# Studies on Transition-metal Peroxo Complexes. Part 7.† Molybdenum(VI) and Tungsten(VI) Carboxylato Peroxo Complexes, and the *X*-Ray Crystal Structure of $K_2[MoO(O_2)_2(glyc)]·2H_2O$‡

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New complexes $[MoO(O_2)_2L]^{2-}$ [L = malate, tartrate (tart), tartronate, quinate, or glycolate (glyc)], $[WO(O_2)_2L]^{2-}$ (L = citrate, tartrate, malate, or glycolate), and $[W_2O_2(O_2)_4(tart)]^{4-}$ are reported, and modified preparations given for $[MO(O_2)_2L]^{2-}$ and $[MO_2(O_2)L(H_2O)]^{2-}$ (M = Mo or W; L = oxalate). Raman and i.r. spectra of the solid complexes, and Raman, $^{13}C$ and $^{95}Mo$ n.m.r. spectra of their aqueous solutions, have been measured and are used to suggest the structures of the species in the solid state and solution. The *X*-ray crystal structure of $K_2[MoO(O_2)_2(glyc)]·2H_2O$ has been determined: triclinic, space group $P\bar{1}$, with $a$ = 7.222(4), $b$ = 7.950(6), $c$ = 10.450(5) Å, $\alpha$ = 67.81(4), $\beta$ = 73.72(7), $\gamma$ = 64.84(4)° at 20 °C, and $Z$ = 2; the structure has been refined to $R$ = 0.035.

We have previously prepared and characterised the oxalato (ox) peroxo complexes $K_2[MO(O_2)_2(ox)]$, $K_2[MO_2(O_2)(ox)(H_2O)]·H_2O$ (M = Mo or W),[1] the citrato (cit) (2-hydroxypropane-1,2,3-tricarboxylate) complex $K_2[MoO(O_2)_2(cit)]·3H_2O·0.5H_2O_2$,[2] and the tartrato (tart) complexes $K_4[M_2O_2(O_2)_4(tart)]·4H_2O$ (M = Mo or W).[3] *X*-Ray crystal structures of the complexes $K_2[MoO(O_2)_2(ox)]$,[4] $K_2[WO(O_2)_2(ox)]$,[5] $K_2[MoO(O_2)_2(cit)]·3H_2O·0.5H_2O_2$,[2] and $K_4[Mo_2O_2(O_2)_4(tart)]·4H_2O$[3] have been reported.

In this paper, we report a number of new, stable carboxylato peroxo complexes and present spectroscopic data for them in the solid state and for their aqueous solutions, as well as the first *X*-ray crystal structure of a glycolato (glyc) peroxo complex, namely $K_2[MoO(O_2)_2(glyc)]·2H_2O$. The work has been undertaken in order to investigate further the chemistry of carboxylato peroxo complexes, as our earlier experiments on oxalato species indicate that carboxylates rival fluorides as co-ligands to impart chemical and thermal stability to peroxo complexes of the Group 4—6 transition metals.

## Results and Discussion

(*a*) *Formation of Complexes.*—We find that carboxylato ligands capable of forming five-membered rings with the metal [*e.g.* oxalate, citrate, tartrate, malate, tartronate, glycolate, quinate (1,3,4,5-tetrahydroxycyclohexanecarboxylate)] generally give stable complexes with peroxo co-ligands. Using the same methods we find that carboxylates which do not form such rings (*e.g.* acetate, adipate, succinate, salicylate, and thiosalicylate) do not form such complexes. Unsaturated acids capable of forming five-membered rings {*e.g.* mandelic (phenylglycolic), atrolactic [methyl(phenyl)glycolic], and 3-phenyl-lactic} do not form stable complexes, presumably due to the electron-withdrawing properties of their aromatic rings. We also find that the formation of some of the carboxylato peroxo complexes can depend on the reacting metal:carboxylate ratio, as with the oxalate and tartrate systems, or on the amount of peroxide present, as with the oxalate system. In all cases the formation of the carboxylato peroxo complex depends markedly on the pH of the reaction mixture: some complexes (oxalate, citrate, non-bridged tartrate, tartronate, malate, and glycolate) are formed at the natural pH of the metal–carboxylate–peroxide mixture, while others [bridged tartrate, quinate (quin)] need pH adjustment for complex formation. Generally high pH (>7—8) leads to the formation of the unstable $[M(O_2)_4]^{2-}$ species, while at low pH (<2—3) formation of the very stable $[M_2O_3(O_2)_4(H_2O)_2]^{2-}$ is favoured rather than the carboxylato peroxo complex. Rates of formation of carboxylato peroxo complexes are markedly greater for molybdenum than for tungsten.

