A Binuclear Dioxomolybdate Chloranilate Complex $[(MoO_2Cl_2)_2(C_6O_4Cl_2)]^{2-}$, Prepared from the Reaction of a Polyoxomolybdate Anion with Tetrachloro-1,2-benzoquinone

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Complexes of 1,2-benzoquinones with transition metals are of general interest in the investigation of ligand-centered redox processes [1–3] and in the preparation of metal-semiquinone species [4, 5]. The reactions of $Mo(CO)_6$ and various *o*-benzoquinones have been shown to produce dramatically different compounds, including the binuclear oxomolybdenum(VI) products $[Mo_2O_2(dibutylcatecholate)_4]$ and $[Mo_2O_5(phenanthrenesemiquinone)_2]$ [6, 7] and, with tetrachloro-1,2-benzoquinone, the dimeric catecholate complex, $[Mo_2(Cl_4cat)_3]$ [8, 9].

As part of our investigations of the coordination chemistry of polyoxomolybdates with oxygen donor ligands in nonaqueous solvents [10], we have prepared a variety of oxomolybdenum complexes of catechol and quinone ligands [11]. In the course of these studies, the reaction of $[Mo_2O_7]^{2-}$ with tetrachloro-1,2-benzoquinone has been shown to yield an unusual binuclear dioxomolybdenum–chloranilate complex, $(n\text{-}Bu_4N)_2[(MoO_2Cl_2)_2(Cl_2C_6O_4)]\cdot 0.5CH_3CN$ (**I**).

Reaction of $(n\text{-}Bu_4N)_2[Mo_2O_7]$ with a two-fold excess of tetrachloro-1,2-benzoquinone in methanol or CH_3CN, followed by the addition of ether, results in the precipitation of a blue product which analyzes for $[(n\text{-}C_4H_9)_4N]_2[Mo_2O_4Cl_4(Cl_2C_6O_4)]$ after recrystallization from CH_3CN/ether. *Anal.* Calc. for $C_{39}H_{73.5}Cl_6Cl_6Mo_2N_{2.5}O_8$: C, 42.2; H, 6.67; N, 3.15; Cl, 19.2. Found: C, 42.3; H, 6.79; N, 3.16; Cl, 18.8%. Infrared (KBr pellet, cm^{-1}): 2960(s), 2880(ms), 1545(vs), 1475(s), 1390(s), 954(vs), 920(vs), 860(ms), 485(w), 345(s). Electronic spectrum (CH_3CN, nm [ϵ, M^{-1} cm^{-1}]): 563 [8.26×10^2], 367 [2.14×10^4], 305 [8.6×10^3]. Extinction coefficients are reported for 1.0×10^{-3} M solution. Since solutions of the complex decolorize over time and particularly upon exposure to light, the solutions exhibit deviations from Beer's law behavior. The infrared spectrum of the complex exhibited strong bands at 954 and 920 cm^{-1} assigned to $\nu_a(MoO_2)$ and $\nu_s(MoO_2)$ of the *cis*-dioxomolybdate(VI) moiety. The single resonance observed at 1001 ppm of the ^{17}O NMR spectrum established exclusively terminal oxo groups in identical chemical environments.

The structure of the anion of **I**, determined by a single crystal X-ray diffraction study, is shown in Fig. 1 and selected geometric parameters are given in the caption. Orthorhombic space group $P222_1$ with $a = 9.804(2)$, $b = 15.465(3)$, $c = 18.951(3)$ Å, $Z = 2$ (based upon binuclear formulation), $V = 2873.3(11)$ Å. Structure solution and refinement based on 1304 reflections with $F_o \geqslant 6\sigma(F_o)$(Mo K$\alpha$ radiation, $\lambda = 0.71073$ Å) converged at a conventional discrepancy factor of 0.060 with a 'goodness of fit' of 1.207.

