

## Synthesis and Structural Characterisation of an Unusual Tetranuclear Oxomolybdenum(vi) Complex of Dihydroxybenzoquinone, $[\text{Mo}_4\text{O}_{10}(\text{O}_4\text{C}_6\text{H}_2)_2]^{2-}$ , and a Comparison with the Mononuclear Chloranilate Complex $[\text{MoO}_2(\text{HO}_4\text{C}_6\text{Cl}_2)(\text{O}_4\text{C}_6\text{Cl}_2)]^{1-}$

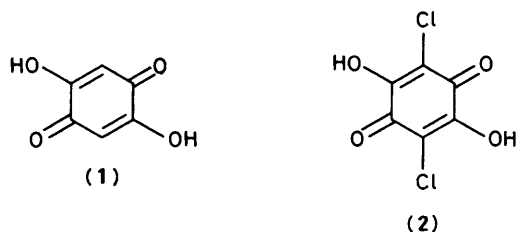
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While reaction of the sterically encumbered chloranil group with  $(\text{Mo}_2\text{O}_7)^{2-}$  yields the mononuclear species  $[\text{MoO}_2(\text{L})(\text{LH})]^{1-}$  ( $\text{L} = \text{C}_6\text{O}_4\text{Cl}_2$ ), dihydroxybenzoquinone under similar conditions yields the tetranuclear cluster  $[(\text{Mo}_2\text{O}_5)_2(\text{C}_6\text{H}_2\text{O}_4)]^{2-}$ , a species with magnetically coupled semiquinone ligands.

Catechol and 1,2-benzoquinone complexes of transition metals are of general interest in the investigation of ligand-centred redox processes<sup>1</sup> and in the preparation of metal semiquinone species.<sup>2</sup> The reactions of  $[\text{Mo}(\text{CO})_6]$  with various *o*-benzoquinones have been shown to produce dramatically different compounds, including the binuclear oxomolybdenum(vi) species  $[\text{Mo}_2\text{O}_2(\text{dibutylcatecholate})_4]$ <sup>3</sup> and  $[\text{Mo}_2\text{O}_5(\text{phenanthrenesemiquinone})_6]$ <sup>4</sup> and, with tetrachloro-1,2-benzoquinone, the dimeric catecholate complex  $[\text{Mo}_2(\text{Cl}_4\text{cat})_3]$ .<sup>5</sup> By exploiting the reactivity of polyoxoanions which are soluble in organic solvents,<sup>6</sup> we have recently extended this series to include both tetranuclear oxomolybdenum(vi) complexes of the class  $[\text{Mo}_4\text{O}_6(\text{OR})_2(\text{Rcat})_2]^{2-}$  (ref. 7) and ligand-bridged binuclear species  $[\text{Mo}_2\text{O}_4\text{Cl}_4(\text{O}_4\text{C}_6\text{X}_2)_2]^{2-}$ ,  $\text{X} = \text{Cl}, \text{Br}$ .<sup>8</sup> As part of these investigations, we have studied the reactions of dihydroxybenzoquinone (**1**) and its chloro-derivative, chloranilic acid (**2**) with  $(\text{Bu}^n_4\text{N})_2[\text{Mo}_2\text{O}_7]$ .

Reaction of  $(\text{Bu}^n_4\text{N})_2[\text{Mo}_2\text{O}_7]$  with an equimolar amount of dihydroxybenzoquinone in methanol yields a



