast to **4** the clearly defined separation of the first and second steps in the alkalimetric titration of **6** is absent (Table XIII). The observed behavior strongly suggests that the tungsten-bound pyridine-2-carboxylato ligand can be hydrolyzed upon addition of aqueous sodium hydroxide much easier and at a lower pH than in the molybdenum analogue **4**.

In methanol and acetonitrile the molar conductivity of **4** (Table XIV) is in the range expected for a two-ion conductor in agreement with the crystal structure. However, in both solvents the molar conductivity of **6** is about half of the molar conductivity of **4**.

All the evidence amassed so far strongly suggests that the structure of the molybdenum anionic moiety in **4**, when dissolved in organic solvents, is the same as that in the solid state. On the other hand, the crystal structure of **4** may not be a perfect model for **6** at least when dissolved in organic solvents. It is proposed that the presence of the forms **6a** and **6b** should also be considered. The forms **6a** and **6b** are nonionic and would agree with the substantial decrease of the molar conductivities of **6** in acetonitrile and methanol.



Spectral and Physical Properties of $H^+[Mo(O)(O_2)_2(C_5H_4NCO_2)]^-\cdot H_2O$ (7) and the Tungsten Analogue $H^+[W(O)(O_2)_2(C_2H_4NCO_2)]^-\cdot H_2O$ (8). It is suggested that the structures of hydrogen oxodiperoxo(pyridine-2-carboxylato)molybdate(VI) monohydrate, $H^+[Mo(O)(O_2)_2(C_5H_4NCO_2)]^-\cdot H_2O$ (**7**), and hydrogen oxodiperoxo(pyridine-2-carboxylato)tungstate(VI) monohydrate, $H^+[W(O)(O_2)_2(C_5H_4NCO_2)]^-\cdot H_2O$ (**8**), are analogous to those of **4** and **6**, respectively. The following evidence supports this statement. The IR spectra of the oxoperoxo moiety of complexes **4** and **6** are practically identical with the IR spectra of **7** and **8**, respectively (Table XI). The IR spectra of **7** and **8** are also analogous, with the exception of small frequency shifts of ν(OH), $\nu(C{=}O)_{as}$, and the fine structure in the ν(O—O) region of 830–860 cm^{-1}.

The chemical shifts in the ^{13}C NMR spectra of the pyridine-2-carboxylato ligand in **7** are in good agreement with the chemical shifts of the metal-bound pyridine-2-carboxylato ligand in **4** (Table XII).[21]

The alkalimetric titration of **7** dissolved in methanol exhibits two inflections (Table XIII). The first at pH 5.08 corresponds to 1 equiv of base/mol of **7**. It is attributed to the neutralization of the outer-sphere proton in analogy to eq 1. The second inflection at pH 10.2 again requires 1 mol of base and can be described by eq 2. Besides the potentiometric jump at pH 7.4, observed in the alkalimetric titration of **4** and assigned to the neutralization of the outer-sphere pyridine-2-carboxylic acid and naturally missing in the titration of **7**, a very good analogy between **4** and **7** is demonstrated.

Three inflections were observed in the alkalimetric titration of **8** (Table XIII). However, the fact that none of the observed inflections corresponds to 1 mol of base/mol of **8** strongly suggests that the pyridine-2-carboxylato ligand is relatively easily hydrolyzed on addition of aqueous sodium hydroxide. The behavior of **8** is again in complete agreement with the properties of **6**. Very close similarities of **4** to **7** and **6** to **8** were also found in the molar conductivities (Table XIV).

Spectral and Physical Properties of $Mo(O)(O_2)[C_5H_3N(CO_2)_2](H_2O)$ (5) and the Tungsten Analogue (9). The IR spectra (Table XI) display typical absorptions of covalent peroxo complexes for both **4** and oxoperoxo(pyridine-2,6-dicarboxylato)aquotungsten(VI) monohydrate, $W(O)(O_2)_2[C_5H_3N(CO_2)_2]H_2O\cdot H_2O$ (**9**); zero molar conductivities (Table XIV) also suggest fully covalent structures.[20]

In the ^{13}C NMR spectra (Table XII) the carboxylic carbon of the pyridine-2,6-dicarboxylato ligand shows a downfield shift of 2.5 and 2.2 ppm in **5** and **9**, respectively. This chemical shift is less than that observed in the ^{13}C NMR spectra of the pyridine-2-carboxylato ligand in **4** and **6**. Nevertheless, it supports a carboxyl bonded to a high-valent metal. The carbon in position 4 of the pyridine-2,6-dicarboxylato ligand displays a much stronger downfield shift of 7.6 and 8.5 ppm in **5** and **9**, respectively, in analogy to the pyridine-2-carboxylato ligand in **4** and **6**. No sign of ligand dissociation has been observed in the NMR spectra.