In a recent paper it was shown that reaction of $MoO_3$ and KOH with malic acid in the presence of an excess of hydrogen peroxide gave $K_2[MoO(O_2)_2(ox)]$ rather than a malato peroxo complex.[6] We find however that a malato (mal) complex, $K_2[MoO(O_2)_2(mal)]·2H_2O$, can be made from $[MoO_4]^{2-}$, malic acid, and an excess of hydrogen peroxide at pH 3.4, a higher pH than that (2.9) obtained by using $MoO_3$ and KOH. We find that recrystallisation of the malato complex from an excess of $H_2O_2$ does however give $K_2[MoO(O_2)_2(ox)]$, indicating that a slow, complicated rearrangement and decarboxylation of the malate ligand has occurred.

Although in general the carboxylato peroxo complexes are formed under very similar conditions for molybdenum and tungsten, there are significant differences for $K_4[Mo_2O_2(O_2)_4(tart)]·4H_2O$ and $K_2[MoO(O_2)_2(quin)]·2H_2O$. The molybdenum tartrate complex was formed only when the pH was adjusted to 4, while the corresponding tungsten complex was formed at pH 2; the molybdenum quinate was formed at pH 3.3, while the tungsten analogue could not be isolated at all.

Several covalent molybdenum(VI) complexes are known to epoxidise simple alkenes in good yield.[7] Using the well documented epoxidation of simple alkenes by the complex $[MoO(O_2)\{P(O)(NMe_2)_3\}]^{7-10}$ as a model, we used n.m.r. spectroscopy to determine whether the complexes $[PPh_4]_2[MoO(O_2)_2(ox)]$ and $[PPh_4]_4[Mo_2O_2(O_2)_4(tart)]$ in acetonitrile would similarly epoxidise alkenes. In no case was epoxidation observed, suggesting it is inhibited by the residual negative charge of these anionic molybdenum(VI) peroxo complexes.

(*b*) *X-Ray Crystal Structure of* $K_2[MoO(O_2)_2(glyc)]·2H_2O$.—Although there have been *X*-ray crystal structure determinations on several glycolato complexes,[11] this is the first peroxo glycolato complex to be so characterised. The glycolate

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† Part 6 is ref. 1*b*.

‡ Dipotassium (glycolato-*OO'*)oxodi(peroxo-*OO'*)molybdate(VI) dihydrate.

*Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

group is of interest in the context of peroxo chemistry in that it has a hydroxyl donor atom as well as the carboxylate donor sites; we wished to establish whether the unusual mode of bonding involving both hydroxyl and carboxylate oxygen atoms found in $K_2[MoO(O_2)_2(cit)]\cdot3H_2O\cdot0.5H_2O_2$[2] was followed in this case as well. The Figure shows the structure of the $[MoO(O_2)_2(glyc)]^{2-}$ anion, and bond lengths and angles are given in Table 1.

The co-ordination about the molybdenum atom is essentially pentagonal bipyramidal, similar to that found by us in the complexes $K_2[MoO(O_2)_2(cit)]\cdot3H_2O\cdot0.5H_2O_2$ (**1**)[2] and $K_4[Mo_2O_2(O_2)_4(tart)]\cdot4H_2O$ (**2**).[3] The axial positions are occupied by the terminal oxo ligand [Mo–O 1.686(6) Å] and the oxygen atom from the deprotonated carboxylate group [Mo–O 2.239(6) Å]. The equatorial positions are occupied by the two slightly asymmetrically bound peroxo ligands [mean Mo–O 1.927(4) and 1.966(4); mean O–O 1.471(7) Å], and the deprotonated hydroxyl group of the glycolate [Mo–O 1.991(5) Å]. As in complexes (**1**) and (**2**), it appears that the deprotonated hydroxyl group assumes the equatorial rather than the axial position, so as to form a strong bond; the long axial Mo–O distance could be due to the *trans* influence of the oxo ligand.

The crystal structure is held together by ionic attraction between the $K^+$ ions and the complex anion, and by hydrogen bonding involving the water molecules. One of the potassium ions K(1) has eight oxygen near neighbours at distances 2.73—2.90 Å, while K(2) is surrounded by nine oxygen atoms at 2.81—3.12 Å. Each of the two water molecules of hydration forms two OH ⋯ O hydrogen bonds to oxygen atoms on the complex anion.

(*c*) *Infrared and Raman Data.*—The i.r. and Raman data are summarised in Table 2. In addition to the bands arising from the carboxylato ligands, all the complexes show strong i.r. and Raman bands near 950 $cm^{-1}$ due to ν(M=O), polarised in the Raman spectra of the aqueous solutions. For the dioxo complexes $[MO_2(O_2)(ox)(H_2O)]^{2-}$, M = Mo or W, two such