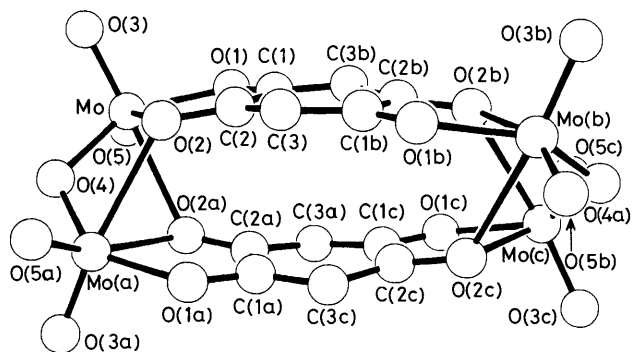
bright red solution from which red blocks of  $(\text{Bu}^n_4\text{N})_2[\text{Mo}_4\text{O}_{10}(\text{O}_4\text{C}_6\text{H}_2)_2]$  (**3**) crystallize over two days in 30% yield.† A copious second crop of crystals was identified as  $\alpha\text{-(Bu}_4\text{N)}_4[\text{Mo}_8\text{O}_{26}]$  (ca. 40%), suggesting a condensation-type reaction producing  $\text{H}_2\text{O}$  as a by-product and resulting in reaggregation of the oxomolybdate cluster. The structure of (**3**), shown in Figure 1, is seen to consist of discrete tetranuclear dianionic units  $[\text{Mo}_4\text{O}_{10}(\text{O}_4\text{C}_6\text{H}_2)_2]^{2-}$ , with two-fold axes passing through O(4) and O(4a) and through the midpoints of the phenyl rings generating the symmetry-related portions of the tetrametallic cluster. The ligands function as chelating tetradentate groups, bridging two  $[\text{Mo}_2\text{O}_5]^{2+}$  units.

While the metrical parameters associated with the

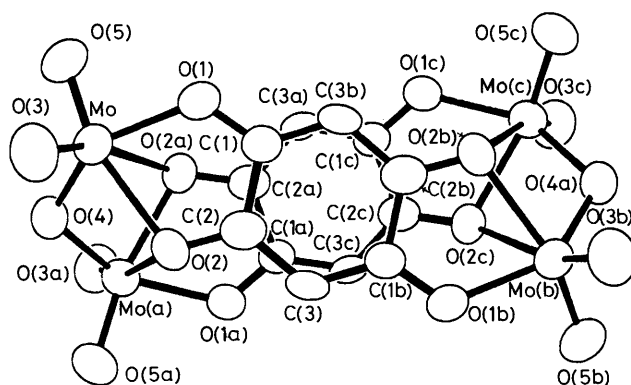
† Satisfactory elemental analyses (C, H, and N) were obtained for (**3**) and (**6**).

Selected spectral data for (**3**): i.r.: 949 and 920  $[\nu_s(\text{Mo}=\text{O})]$  and  $\nu_s(\text{Mo}=\text{O})$ , 735  $\text{cm}^{-1}$   $[\nu(\text{Mo}-\text{O}-\text{Mo})]$ ; u.v.-vis.: 569 ( $\epsilon$   $9.4 \times 10^2$ ), 411 ( $1.4 \times 10^3$ ), 365 ( $2.9 \times 10^3$ ), 305 nm ( $2.8 \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ).

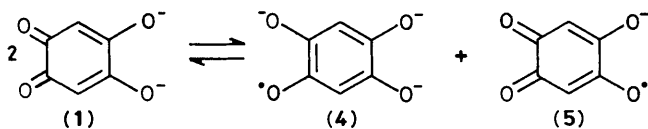
Crystal data for (**3**):  $\text{C}_{44}\text{H}_{76}\text{N}_2\text{O}_{18}\text{Mo}_4$ , space group *Ccca*,  $a = 15.527(3)$ ,  $b = 21.094(4)$ ,  $c = 17.192(3)$  Å,  $U = 5630.6(12)$  Å<sup>3</sup>,  $Z = 4$  (based on tetranuclear formulation),  $D_c = 1.54 \text{ g cm}^{-3}$ . Structure solution and refinement based on 1022 reflections with  $F_o \geq 6\sigma(F_o)$  (2730 collected in the range  $2 > 2\theta \geq 45^\circ$ ; Mo- $K_\alpha$  radiation,  $\lambda = 0.71073$  Å) gave  $R = 0.056$ . The cation was disordered about the two-fold axis passing through the N atom. Partial populations of 0.6 and 0.4 were assigned to C(11)–C(18) and C(11')–C(18'), respectively, an expedient which appeared adequately to model the disorder. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