Table VIII

Weighted Least-Squares Planes for Complex **4**

plane	atoms in plane	equation of plane
1	Mo, N1, C1, C2, C3, C4, C5, C6, O6	$-0.8363x + 0.4218y - 0.3501z = -7.6795$
2	N2, C7, C8, C9, C10, C11, C12	$-0.9313x + 0.2783y - 0.2349z = -6.7955$
3	N3, C13, C14, C15, C16, C17, C18	$-0.8735x + 0.3614y - 0.3261z = -10.8367$
4	O2, O3, O4, O5, O6	$0.5155x + 0.7698y - 0.3764z = -4.4593$

Distance of Atoms from Plane (Å)

plane 1		plane 2		plane 3		plane 4	
Mo	0.000	N2	0.001	N3	0.007	O2	−0.018
N1	−0.006	C7	0.004	C13	−0.004	O3	0.026
C1	−0.047	C8	−0.010	C14	−0.008	O4	0.019
C2	−0.034	C9	0.006	C15	−0.000	O5	−0.009
C3	0.034	C10	−0.000	C16	0.007	O6	−0.017
C4	0.042	C11	0.002	C17	0.002	Mo	−0.349
C5	0.026	C12	−0.003	C18	−0.009	O1	−2.023
C6	−0.014	O8	−0.058	O10	−0.204	N1	1.973
O6	−0.029	O9	+0.060	O11	0.153		
O1	−0.060						
O7	−0.069						

Table IX

Weighted Least-Squares Planes for Complex **5**

plane	atoms in plane	equation of plane
1	N, O2, O3, O5, O6	$-0.0156x - 0.5200y - 0.8540z = -1.2655$
2	N, C1, C2, C3, C4, C5, C6, C7, O5, O6	$-0.113x - 0.4862y - 0.8667z = -1.5300$

Distance of Atoms from Plane (Å)

plane 1		plane 2		plane 2	
N	0.069	N	−0.009	C7	−0.005
O2	0.022	C1	−0.036	O5	0.046
O3	0.025	C2	−0.013	O6	0.002
O5	−0.058	C3	−0.004	Mo	−0.142
O6	−0.058	C4	0.026	O2	−0.341
Mo	−0.277	C5	0.003	O3	0.328
		C6	−0.004		

Table X. Hydrogen Bond Distances and Angles for the Water Molecule in Complex **5** and for the Outer-Sphere Molecules in Complex **4**

Complex **4**

N2–0.96 (4) Å–H5–1.77 (4) Å–O12, angle = 154.7 (32)°
O7–2.10 (4) Å–H15–0.66 (4) Å–O12, angle = 170.1 (46)°
O7–2.23 (6) Å–H16–0.76 (6) Å–O12, angle = 149.2 (51)°

Complex **5**

O4–0.72 (6) Å–H4–2.21 (7) Å–O7, angle = 159 (46)°
O4–0.63 (7) Å–H5–2.14 (8) Å–O8, angle = 170 (48)°

The alkalimetric titration (Table XIII) of complexes **5** and **9** in methanol with aqueous sodium hydroxide exhibits only one inflection at pH 9.2 corresponding to 3 equiv of base/mol of the complex. The neutralization, which can be described by eq 3 for **5**, clearly establishes that the pyridine-2,6-dicarboxylato ligand is solvolyzed in aqueous media only at high pH.

$$2Mo(O)(O_2)[C_5H_3N(CO_2)_2](H_2O) + 6NaOH \rightarrow Na^+{}_2Mo_2O_9{}^{2-} + 2C_5H_3N(CO_2{}^-Na^+)_2 + 5H_2O \quad (3)$$