**Table 1.** Bond lengths (Å) and angles(°) in $K_2[MoO(O_2)_2(glyc)]\cdot2H_2O$ with estimated standard deviations (e.s.d.s) in parentheses

| | | | |
|---|---|---|---|
| Mo(1)–O(1) | 1.686(6) | Mo(1)–O(7) | 2.239(6) |
| Mo(1)–O(2) | 1.970(4) | Mo(1)–O(4) | 1.961(4) |
| Mo(1)–O(3) | 1.926(4) | Mo(1)–O(5) | 1.928(4) |
| Mo(1)–O(6) | 1.991(5) | | |
| | | O(4)–O(5) | 1.472(7) |
| O(2)–O(3) | 1.469(7) | C(2)–O(10) | 1.231(11) |
| C(2)–O(7) | 1.279(9) | C(1)–C(2) | 1.528(9) |
| C(1)–O(6) | 1.413(11) | | |
| O(1)–Mo(1)–O(2) | 99.9(2) | O(1)–Mo(1)–O(3) | 101.6(2) |
| O(1)–Mo(1)–O(4) | 99.8(2) | O(1)–Mo(1)–O(5) | 102.4(2) |
| O(1)–Mo(1)–O(6) | 92.8(2) | O(3)–Mo(1)–O(5) | 87.0(2) |
| O(2)–Mo(1)–O(3) | 44.3(2) | O(4)–Mo(1)–O(5) | 44.5(2) |
| O(2)–Mo(1)–O(6) | 89.3(2) | O(4)–Mo(1)–O(6) | 89.9(2) |
| O(7)–Mo(1)–O(1) | 168.2(2) | O(7)–Mo(1)–O(6) | 75.4(2) |
| O(7)–Mo(1)–O(2) | 79.9(2) | O(7)–Mo(1)–O(3) | 86.6(2) |
| O(7)–Mo(1)–O(4) | 80.8(2) | O(7)–Mo(1)–O(5) | 86.4(2) |
| Mo(1)–O(2)–O(3) | 66.3(2) | Mo(1)–O(3)–O(2) | 69.5(2) |
| Mo(1)–O(4)–O(5) | 66.6(2) | Mo(1)–O(5)–O(4) | 68.9(2) |
| Mo(1)–O(6)–C(1) | 120.3(3) | Mo(1)–O(7)–C(2) | 115.8(4) |
| O(6)–C(1)–C(2) | 111.6(6) | O(7)–C(2)–C(1) | 114.9(7) |
| O(10)–C(2)–C(1) | 120.2(7) | O(7)–C(2)–O(10) | 124.9(6) |

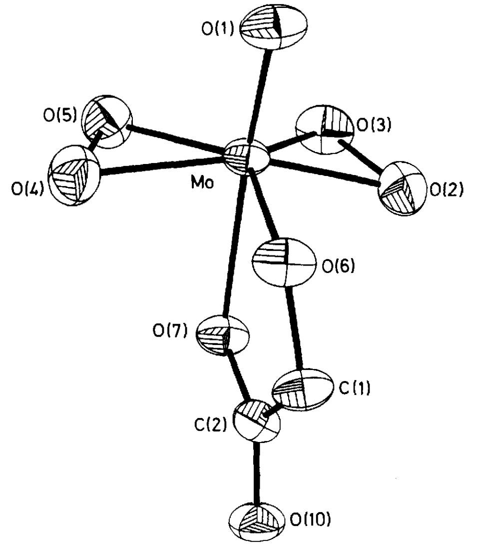

**Figure.** Structure of the $[MoO(O_2)_2(glyc)]^{2-}$ anion. Thermal vibration ellipsoids are scaled to enclose 50% probability

**Table 2.** Vibrational and n.m.r. data

| | | Vibrational data ($cm^{-1}$)[a] | | | | N.m.r. data[b] | |
|---|---|---|---|---|---|---|---|
| Complex | | ν(M=O) | ν(O–O) | $\nu_{sym}[M(O_2)]$ | $\nu_{asym}[M(O_2)]$ | $^{95}Mo$ | $^{13}C$ |
| $K_2[MoO(O_2)_2(ox)]$ | I.r. | 972vs | 872s | 661m | 606m | −228.3 | |
| | R | 965(10) | 880(9) | 655(5) | 587(7) | | |
| | R | *968(10)* | *876(8)* | *653(6)* | *588(7)* | | |
| $K_2[WO(O_2)_2(ox)]$ | I.r. | 985s | 871m<br>855m | 661s | 614m | | |
| | R | 970(10) | 885(9) | 645(4) | 592(7) | | |
| | R | *961(10)* | *856(9)* | *649(4)* | *595(6)* | | |
| $K_2[MoO_2(O_2)(ox)(H_2O)]\cdot H_2O$ | I.r. | 975s[c]<br>915m[d] | 870s | 656m | 601m | −229.7<br>+4.4 | |
| | R | 962(8)[c]<br>909(7)[d] | 877(6) | 653(4) | 581(5) | | |
| | R | *964(10)* | *875(9)* | *640(6)* | *584(7)* | | |
| $K_2[WO_2(O_2)(ox)(H_2O)]\cdot H_2O$ | I.r. | 985vs[c]<br>919m[d] | 869m<br>853m | 659m | 613m | | |
| | R | 966(10)[c]<br>908(4)[d] | 877(8) | 655(6) | 592(7) | | |
| | R | *967(10)* | *876(8)* | *650(5)* | *596(7)* | | |
| $K_2[MoO(O_2)_2(cit)]\cdot3H_2O\cdot0.5H_2O_2$ | I.r. | 957s | 875m<br>861s | 653m | 603m | −247br | *ca.* 179<br>88.2 |
| | R | 962(10) | 877(8) | 652(6) | 590(7) | | 47.1 |
| | R | *959(10)* | *870(9)* | *640(6)* | *583(7)* | | |