**Figure 1.** ORTEP view of the structure of  $[\text{Mo}_4\text{O}_{10}(\text{O}_4\text{C}_6\text{H}_2)_2]^{2-}$ , the anion in (3), showing the atom labelling scheme. Selected bond lengths (Å) and angles ( $^\circ$ ): Mo–O(1) 2.003(9), Mo–O(2) 2.232(9), Mo–O(3) 1.705(9), Mo–O(4) 1.906(6), Mo–O(5) 1.708(9), Mo–O(2a) 2.594(8), C(1)–O(1) 1.28(1), C(2)–O(2) 1.30(1), C(1)–C(2) 1.49(1), C(2)–C(3) 1.43(2); O(1)–Mo–O(2) 75.2(3), O(1)–Mo–O(3) 104.1(4), O(1)–Mo–O(4) 142.5(4), O(1)–Mo–O(5) 93.2(4), O(2)–Mo–O(3) 96.0(4), O(2)–Mo–O(4) 77.4(3), O(2)–Mo–O(5) 158.1(4), O(3)–Mo–O(4) 103.9(4), O(3)–Mo–O(5), 104.9(5), O(4)–Mo–O(5) 103.3(4).



**Figure 2.** View of the structure of  $[\text{Mo}_4\text{O}_{10}(\text{O}_4\text{C}_6\text{H}_2)_2]^{2-}$  normal to the ring plane, showing the staggered configuration of the rings.

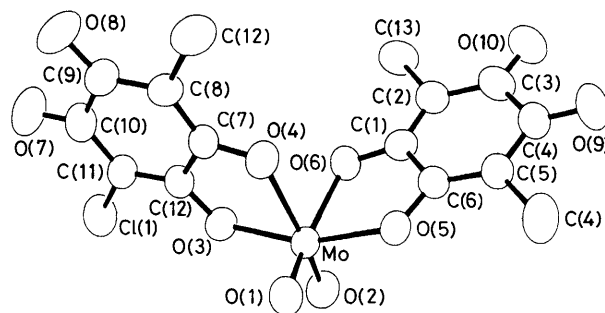


$[\text{Mo}_2\text{O}_5]^{2+}$  moieties are unexceptional, the highly distorted  $[\text{MoO}_6]$  geometry, which approaches the square pyramidal limit with an additional long  $\text{Mo} \cdots \text{O}$  contact, is unusual, as other examples of this unit display simple pseudo-octahedral geometry.<sup>3,9</sup> The *trans* influence of the oxo groups is evident in the Mo–ligand oxygen distances of 2.232(9) and 2.003(9) Å for O(2) *trans* to the terminal oxo group O(5) and O(1) *trans* to the bridging oxo group O(4), respectively, and most noticeable in the Mo–O(2a) (ligand) distance of 2.594(8) Å for the doubly-bridging quinone oxygen *trans* to O(3).

A most unusual feature of the complex is the requirement that the ligands co-ordinate formally as trinegative radical anions. Since the Mo(vi) centres are uninvolved in redox transformations at the ligand sites, disproportionation of (1) to semiquinone forms must be invoked to account for this formulation. Although the ultimate fate of the unreacted semiquinone has not been established, such equilibria occur readily in quinoid chemistry and have been extensively documented.<sup>10</sup>

The observed diamagnetism of (3) requires that the semiquinone ligands be magnetically coupled. The crystallographically imposed parallel orientation of the quinoid ligands in (3), together with the staggered ring configuration shown in Figure 2, suggests direct interaction between radical anions. The interplanar separation of 2.88 Å is extremely short compared with 3.15 Å for tetracyanoquinodimethane (TCNQ) molecules in conductive crystals and may be compared to an interplanar separation of *ca.* 3.10 Å in  $[\text{Mo}_2\text{O}_5(9,10\text{-phenanthrenesemiquinone})_2]$ , a complex which also exhibits magnetic coupling of quinone radical anions.<sup>3</sup>

The short interplanar separation of the quinoid ligands suggests that steric constraints would dramatically affect the aggregation through parallel stacked bridging quinoid groups. To test this hypothesis, similar reactions were carried out using chloranilic acid (2) as a ligand. Under a variety of