In conclusion, we stress that all of the data strongly suggest that the single-crystal structure of **5** is representative of the structures of complex **9** in the solid state as well as of both

Table **XI.** Infrared Spectra of the Peroxo Complexes in Nujol

	bands, cm^{-1}					
compd	$\nu(OH)$	$\nu(C{=}O)_{as}$	$\nu(M{=}O)$	$\nu(O{-}O)$	$\nu(\mathrm{M}{<}^{\mathrm{O}}_{\mathrm{O}}{|})_{\mathrm{as}}$	$\nu(\mathrm{M}{<}^{\mathrm{O}}_{\mathrm{O}}{|})_{\mathrm{sym}}$
4	3530 m, 3340 m	1650 s, 1640 s, 1630 s	938 s	860 s	580 s	550 m[a]
6	none	1735 m, 1690 s	935 s	850 m 840 m 830 m	595 s	560 m
7	3480 s	1685 s	973 s	850 s	572 s	542 m
8	3440 s	1695 s	978 s	845 m 836 m 825 s	560 s	538 s
5	3425 br 3100 br	1710 s, 1690 s	970 s	900 s	592 m	575 s
9	3570 s 3480 m	1705 s, 1685 s	982 s	875 s	602 m	571 s
10	none	1720 s	955 s	845 s	584 s	554 m
11	none	1745 s, 1680 s	945 s	850 s	575 s	539 w
12	none	1700 s	950 s	895 s	583 m	557 s
13	3420 w	1710 s, 1730 s	968 s	880 s	594 m	569 s

[a] Not a very well-defined shoulder, assignment uncertain.

Table **XII.** Chemical Shift Relative to Me_4Si in ^{13}C NMR of Peroxo Complexes

		ring carbons					carboxylic carbons	
compd	solvent	C2	C3	C4	C5	C6	C7	C8
pyridine-2-carboxylic acid	CD_3OD	148.9	126.8	142.1	129.0	148.2	166.8	
4 *a*	CD_3OD	140.2	127.0	145.8	129.5	144.4	163.2	
b		141.7	124.7	147.9	128.1	144.8	170.4	
7	CD_3OD	141.4	125.8	148.3	129.4	146.3	171.6	
11 *c*	CD_3OD	140.3	128.0	147.7	130.9	145.8	160.3	51.1[d]
b		140.3	124.7	147.7	128.0	144.2	170.3	
pyridine-2,6-dicarboxylic acid	THF-d_8	149.3	129.3	141.1	129.3	149.3	166.2	166.2
5	THF-d_8	149.7	130.9	149.4	130.9	149.7	168.7	168.7
9	THF-d_8	148.9	131.1	149.7	131.1	148.9	168.4	168.4

[a] Outer-sphere pyridine-2-carboxylic acid (signal intensity twice that in *b*). [b] Pyridine-2-carboxylato ligand bonded to molybdenum. [c] Outer-sphere methyl pyridine-2-carboxylate. [d] Carbon of the methyl group of the outer-sphere methyl pyridine-2-carboxylate.

Table **XIII.** Titration of Methanolic Solutions of Peroxo Complexes by Aqueous Sodium Hydroxide

complex	equivalence point pH	no. of NaOH equiv/mole of complex
4	3.6	0.9
	7.4	2.1
	10.2	1.1
7	5.1	1.0
	10.2	1.1
11	4.9	1.0
	10.2	1.1
10	3.7	0.9
	7.3	1.1
	10.0	1.0
6	3.1	0.3
	7.4	2.8
	9.9	0.9
8	3.0	0.5
	7.2	0.9
	10.1	0.6
5	9.2	3.1
9	9.4	3.1

Table **XIV.** Molar Conductivities of Peroxo Complexes

	λ, ohm mol^{-1}	
complex	methanol	acetonitrile
$Bu_4N^+Br^-$	57	116
pyridine-2-carboxylic acid	2	1
4	32	103
7	35	146
6	12	59
8	14	*a*
5	2	2
9	2	3

[a] Complex 8 is insoluble in acetonitrile.

complexes **5** and **9** in organic solvents and aqueous media at pH ≤8.