**Table 2** (*continued*)

| Complex | | Vibrational data (cm$^{-1}$)[a] | | | | N.m.r. data[b] | |
|---|---|---|---|---|---|---|---|
| | | ν(M=O) | ν(O–O) | $\nu_{sym}[M(O_2)]$ | $\nu_{asym}[M(O_2)]$ | $^{95}$Mo | $^{13}$C |
| $K_2[WO(O_2)_2(cit)]\cdot 3H_2O\cdot 0.5H_2O_2$ | I.r. | 963s | 875m | 655w | 602w | | |
| | | | 862w | | | | |
| | R | 952(10) | 848(9) | 637(7) | 580(8) | | |
| $K_4[Mo_2O_2(O_2)_4(tart)]\cdot 4H_2O$ | I.r. | 929s | 857s | 638s | 578m | −235.0 | 186.0 |
| | | | 847s | | | | 89.0 |
| | R | 935(10) | 857(7) | 640(4) | 592(6) | | |
| | R | *954(10)* | *869(8)* | *639(5)* | *582(7)* | | |
| $K_4[W_2O_2(O_2)_4(tart)]\cdot 4H_2O$ | I.r. | 924s | 831s | 622m | 570w | | 175.1 |
| | R | 957(10) | 852(9) | 628(5) | 571(6) | | 88.5 |
| | R | *952(10)* | *852(9)* | *628(7)* | *566(8)* | | |
| $K_2[MoO(O_2)_2(mal)]\cdot 2H_2O$ | I.r. | 930s | 855s | 633m | 584m | −233.0 | 186.3 |
| | | | | | | | 178.6 |
| | R | 949(10) | 873(8) | 638(6) | 590(7) | | 82.0 |
| | | | | | | | 44.2 |
| | R | *965(10)* | *875(8)* | *641(5)* | *580(6)* | | |
| $K_2[WO(O_2)_2(mal)]\cdot 2H_2O$ | I.r. | 925s | 830s | 625m | 575w | | |
| | R | 945(10) | 845(9) | 625(6) | 565(8) | | |
| $K_2[MoO(O_2)_2(tron)]\cdot 2H_2O$ | I.r. | 947vs | 855vs | 640m | 584s | −227.7 | |
| | R | 958(10) | 874(8) | 640(6) | 585(7) | | |
| | R | *968(10)* | *875(8)* | *640(6)* | *585(7)* | | |
| $K_2[MoO(O_2)_2(glyc)]\cdot 2H_2O$ | I.r. | 937vs | 849s | 635m | 584m | −220.6 | 186.6 |
| | | 922vs | | | | | 74.9 |
| | R | 943(10) | 864(9) | 642(5) | 596(6) | | |
| | | 925(7) | | | | | |
| | R | *958(10)* | *868(9)* | *639(5)* | *581(6)* | | |
| | | *930(7)* | | | | | |
| $K_2[MoO(O_2)_2(quin)]\cdot 2H_2O$ | I.r. | 935s | 848s | 627m | 580m | −245.0 | |
| | R | 946(10) | 868(7) | 631(4) | 588(7) | | |
| | R | *952(10)* | *870(8)* | *640(6)* | *585(7)* | | |
| $K_2[MoO(O_2)_2(tart)]\cdot 2H_2O$ | I.r. | 937vs | 871s | 656s | 608m | −252.0 | 185.9 |
| | | | 859s | | | −231.7 | 185.5 |
| | | | | | | | 89.5 |
| | R | 936(9) | 874(8) | 637(6) | 600(5) | | 88.8 |
| | R | *954(10)* | *862(9)* | *640(6)* | *602(5)* | | |
| $K_2[WO(O_2)_2(tart)]\cdot 2H_2O$ | I.r. | 939s | 859w | 641m | 603w | | |
| | R | 934(10) | 880(8) | 635(6) | 598(5) | | |
| $[PPh_4]_2[MoO(O_2)_2(ox)]$ | I.r. | 962s | 871s | 648s | 585s | | |
| | | | 851s | | | | |
| | R | 942(9) | 874(4) | 616(6) | 588(5) | | |
| | R[e] | *943(8)* | *870(5)* | *616(6)* | *583(4)* | | |
| $[PPh_4]_4[Mo_2O_2(O_2)_4(tart)]$ | I.r. | 962vs | 862vs | 629m | 598m | | |
| | R | 960(7) | 873(6) | 616(4) | 561(5) | | |
| $K_2[MoO_3(ox)]\cdot 2H_2O$ | I.r.[f] | 903s[s] | | | | 5.1 | |
| | | 869vs[d] | | | | | |
| | R[f] | 901[c] | | | | | |
| | | 869[d] | | | | | |
| $K_2[WO(O_2)_2(glyc)]\cdot 2H_2O$ | I.r. | 940s | 841m | 624s | 581m | | 187.5 |
| | | 918s | 827s | | | | 75.3 |
| | R | 938(9) | 840(8) | 620(4) | 572(6) | | |
| | | 922(7) | | | | | |
| | R | *957(10)* | *854(9)* | *632(6)* | *565(7)* | | |
| | | *932(8)* | | | | | |