**Figure 3.** ORTEP view of the structure of  $[\text{MoO}_2(\text{O}_4\text{C}_6\text{Cl}_2)(\text{HO}_4\text{C}_6\text{Cl}_2)]^{1-}$ , the anion in complex (6), showing the atom labelling scheme. Selected bond lengths (Å) and angles ( $^\circ$ ): Mo–O(1) 1.709(5), Mo–O(2) 1.691(5), Mo–O(3) 2.043(5), Mo–O(4) 2.202(5), Mo–O(5) 2.030(5), Mo–O(6) 2.187(5), C(12)–O(3) 1.311(8), C(7)–O(4) 1.292(8), C(6)–O(5) 1.317(8), C(1)–O(6) 1.276(8); O(1)–Mo–O(2) 104.1(3), O(1)–Mo–O(3) 104.3(2), O(1)–Mo–O(4) 89.9(2), O(1)–Mo–O(5) 88.4(2), O(1)–Mo–O(6) 158.0(2), O(2)–Mo–O(3) 88.8(2), O(2)–Mo–O(4) 160.5(2), O(2)–Mo–O(5) 102.8(2), O(2)–Mo–O(6) 92.7(2), O(3)–Mo–O(4) 74.4(2), O(3)–Mo–O(5) 160.3(2), O(3)–Mo–O(6) 90.0(2), O(4)–Mo–O(5) 90.9(2), O(4)–Mo–O(6) 77.8(2), O(5)–Mo–O(6) 73.8(2).

conditions, the unique product of the reaction was the diamagnetic, dark purple crystalline complex  $(\text{Bu}_4\text{N})-[\text{MoO}_2(\text{HO}_4\text{C}_6\text{Cl}_2)(\text{O}_4\text{C}_6\text{Cl}_2)]$  (6).<sup>‡</sup>

As shown in Figure 3, (6) displays the *cis*-dioxo geometry characteristic of mononuclear Mo(vi) complexes. That the complex is a monoanion suggests that one ligand is doubly deprotonated while the second is singly deprotonated. A broad peak at 3540  $\text{cm}^{-1}$  in the i.r. spectrum of (6), confirms

<sup>‡</sup>  $(\text{Bu}_4\text{N})_2[\text{Mo}_2\text{O}_7]$  was reacted with a three-fold excess of chloranilic acid in acetonitrile. The resulting purple solution was carefully layered with ether, and after standing for two weeks, lustrous purple crystals of (6) were isolated in 40% yield.

Selected spectral data for (6): i.r.: 927 and 900  $[\nu_s(\text{Mo}=\text{O})]$  and  $\nu_s(\text{Mo}=\text{O})$ , 1650  $\text{cm}^{-1}$   $[\nu(\text{C}=\text{O})]$ ; u.v.–vis.: 530 ( $\epsilon 1.7 \times 10^3$ ), 325 nm ( $2.4 \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ).

Crystal data for (6):  $\text{C}_{28}\text{H}_{37}\text{NO}_{10}\text{Cl}_4\text{Mo}$ , space group  $\text{P}\bar{1}$ ,  $a = 10.383(2)$ ,  $b = 13.197(3)$ ,  $c = 14.191(3)$  Å,  $\alpha = 88.11(1)$ ,  $\beta = 87.56(1)$ ,  $\gamma = 78.11(1)^\circ$ ,  $U = 1900.3(11)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.37 \text{ g cm}^{-3}$ . Structure solution and refinement based on 4239 reflections with  $F_o \geq 6\sigma(F_o)$  (6458 collected,  $+h, \pm k, \pm l$  and  $2 \geq 2\theta \geq 45^\circ$ , Mo- $K_\alpha$  radiation,  $\lambda = 0.71073$  Å) gave  $R = 0.055$ . Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

the presence of the exchangeable proton on one ligand site. Rapid exchange apparently precluded observation of this proton in the  $^1\text{H}$  n.m.r. spectrum of (6). The intense colour associated with the complex is attributed to charge transfer interactions, predominantly associated with the ligand itself. Indeed, solutions of (2) to which  $\text{NEt}_3$  is added, display electronic spectra similar to those of (6), with small differences attributable to metal participation.

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