Reactivity of Peroxo Complexes Containing Pyridine-2-carboxylato and Pyridine-2,6-dicarboxylato Ligands in Solution. Complex **4** dissolved in methanol is expected to dissociate the outer-sphere pyridine-2-carboxylic acids, which should manifest itself in the formation of **7**. However, complex **4** on stirring overnight in methanol forms a precipitate. The precipitate, based on chemical analysis and IR spectra (Table XI) and in analogy to **4**, can be formulated as hydrogen oxodiperoxo(pyridine-2-carboxylato)molybdate(VI) mono(pyridine-2-carboxylic acid) monohydrate, $H^+[Mo(O)(O_2)_2(C_5H_4NCO_2)]^-\cdot C_5H_4NCO_2H\cdot H_2O$ (**10**). It is apparently the low solubility of **10** which enables it to precipitate as a chemical entity. The same complex can be prepared by addition of 2 mol of pyridine-2-carboxylic acid to a solution of MoO_3 in 30% aqueous hydrogen peroxide.

Another interesting observation is the formation of a precipitate from either **10** or **7** when dissolved in methanol and stirred overnight. The precipitate is formulated as hydrogen oxodiperoxo(pyridine-2-carboxylato)molybdate(VI) monomethyl pyridine-2-carboxylate, $H^+[Mo(O)(O_2)_2(C_5H_4NCO_2)]^-\cdot C_5H_4NCO_2CH_3$ (**11**), in agreement with elemental analysis and in analogy to **10**. Conversion of complex **7** to complex **11** requires dissociation and esterification of the carboxylato ligand from at least 50% of the complex. The low yield (29%) is therefore not surprising. Besides the typical bands for the molybdenum peroxo moiety, the IR spectrum of **11** (Table XI) displays an ester carbonyl at 1745 cm^{-1} and a carboxylic acid carbonyl at 1680 cm^{-1}. The ^1H NMR shows a methyl group at δ 4.4. The structure **11** is also in agreement with ^{13}C NMR (Table XII) which shows the presence of two pyridine nuclei in a 1:1 ratio and carbon of a methyl ester at δ 54.14. The alkalimetric titration of **11**, which is completely analogous to that of **7** (Table XIII), lends further support to structure **11**.

The pyridine-2,6-dicarboxylato ligand in **5** and **9** is far less reactive than the pyridine-2-carboxylato ligand in **7** or **8**. No reaction was observed in methanol at room temperature and in acetonitrile at 70 °C even in the presence of H_2O_2. However, when H_2O_2 is added to a methanol solution of **5** at 70 °C, about 10% of the ligand is converted into dimethyl pyridine-2,6-dicarboxylate. Under identical conditions, **9** yields ~10% of an apparently polymeric precipitate which has not been characterized.

The metal bonded water in **5** cannot be removed even after 36 h at 100 °C over P_2O_5 under vacuum.[26] However, it can be displaced by other nucleophiles such as HMPA, acetone, methanol, and tetrahydrofuran. An equimolar quantity of HMPA can displace the water quantitatively. Recrystallization from acetone, methanol, or tetrahydrofuran results in replacement of water for the respective solvent. The analogous tungsten complex **9** contains two molecules of water as determined by NMR and elemental analysis. One molecule of water is bonded to tungsten as in **5** and the second one is a solvate. The solvate water molecule can be removed at 100 °C under vacuum. In analogy to **5** the tungsten-bonded water molecule can be displaced only by nucleophiles such as HMPA.

Experimental Section

General Procedures. Infrared spectra (Nujol mulls) were recorded with a Perkin-Elmer 283 spectrophotometer. ^1H NMR and ^{13}C NMR spectra of the complexes dissolved in perdeuteriomethanol or perdeuteriotetrahydrofuran were collected on Varian T-60 and CFT-20 spectrometers, respectively. Tetramethylsilane was employed as internal standard.

Complexes dissolved in methanol were titrated by aqueous sodium hydroxide using as an indicator a glass electrode in connection with a Corning Digital 110 expanded scale pH meter. The conductivities of the complexes in methanol and acetonitrile were measured on an YSI Model 31 conductivity bridge.