[a] Data for solids or (italicised) aqueous solutions; relative Raman intensities given in parentheses. [b] In p.p.m. *vs.* $SiMe_4$ for $^{13}$C and *vs.* $[MoO_4]^{2-}$ for $^{95}$Mo. [c] $\nu_{sym}$. [d] $\nu_{asym}$. [e] In dichloromethane solution. [f] W. P. Griffith and T. D. Wickins, *J. Chem. Soc. A*, 1968, 400.

bands are observed, as in other *cis*-dioxo complexes,[12] near 980 and 915 cm$^{-1}$; these are assigned to $\nu_{sym}(MO_2)$ (polarised in the Raman spectrum of the aqueous solutions) and $\nu_{asym}(MO_2)$ (depolarised). Three i.r. and Raman bands due to the peroxo group are present, as in other peroxo complexes:[1] ν(O–O) near 880 cm$^{-1}$ (polarised in aqueous solution), $\nu_{sym}[M(O_2)]$ near 650 cm$^{-1}$ (polarised), and $\nu_{asym}[M(O_2)]$ near 600 cm$^{-1}$ (depolarised). For most cases studied the profiles of the Raman spectra of the solids and aqueous solutions are very similar, which suggests that there is no structural change from solid to solution. For the monoperoxo complex $[MoO_2(O_2)(ox)(H_2O)]^{2-}$ however, although the three peroxo bands are similar in solid and solution, the Raman spectrum of the aqueous solution shows only one broad ν(M=O) band, due to decomposition to $[MoO(O_2)_2(ox)]^{2-}$ and $[MoO_3(ox)]^{2-}$ [see section (*d*)].

(*d*) *Molybdenum*-95 *and* $^{13}$C *N.M.R. Data*.—The $^{95}$Mo n.m.r. data presented in Table 2 show that this is a useful and sensitive technique for study of the structure of molybdenum carboxylato peroxo complexes in aqueous solution. Changes of the carboxylate ligand (L) in the complexes $[MoO(O_2)_2L]^{2-}$ result in appreciable shifts of the $^{95}$Mo resonance; for example δ −220.6 p.p.m. (relative to $[MoO_4]^{2}$) for L = glycolate, −228.3 p.p.m. for oxalate, −233.0 p.p.m. for malate, and −247.0 p.p.m. for citrate. The bridged peroxo tartrate complex $[Mo_2O_2(O_2)_4(tart)]^{4-}$ gives a single sharp resonance at δ −235.0 p.p.m., which reflects the symmetry of the species with respect to its two molybdenum centres. The sensitivity of $^{95}$Mo n.m.r. shifts towards change of co-ordinated ligand has been noted before.[13]

We have also used the technique to investigate the nature of the monoperoxo complex $[MoO_2(O_2)(ox)(H_2O)]^{2-}$ in aqueous solution. Whereas the other carboxylato peroxo complexes studied show only one $^{95}$Mo resonance, the monoperoxo complex shows two, at $\delta$ −229.7 and +4.4 p.p.m. We find that a solution of $K_2[MoO(O_2)_2(ox)]$ gives a band at −228.3 p.p.m., and $K_2[MoO_3(ox)]\cdot 2H_2O$ one at +5.1 p.p.m., so in aqueous solution the reaction (1) clearly occurs. On addition of an excess

$$2[MoO_2(O_2)(ox)(H_2O)]^{2-} \longrightarrow [MoO(O_2)_2(ox)]^{2-} + [MoO_3(ox)]^{2-} + 2H_2O \quad (1)$$

of $H_2O_2$ to the solution, these two resonances disappeared and were replaced by a single one at $\delta$ −228.3 p.p.m., coincident with that found for $K_2[MoO(O_2)_2(ox)]$.

