The Crystal Structure of Dipyridinium μ-Oxo-tetraperoxodioxobis(aquo)-dimolybdate(VI) and Dipyridinium Di-μ-hydroperoxo-tetraperoxo-dioxodimolybdate(IV)

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PYRIDINE derivatives of peroxomolybdic acid with the peroxide:metal ratio of 2:1 and 3:1 have been isolated[1] and formulated as $[(pyH_2)][MoO_6]$ and $[(pyH)_2][MoO_7]$. Analysis, i.r., and Raman spectra studies of solid samples and aqueous solutions of these peroxomolybdates[2] suggested that these compounds should be formulated as binuclear species containing the $[Mo_2O_{11}]^{2-}$ ion, *i.e.* $[(pyH)_2][Mo_2O_{11}],H_2O$ and $[(pyH)_2][Mo_2O_{11}],2H_2O_2$. It was presumed that this ion exists in both compounds, the second being considered as a perhydrate containing hydrogen peroxide of crystallization.

We have now studied the crystal structures of these compounds. Our results indicate that both foregoing interpretations are in error and that the compounds should be formulated as dipyridinium μ-oxo-tetraperoxodioxobis(aquo)dimolybdate(VI); $[(PyH)_2][O(OH_2)(O_2)_2Mo\text{-}O\text{-}Mo(O_2)_2(OH_2)O]$ (I), and dipyridinium di-μ-hydroperoxo-tetraperoxo-dioxodimolybdate(VI), $[(PyH)_2][O(O_2)_2Mo(OOH)_2Mo(O_2)_2O]$ (II).

In each compound the molybdenum atoms are surrounded by seven oxygen atoms, forming a pentagonal bipyramid. In (I), the anion consists of two pentagonal bipyramids joined by one corner (C_2 symetry, see Figure 1). In (II), the anion consists of two pentagonal bipyramids sharing one edge (C_i symmetry, see Figure 2). Approximate standard deviations of the inter-atomic distances indicated in the Figures are: $\sigma(\text{Mo–O}) = 0{\cdot}010$ and $\sigma(\text{O–O}) = 0{\cdot}015$ Å.

Crystal data: (I) $[(PyH)_2][Mo_2O_{11}(H_2O)_2]$, $M = 564$, monoclinic, $a = 22{\cdot}485(23)$, $b = 7{\cdot}173(7)$, $c = 17{\cdot}211(18)$ Å, $\beta = 140{\cdot}64 \pm 0{\cdot}3°$, $U = 1760$ Å^3, $D_m = 2{\cdot}14$, $Z = 4$, $D_c = 2{\cdot}13$, space group $C2/C$ (No. 15), $\lambda = 0{\cdot}71069$ Å.

(II) $[(PyH)_2][Mo_2O_{10}(OOH)_2]$, $M = 578$, triclinic, $a = 6{\cdot}587(7)$, $b = 7{\cdot}620(8)$, $c = 10{\cdot}903(II)$ Å, $\alpha = 105{\cdot}22°$, $\beta = 117{\cdot}39°$, $\gamma = 100{\cdot}49°$ (each $\pm$ $0{\cdot}3°$), $U = 438$ Å^3, $D_m = 2{\cdot}16$, $Z = 1$, $D_c = 2{\cdot}19$ space group $P\bar{1}$ (No. 2), $\lambda = 0{\cdot}71069$ Å.

Intensities of 1800 and 2370 independent non-zero reflections respectively for the compounds (I) and (II) were recorded on a PAILRED diffractometer using Mo-K_α radiation.

The dimensions of the crystals used for intensity measurements are: (I), 0·25 × 0·25 × 0·60 mm., and (II) 0·35 × 0·34 × 0·80 mm. No absorption corrections were applied $\mu(\text{I}) = 14{\cdot}8\ \text{cm.}^{-1}$, $\mu(\text{II}) = 14{\cdot}7\ \text{cm.}^{-1}$.

The structures were derived by Patterson and Fourier techniques and refined to R 0·082 for (I) and 0·065 for (II) by isotropic full-matrix least-squares analysis and difference synthesis. Refinement with anisotropic temperature factors will be carried out.

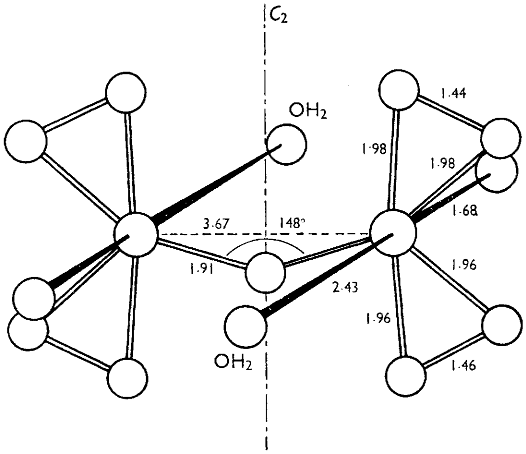

FIGURE 1

We thank the Director of the Institut Francais du Pétrole (Recherche Chimique de base) for interest in this work and for financial support.

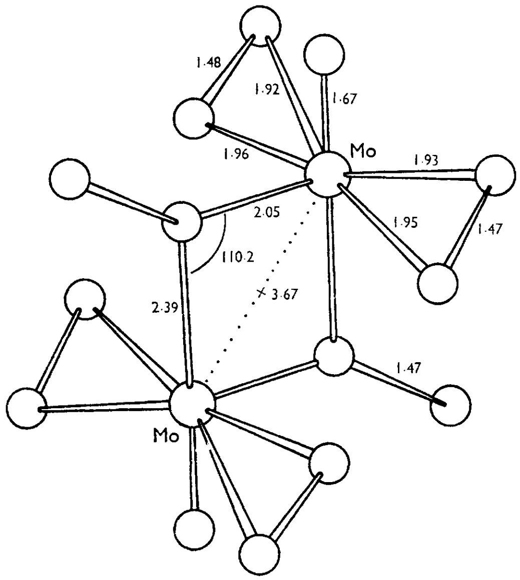

FIGURE 2

(*Received, July* 18*th*, 1968; *Com.* 964.)

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