Preparation of $H^+[Mo(O)(O_2)_2(C_5H_4NCO_2)]^-\cdot 2C_5H_4NCO_2H\cdot H_2O$ (4). A suspension of molybdenum trioxide (5.0 g, 34.7 mmol) in 50 mL of 30% aqueous hydrogen peroxide was stirred and heated at 40–45 °C until a clear solution was obtained (usually overnight). To this solution cooled to 0 °C, a solution of pyridine-2-carboxylic acid (12.8 g, 104 mmol) in 15 mL of water was added. After 10 min, the resulting solution was allowed to warm to room temperature and stirring was continued. A bright yellow precipitate (13.6 g, 24.2 mmol, 70%) was formed. It was filtered off and washed well with ether. If needed, the product was recrystallized from 30% H_2O_2. Anal. Calcd for ($C_{18}H_{17}MoN_3O_{12}$): C, 38.38; H, 3.04; Mo, 17.03; N, 7.46. Found: C, 38.41; H, 3.26; Mo, 17.31; N, 7.39.

Preparation of $H^+[W(O)(O_2)_2(C_5H_4NCO_2)]^-\cdot 2C_5H_4NCO_2H$ (6). Tungstic acid, $WO_3\cdot H_2O$ (15 g, 60 mmol), was stirred at 45 °C in 130 mL of 30% aqueous hydrogen peroxide. The resulting solution was cooled to room temperature and filtered. Pyridine-2-carboxylic acid (22.6 g, 184 mmol) was dissolved in 40 mL of water and slowly added to the solution of tungstic acid chilled to 0 °C. After 48 h at room temperature, a white precipitate was filtered off. The filtrate was kept at 0 °C for 48 h. White crystals (16.7 g, 25.7 mmol, 43%) were filtered and washed with ether. Anal. Calcd for ($C_{18}H_{17}N_3O_{12}W$): C, 33.22; H, 2.63; N, 6.46; O(active), 9.83; W, 28.17. Found: C, 32.82; H, 2.45; N, 6.25; O(active), 9.25; W, 27.7.

Preparation of $Mo(O)(O_2)[C_5H_3N(CO_2)_2](H_2O)$ (5). Solid 2,6-pyridinedicarboxylic acid (17.9 g, 107 mmol) was added to a solution of molybdenum trioxide (18.2 g, 126.5 mmol) in 300 mL of 30% aqueous hydrogen peroxide at 60 °C. After 8 h, the reaction mixture was cooled and the orange precipitate filtered (30.5 g, 94 mmol, 88% yield). Anal. Calcd for ($C_7H_5NO_8Mo$): C, 25.71; H, 1.54; N, 4.28; O(active), 10.25; Mo, 29.33. Found: C, 26.03, H, 1.72; N, 4.23; O(active), 9.63; Mo, 29.64.

Preparation of $H^+[Mo(O)(O_2)_2(C_5H_4NCO_2)]^-\cdot H_2O$ (7). A solution of pyridine-2-carboxylic acid (12.8 g, 104 mmol) in 20 mL of water[27] was added to a solution of molybdenum trioxide (15 g, 104 mmol) in 30% aqueous hydrogen peroxide cooled to 0 °C. A light yellow precipitate of the product (28 g, 89 mmol, 86% yield) was obtained. Anal. Calcd for ($C_6H_7MoNO_8$): C, 22.72; H, 2.23; Mo, 30.26; N, 4.42; O(active), 20.18. Found: C, 23.14; H, 2.42; Mo, 29.67; N, 4.23; O(active), 19.81.

Preparation of $H^+[W(O)(O_2)_2(C_5H_4NCO_2)]^-\cdot H_2O$ (8). A solution of pyridine-2-carboxylic acid (7.4 g, 60 mmol) in 10 mL of water was added to a solution of tungstic acid (15 g, 60 mmol) dissolved in 75 mL of 30% hydrogen peroxide chilled to 0 °C. The resulting solution was stirred overnight at room temperature. The volume of the solution was then reduced to 30 mL by evaporation under vacuum. The product, a white solid (15 g, 27 mmol, 74%), then precipitated.[28] Anal. Calcd for ($C_6H_7NO_8W$): C, 17.84; H, 1.75; N, 3.45; W, 45.41. Found: C, 17.99; H, 1.89; N, 3.27; W, 44.74.