We have not measured $^1$H n.m.r. spectra, since they are likely to be complicated in some cases, and because $^{13}$C n.m.r. is more informative. The $^{13}$C n.m.r. spectrum of the $[Mo_2O_2(O_2)_4(tart)]^{4-}$ anion shows two singlets at 186.0 and 89.0 p.p.m. due to the carboxylate and –C(H)O– carbon atoms respectively. This shows that the anion retains its symmetrical structure and quadridentate co-ordination of the tartrate, with just two types of carbon environment. The spectrum of the $[MoO(O_2)_2(tart)]^{2-}$ complex is interesting in that it shows several closely spaced resonances near 185 and near 89 p.p.m. This indicates that the bridged $[Mo_2O_2(O_2)_4(tart)]^{4-}$ species may also be present in solution, formed from the oxodiperoxomolybdate(VI) species with the release of free tartrate. It seems that a similar situation may arise with the citrato peroxo complex $K_2[MoO(O_2)_2(cit)]\cdot 3H_2O\cdot 0.5H_2O_2$ in solution. The spectrum shows only one broad carboxyl resonance, as well as the expected resonances near 47 ($CH_2$ carbons) and 88 p.p.m. (hydroxyl carbon). The $^{13}$C n.m.r. spectrum of the peroxo glycolato complex $K_2[MoO(O_2)_2(glyc)]\cdot 2H_2O$ is consistent with retention of the solid-state structure in solution.

## Experimental

*Preparations.*—$K_2[MoO(O_2)_2(ox)]$ (M = Mo *or* W). Potassium molybdate, $K_2[MoO_4]$ (1.0 g, 4.2 mmol), was dissolved in water (20 cm$^3$), and a slight excess of oxalic acid dihydrate (0.63 g, 5.0 mmol) added with stirring. The solution was treated with an excess of 30% $H_2O_2$ (10 cm$^3$). Addition of ethanol precipitated a yellow microcrystalline solid which was filtered off, washed with ethanol, and air-dried. The tungsten analogue was prepared similarly. This method is an improvement of that reported by Mazzucchelli and co-workers,[14,15] in which equimolar quantities of the metal and oxalic acid can produce a pH high enough for traces of the explosive $[Mo(O_2)_4]^{2-}$ to form [Found: C, 7.0; K, 23.1; $(O_2)^{2-}$, 18.6. $C_2K_2MoO_9$ requires C, 7.0; K, 22.9; $(O_2)^{2-}$, 18.7. Found: C, 5.9; K, 18.1; $(O_2)^{2-}$, 14.6. $C_2K_2O_9W$ requires C, 5.6; K, 18.2; $(O_2)^{2-}$, 14.9%].

$K_2[MoO_2(O_2)(ox)(H_2O)]\cdot H_2O$ (M = Mo *or* W). The method used was essentially that of Rodriguez,[16] with modification of the isolation procedure. Potassium molybdate (1.0 g, 4.2 mmol) and oxalic acid dihydrate (0.53 g, 4.2 mmol) were dissolved in water (10 cm$^3$), and the solution stirred and treated with 30% $H_2O_2$ (0.35 cm$^3$, 4.2 mmol). Yellow crystals were obtained by addition of a few drops of ethanol and cooling to 5 °C, filtered off, and washed with ethanol. The tungsten analogue was prepared similarly [Found: C, 7.0; H, 0.6; K, 22.2; $(O_2)^{2-}$, 9.5. $C_2H_4K_2MoO_{10}$ requires C, 6.6; H, 1.1; K, 21.6; $(O_2)^{2-}$, 8.8. Found: C, 5.5; H, 0.4; K, 17.0; $(O_2)^{2-}$, 7.8. $C_2H_4K_2O_{10}W$ requires C, 5.3; H, 0.9; K, 17.4; $(O_2)^{2-}$, 7.1%].

$K_2[MO(O_2)_2(cit)]\cdot 3H_2O\cdot 0.5H_2O_2$ (M = Mo *or* W). The method used for both salts is that described by us previously for the molybdenum complex.[2] An excess of 30% $H_2O_2$ (15 cm$^3$) was added at 0 °C to a solution of potassium molybdate (1.0 g, 4.2 mmol) and citric acid (0.88 g, 4.2 mmol) in water (15 cm$^3$). Addition of ethanol produced yellow crystals, which were filtered off and washed with ethanol [Found: C, 14.0; H, 2.2; K, 15.3; $(O_2)^{2-}$, 15.6. $C_6H_{13}K_2MoO_{16}$ requires C, 14.0; H, 2.5; K, 15.2; $(O_2)^{2-}$, 15.5. Found: C, 12.5; H, 1.5; K, 12.6; $(O_2)^{2-}$, 12.0. $C_6H_{13}K_2O_{16}W$ requires C, 12.0; H, 2.2; K, 13.0; $(O_2)^{2-}$ 13.3%].

$K_2[M_2O_2(O_2)_4(tart)]\cdot 4H_2O$ (M = Mo *or* W). Potassium molybdate (1.0 g, 4.2 mmol) and (+)-tartaric acid (0.31 g, 2.1 mmol) were dissolved in water (10 cm$^3$). Addition of 30% $H_2O_2$ (10 cm$^3$) produced a dark red solution, which was adjusted to pH 4.0 to give a yellow colour by dropwise addition of dilute HCl. The yellow complex was precipitated with ethanol, and recrystallised from water–ethanol at 5 °C as yellow needles [Found: C, 6.8; H, 1.3; K, 21.8; $(O_2)^{2-}$, 17.8. $C_4H_{10}K_4Mo_2O_{20}$ requires C, 6.6; H, 1.4; K, 21.5; $(O_2)^2$, 17.6%]. The tungsten complex was similarly prepared, except that the solution (pH 2.0) needed no pH adjustment, and gave extremely thin off-white crystals [Found: C, 5.6; H, 0.9; K, 16.8; $(O_2)^{2-}$, 15.6. $C_4H_{10}K_4O_{20}W_2$ requires C, 5.3; H, 1.1; K, 17.3; $(O_2)^{2-}$, 14.2%].

$K_2[MoO(O_2)_2L]\cdot 2H_2O$ [L = *tart* (**3**), *mal* (**4**), *glyc* (**5**), *or tartronate* (*tron*) (**6**)] *and* $K_2[WO(O_2)_2L]\cdot 2H_2O$ [L = *tart* (**7**), *mal* (**8**) *or glyc* (**9**)]. These complexes were prepared by addition of an excess of 30% $H_2O_2$ to solutions equimolar in $[MO_4]^{2-}$ (M = Mo or W) and the carboxylic acid, and isolated in the manner of the citrato and oxalato complexes. [Found for (**3**): C, 11.2; H, 1.6; K, 18.2; $(O_2)^{2-}$, 14.1. $C_4H_8K_2MoO_{13}$ requires C, 11.0; H, 1.8; K, 17.8; $(O_2)^{2-}$, 14.6. Found for (**4**): C, 11.1; H, 1.2; K, 18.8; $(O_2)^{2-}$, 15.3. $C_4H_8K_2MoO_{12}$ requires C, 11.4; H, 1.9; K, 18.5; $(O_2)^{2-}$, 15.2. Found for (**5**): C, 6.6; H, 1.5; K, 21.4; $(O_2)^{2-}$, 17.7. $C_2H_6K_2MoO_{10}$ requires C, 6.6; H, 1.7; K, 21.5; $(O_2)^{2-}$, 17.6. Found for (**6**): C, 8.2; H, 0.5; K, 19.6; $(O_2)^{2-}$, 16.8. $C_3H_6K_2MoO_{12}$ requires C, 8.8; H, 1.5; K, 19.2; $(O_2)^{2-}$, 15.7. Found for (**7**): C, 8.8; H, 1.0; K, 14.4; $(O_2)^{2-}$, 12.7. $C_4H_8K_2O_{13}W$ requires C, 9.1; H, 1.5; K, 14.9; $(O_2)^{2-}$, 12.2. Found for (**8**): C, 9.7; H, 1.1; K, 15.0; $(O_2)^{2-}$, 12.9. $C_4H_8K_2O_{12}W$ requires C, 9.4; H, 1.6; K, 15.3; $(O_2)^{2-}$, 12.6. Found for (**9**): C, 5.6; H, 0.8; K, 17.0; $(O_2)^{2-}$, 14.7. $C_2H_6K_2O_{10}W$ requires C, 5.3; H, 1.3; K, 17.3; $(O_2)^{2-}$, 14.2%].

$K_2[MoO(O_2)_2(quin)]\cdot 2H_2O$. Potassium molybdate (1.0 g, 4.2 mmol) and quinic acid (0.81 g, 4.2 mmol) were dissolved in water (10 cm$^3$). Addition of an excess of 30% $H_2O_2$ gave a dark red solution, to which dilute HCl was added dropwise until the colour just changed to light yellow (pH 3.3). Storage at 5 °C for 24 h, after addition of ethanol, produced a yellow oil, which was dried and the residue crushed to a yellow powder [Found: C, 16.3; H, 2.1; K, 15.3; $(O_2)^{2-}$, 14.4. $C_7H_{14}K_2MoO_{13}$ requires C, 17.5; H, 2.9; K, 16.3; $(O_2)^{2-}$, 13.3%].

$[PPh_4]_2[MoO(O_2)_2(ox)]$. Tetraphenylphosphonium chloride (2.19 g, 5.8 mmol) was added to a solution of $K_2[MoO(O_2)_2(ox)]$ (1.0 g, 2.9 mmol; in 25 cm$^3$ of water), and the mixture stirred for 24 h. The yellow product was filtered off, washed with water, and dried in a vacuum desiccator over silica gel (Found: C, 61.9; H, 4.3; P, 6.8. $C_{50}H_{40}MoO_9P_2$ requires C, 63.7; H, 4.3; P, 6.6%).