Preparation of $W(O)(O_2)[C_5H_3N(CO_2)_2](H_2O)\cdot H_2O$ (9). Solid 2,6-pyridinedicarboxylic acid (14.9 g, 89 mmol) was added to a solution of tungstic acid (31.0 g, 105 mmol) in 300 mL of 30% aqueous hydrogen peroxide at 45 °C. After 4 h, the cloudy light yellow solution was filtered. The filtrate was kept at room temperature for 48 h. Yellow crystals (16.9 g, 41 mmol, 46%) were filtered and washed with ether. Anal. Calcd for ($C_7H_7NO_9W$): C, 19.39; H, 1.62; N, 3.24; W, 42.46. Found: C, 19.34; H, 1.83; N, 3.22; W, 42.21. Molecular weight calcd, 434; found, 428 (THF solvent).

Preparation of $H^+[Mo(O)(O_2)_2(C_5H_4NCO_2)]^-\cdot C_5H_4NCO_2H\cdot H_2O$ (10). A. In analogy to complex **4**, pyridine-2-carboxylic acid (8.5 g, 69 mmol) was added to a solution of molybdenum trioxide (5 g, 34 mmol) in 50 mL of 30% H_2O_2. The complex **10** (7.0 g, 16 mmol, 47%) precipitated.

B. Complex **4** (1 g, 1.78 mmol) was stirred in methanol overnight at room temperature. The yellow complex **10** precipitated (0.35 g, 0.79 mmol, 44%).

Anal. Calcd for ($C_{13}H_{13}MoN_2O_{10}$): C, 34.45; H, 2.89; Mo, 21.17; N, 6.18. Found: C, 34.06; H, 2.48; Mo, 21.46; N, 6.55.

Preparation of $H^+[Mo(O)(O_2)_2(C_5H_4NCO_2)]^-\cdot C_5H_4NCO_2CH_3$ (11). Complex **4** (1 g, 3.2 mmol) was dissolved in methanol (10 mL) and the resulting solution was stirred overnight. At that time 0.4 g (0.9 mmol, 29%) of crystals was formed. ^1H NMR (δ, C_5D_5N): 4.4 [s, 3 H, $C(O)OCH_3$], 8.2–10.4 [m, 8 H, $(C_5H_4N)_2$]. Anal. Calcd for ($C_{13}H_{12}MoN_2O_9$): C, 35.79; H, 2.77; Mo, 21.99; N, 6.42; O(active), 14.67. Found: C, 35.79; H, 2.90; Mo, 22.23; N, 6.26; O(active), 14.11.

Preparation of $W(O)(O_2)[C_5H_3N(CO_2)_2]\{OP[N(CH_3)_2]_3\}(H_2O)$ (13). Complex **9** (1.5 g, 3.6 mmol) was dissolved in tetrahydrofuran and HMPA (0.63 g, 3.5 mmol) was slowly added. A white precipitate immediately formed (1.9 g, 3.2 mmol, 91%). Anal. Calcd for $C_{13}H_{23}N_4O_9PW$: C, 26.31; H, 3.88; N, 9.44; P, 5.23; W, 31.03. Found: C, 25.84; H, 3.76; N, 9.25; P, 5.29; W, 31.11. ^1H NMR (δ, $CDCl_3$): 2.34 (d, J_{H-P} = 9 Hz, 18 H, $[N(CH_3)_2]_3$), 8.2–8.6 [m, 3 H, (C_5H_3N)].

Preparation of $Mo(O)(O_2)[C_5H_3N(CO_2)_2]\{OP[N(CH_3)_2]_3\}$ (12). Complex **5** (1.0 g, 3.1 mmol) was dissolved in tetrahydrofuran (50 mL). HMPA (0.55 g, 3.1 mmol) was slowly added and an orange precipitate immediately formed (1.2 g, 2.5 mmol, 79%). Anal. Calcd for $C_{13}H_{21}N_4O_8PMo$: C, 32.02; H, 4.35; N, 11.48; Mo, 19.5. Found: C, 32.01; H, 4.43; N, 11.27; Mo, 19.02. ^1H NMR (δ,$CDCl_3$): 2.31 [d, J_{H-P} = 9 Hz, 11 H, HMPA(bound)], 2.63 [d, J_{H-P} = 9 Hz, 7 H, HMPA(free)]; 8.3–8.5 [m, 3 H, (C_5H_3N)].