*General Experimental.*—Infrared spectra were measured on a Perkin-Elmer 683 spectrometer, as mulls in liquid paraffin between potassium bromide plates. Raman spectra were measured on a Spex Ramalog V instrument and Spex Datamate computer control unit, using the exciting lines at 568.2 and 530.9 nm from a Coherent model 52 krypton-ion laser. Spectra of solids were taken as spinning KBr discs, and of aqueous solutions in capillary tubes. The $^{95}$Mo and $^{13}$C n.m.r. spectra were recorded on a Bruker WM250 Fourier-transform spectrometer. Proton n.m.r. spectra in the epoxidation

**Table 3.** Atomic co-ordinates of the non-hydrogen atoms ( × $10^4$) with e.s.d.s in parentheses

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Mo | 1 540(1) | 3 577(1) | 2 794(1) |
| K(1) | 2 999(2) | 2 043(2) | 6 405(2) |
| K(2) | 2 958(2) | 8 129(2) | 649(2) |
| O(1) | 1 247(7) | 5 270(7) | 3 509(5) |
| O(2) | 1 549(8) | 1 367(7) | 4 493(5) |
| O(3) | 3 624(7) | 1 333(6) | 3 780(5) |
| O(4) | 1 656(8) | 5 100(7) | 816(5) |
| O(5) | 3 706(7) | 3 857(7) | 1 247(5) |
| O(6) | −1 498(6) | 4 328(6) | 2 931(5) |
| O(7) | 1 215(6) | 1 559(6) | 1 919(4) |
| O(8) | 3 148(7) | 2 067(6) | 9 131(5) |
| O(9) | 3 410(8) | 7 520(7) | 3 695(6) |
| O(10) | −1 075(7) | 499(6) | 1 741(5) |
| C(1) | −2 298(10) | 3 104(9) | 2 747(7) |
| C(2) | −618(10) | 1 585(9) | 2 079(6) |

experiments were measured on a JEOL FX 90Q Fourier-transform spectrometer. Microanalyses were performed by Mr. K. Jones of the Imperial College Microanalytical Department, peroxide analyses by iodometric titration, and potassium analyses gravimetrically.

Absolute ethanol and other reagents were used as supplied, except for potassium tungstate which was prepared by acidification of sodium tungstate to $WO_3$, followed by the addition of KOH until pH 7—8.

*X-Ray Crystal Structure of* $K_2[MoO(O_2)_2(glyc)]\cdot 2H_2O$.—Yellow crystals of the complex were prepared as described in the Experimental section. That selected for intensity data collection was an elongated prism, approximately 0.25 × 0.04 × 0.03 mm. Measurements were carried out on a Nicolet *R*3*m*/Eclipse S140 diffractometer system with graphite-monochromated Cu-$K_\alpha$ radiation. Unit-cell dimensions were determined by least-squares refinement of the angular settings of 17 automatically centred reflections.

*Crystal data.* $C_2H_6K_2MoO_{10}$, $M = 364.21$, triclinic, space group $P\bar{1}$, $a = 7.222(4)$, $b = 7.950(6)$, $c = 10.450(5)$ Å, $\alpha = 67.81(4)$, $\beta = 73.72(7)$, $\gamma = 64.84(4)°$, $U = 497.7$ Å$^3$ at 20 °C, $Z = 2$, $D_c = 2.43$ g cm$^{-3}$, $F(000) = 351.9$, $\lambda$(Cu-$K_\alpha$) = 1.541 8 Å, $\mu$(Cu-$K_\alpha$) = 191.2 cm$^{-1}$.

Integrated intensities in one hemisphere were measured using the ω-scan technique. Two reflections (110 and $1\bar{1}\bar{1}$) were monitored every 50 measurements, and these decreased by *ca.* 6% over the period of data collection (1 d). A total of 1 518 independent reflections were measured (to $\theta = 57°$), of which 49 were judged to be 'unobserved' [$I < 3\sigma(I)$]. The data were scaled using the reference reflections and were corrected for Lorentz and polarisation effects. At a later stage an empirical absorption correction was applied,[17] based on 36 psi-scan measurements for each of eight representative reflections. All calculations and drawings were made using the SHELXTL program system,[17] and atomic scattering factors and anomalous dispersion corrections were taken from ref. 18.

The co-ordinates of the molybdenum atom were derived from an initial Patterson synthesis and the positions of all the other atoms were found from subsequent Fourier difference syntheses. Least-squares refinement was by the block-cascade method, typical of the SHELXTL system. All non-hydrogen atoms were refined with anisotropic thermal parameters, while the positions of the glycolate hydrogen atoms were tied to those of the parent carbon atom; those of the water hydrogens were fixed and their isotropic thermal parameters were allowed to refine. A weighting scheme was applied so that $w = 1/[\sigma(F_o)^2 + 0.0007F_o^2]$ for the last cycle; $R$ reduced to 0.035, and $R' = [\Sigma w|\Delta F|^2/\Sigma w|\Delta F_o|^2]^{\frac{1}{2}}$ was 0.038.

Fractional co-ordinates of the non-hydrogen atoms are listed in Table 3.

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