Collection of X-ray Data and Structure Determination. For the single-crystal X-ray work, crystals of **4** and **5** were mounted in glass fibers. Cell constants were obtained by computer centering of 25 reflections, on an Enraf-Nonius CAD4 automatic diffractometer for **4** and of 15 reflections on a Syntex $P\bar{1}$ automatic diffractometer for **5**. Least-squares refinement of the setting angles for **4** provided the following values: a = 7.337 (9) Å, b = 10.816 (4) Å, c = 27.004 (6) Å, V = 2142.9 Å^3, β = 90.35 (2)°. For **5** the following values were obtained: a = 9.495 (2) Å, b = 11.607 (2) Å, c = 9.145 (2) Å, V = 974.0 (2) Å^3, β = 104.90 (2)°. The number of formula units of $MoO_{12}N_3C_{18}H_{16}$ per unit cell was computed to be 4 (ρ_{calcd} = 1.743 g/cm^3) for **4**. The number of formula units of $MoO_8NC_7H_5$ per unit cell was computed to be 4 (ρ_{calcd} = 2.23 g/cm^3) for **5**. The systematic absences $h0l$, $l \neq 2n$, and $0k0$, $k \neq 2n$, indicated space group $P2_1/c$ for **4**, and hkl, $h + k \neq 2n$, and $h0l$, $l \neq 2n$, indicated space groups

$C2/c$ or Cc for **5**. Cc was confirmed by a systematic refinement of the structure.

For the data collection, prismatic crystals of dimensions 0.3 × 0.3 × 0.35 mm for **4** and 0.12 × 0.13 × 0.15 mm for **5** were mounted on the diffractometer. Molybdenum Kα radiation (λ 0.71073 Å) filtered by a graphite-crystal incident-beam monochromator was employed. Data were taken in the range of $0 < 2\theta$ (Mo Kα) $< 55°$ with a scan width of [2θ(Mo Kα_1) − 0.8°] to [2θ(Mo Kα_2) + 0.8°] (crystal at 23 ± 1 °C). A variable scan rate of 4–24°/min was used so as to allow rapid data collection and good counting statistics for weak reflections. A total of 5200 independent reflections for **4** and 1481 for **5** were collected. As a check on crystal and electronic stability, three representative reflections were measured periodically. Standard reflections were found to decrease by about 20% during data collection for **4**; no significant change was noted for **5**.

Intensities and standard deviations on intensities were calculated using the following formulas:

$$I = S(C - RB)$$

$$\sigma(I) = [S^2(C + R^2B) + (pI)^2]^{1/2}$$

where S = scan rate, C = total integrated peak count, R = scan time/background count time, B = total background count, and the parameter p is a factor introduced to downweight intense reflections. Here p was set to 0.06 for complex **4** and 0.05 for complex **5**. Lorentz and polarization corrections were applied to the data. A correction for changes in intensity of the standard reflections was made for complex **4** and was not necessary for **5**. An extinction correction was not necessary for either complex.

The calculated values of μ (Mo Kα radiation) for complexes **4** and **5** are 6.81 and 13.64 cm^{-1}, respectively. The calculated maximum and minimum transmission factors are 0.82 and 0.79 for **4** and 0.85 and 0.815 for **5**. No corrections for the effects of absorption were made.

The structures were solved using the Patterson method. The Patterson maps showed the position of the molybdenum atoms. Least-squares refinement of the atoms resulted in agreement factors of $R_1 = 0.55$ and $R_2 = 0.62$ for **4** and $R_1 = 0.33$ and $R_2 = 0.39$ for **5**, where R_1 and R_2 are defined as

$$R_1 = \sum||F_o| - |F_c||/\sum|F_o|$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$$

$$w = 4F_o^2/\sigma^2(F_o^2)$$

The remaining nonhydrogen atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms for both complexes were located after anisotropic refinement of all nonhydrogen atoms. The structure was refined by minimizing the function $\sum w(|F_o| - |F_c|)^2$. Scattering factors were taken from tables by Cromer and Waber.[29] Anomalous dispersion effects were included in F_c; the values of $\Delta f'$ and $\Delta f''$ were those of Cromer and Liberman.[30] Only the 3574 reflections for **4** having $F_o^2 > 3\sigma(F_o^2)$ and the 761 reflections for **5** having $F_o^2 > 2\sigma(F_o^2)$ were used in the refinement. In the last cycle of least-squares refinement R_1 and R_2 were 0.0444 and 0.057 for **4** and 0.018 and 0.025 for **5**, respectively. The final difference Fourier map for **4** showed only one peak as high as hydrogen atoms on a previous Fourier map. The peak was 1.6 Å from H(1), not bonded to any other atoms, and of doubtful chemical significance. The final Fourier map of **5** showed no peaks as high as hydrogen atoms in the previous difference Fourier map.

Lists of refined positional and thermal parameters for all the atoms, and also tables of observed and calculated structure factors, are available as supplementary material.

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Registry No. **4**, 67584-11-6; **5**, 55173-45-0; **6**, 67584-10-5; **10**, 67584-09-2; **11**, 67584-08-1; **12**, 67584-07-0; $H^+[Mo(O)(O_2)_2(C_5H_4NCO_2)]^-$, 67584-06-9; $H^+[W(O)(O_2)_2(C_5H_4NCO_2)]^-$, 67584-05-8; $W(O)(O_2)[C_5H_3N(CO_2)_2](H_2O)$, 55173-46-1; $W(O)(O_2)[C_5H_3N(CO_2)_2]\{OP[N(CH_3)_2]_3\}$, 67584-04-7; MoO_3, 1313-27-5; WO_3, 1314-35-8; $Bu_4N^+Br^-$, 1643-19-2; $C_5H_4NCO_2H$, 98-98-6.

Supplementary Material Available: Listings of refined positional and thermal parameters for all atoms and also tables of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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(8) (a) The X-ray diffraction work described here was done by Dr. Jan M. Troup, Molecular Structure Corp., College Station, Texas. (b) In order to facilitate the reader's orientation, the complexes discussed in the paper are listed in Table I.

(9) Two crystal modifications are present. The other one is orthorhombic, space group *Pbca*. Both modifications are identical from other physical and chemical measurements so only the monoclinic was subjected to structural investigation.

(10) The deviation of O1 from plane 1 (Table VII) is so small that it could be considered a part of the plane.

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(18) The Fourier map, after anisotropic refinement of all nonhydrogen atoms, shows only one peak as high an intensity as hydrogen. This peak is 1.6 Å from H1 (Figure 3) and not bonded to any other atom. However, its significance is in doubt.

(19) The authors cited in reference 6a prepared a complex which according to the elemental analysis contain three molecules of pyridine-2-carboxylic acid per molybdenum. Without any additional information, they suggested a structure containing $Mo_2O_{11}^{2-}$ anions and the protonated form of pyridine-2-carboxylic acid. Since no spectral data were reported, we were unable to relate their complexes to ours.

(20) When this work was in progress, the authors cited in ref 6b prepared the same complexes in a much lower yield by a route different from ours. Based on molar conductivities in acetonitrile and IR spectra in Nujol which are identical with our data, Westlake and co-workers (ref 6b) suggested the correct arrangement of the ligands around Mo and W in complexes **5** and **9**.

(21) Because of low solubility, ^{13}C NMR spectra of **6** and **8** cannot be measured.

(22) (a) A. J. Jones, D. M. Grant, J. G. Russel, and G. Fraenkel, *J. Phys. Chem.*, **73**, 1624 (1969); (b) D. K. Lavallee, M. D. Baughman, and M. P. Phillips, *J. Am. Chem. Soc.*, **99**, 718 (1977).

(23) The titration has been done in methanol with aqueous NaOH. Therefore, no absolute pH values have been obtained. However, the pH scale was retained for convenience.

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(25) The equilibrium between monomeric peroxo species and the dimeric $Mo_2O_{11}^{2-}$ is well established even at lower pH for peroxo complexes stabilized by monodentate ligands such as HMPA and pyridine (see ref 13).

(26) The water in $Mo(O)(O_2)_2(HMPA)(H_2O)$ can be removed under vacuum if the complex is stored over P_2O_5.

(27) Greater quantities of water used to dissolve pyridine-2-carboxylic acid result in immediate formation of a bright yellow precipitate which in contrast to **7** is insoluble in methanol and gives a different elemental analysis. This product has not been characterized.

(28) An analogous procedure using WO_3 gave no complex.

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