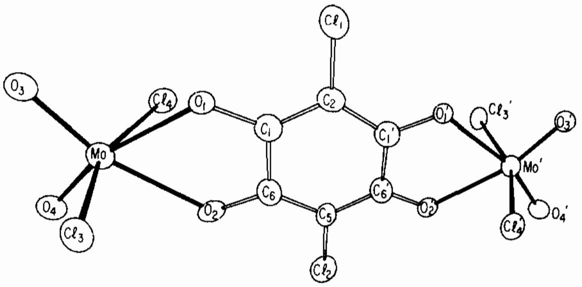

Fig. 1. ORTEP view of the complex dianion $[Mo_2O_4Cl_4(Cl_2C_6O_4)]^{2-}$, showing the atom-labelling scheme. Selected bond lengths (Å) and angles (°): Mo–Cl3, 2.353(5); Mo–Cl4, 2.348(6); Mo–O1, 2.24(1); Mo–O2, 2.24(1); Mo–O3, 1.64(1); Mo–O4, 1.66(1); Cl–O1, 1.27(2); C6–O2, 1.27(2). Cl3–Mo–Cl4, 158.3(2); Cl3–Mo–O3, 95.8(5); Cl3–Mo–O4, 98.1(5); Cl4–Mo–O3, 97.3(6); Cl4–Mo–O4, 95.3(5); O1–Mo–O4, 162.2(5); O2–Mo–O3, 163.4(6); O3–Mo–O4, 104.5(7).

Compound **I** contains discrete $[(MoO_2Cl_2)_2(Cl_2C_6O_4)]^{2-}$ anions, possessing a crystallographic two-fold axis passing through Cl1, C2, C5 and Cl2. The structure may be described as two *cis*-dioxodichloromolybdenum(VI) units bridged by a chloranilate dianion $(Cl_2C_6O_4)^{2-}$, producing pseudo-octahedral $[MoO_4Cl_2]$ coordination about the Mo centers. The $[MoO_2(Cl_2C_6O_4)MoO_2]^{2+}$ moiety is essentially planar, with a maximum deviation from the best plane through these atoms of 0.1 Å.

Complex **I** is formed as a consequence of chloride transfer from tetrachloro-1,2-benzoquinone to the molybdate center, coupled to addition of a *cis*-dioxomolybdate unit to the quinone ligand. Since the product is best described as a molybdenum(VI) complex of the chloranilate dianion $(Cl_2C_6O_4)^{2-}$, the unusual chemical transformation results from substitution reactions alone, with no net redox chemistry of either the metal or ligand centers. Although tetrachloro-1,2-benzoquinone has been used as a chloride transfer reagent in organic reactions and in reactions with manganese [12], the reaction chemistry with

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metals has been limited to chelation through the oxygen donors [8, 13]. The ability of molybdate to abstract chloride from chlorohydrocarbons has precedents in the synthesis of $[Mo_2O_2Cl_5(SPh)_2]^-$ via chloro abstraction from chloroform by molybdate [14] and in the reaction of $[MoO_4]^{2-}$ with CH_2Cl_2 to yield $[CH_2Mo_4O_{15}H]^{3-}$ [15]. That complex **I** may also be synthesized from the reaction of $MoO_2Cl_2 \cdot (dmf)_2$ with chloranilic acid confirms the identity of the bridging ligand.

Complex I is electrochemically active, displaying a one-electron reduction at −0.10 V, a process which behaves reversibly only at sweep rates greater than 2000 mV/s in cyclic voltammetry and which exhibits characteristics associated with reduction followed by an irreversible chemical reaction [16]. Controlled potential electrolysis at −0.20 V bleaches the characteristic blue color of the solution of **I** and yields a yellow microcrystalline material currently under investigation.

The analogous bromide species $(n\text{-}Bu_4N)_2[(MoO_2Br_2)_2(Br_2C_6O_4)]$ (**II**) may be synthesized from the reaction of $[Mo_2O_7]^{2-}$ with tetrabromo-1,2-benzoquinone. Calc. for $C_{38}H_{72}Br_6Mo_2N_2O_8$: C, 33.65; H, 5.35; N, 2.06, Br, 35.35. Found: C, 33.82; H, 5.47; N, 2.02; Br, 34.53%. Infrared (KBr pellet, cm^{-1}): 2955(m, s), 2862(m), 1522(vs), 1465(ms), 1370(s), 945(s), 910(s), 820(m), 482(ms), 375(m). Electronic spectrum (CH_3CN, nm [ϵ, M^{-1} cm^{-1}]): 579[2.5×10^2], 386[6.4×10^3, sh], 363[1.65×10^4]. Reactions with potentially binucleating ligands, analogous to chloranilic acid, such as 2,5-dihydroxy-1,4-benzoquinone and squaric acid, yield a variety of binuclear and oligomeric species upon reaction with $[Mo_2O_7]^{2-}$ and $MoO_2Cl_2 \cdot (dmf)_2$ whose structures and properties will be reported and compared to those of I and II.

Supplementary Material

Tables of atomic coordinates, bond lengths and angles and observed and calculated structure factors (20 pages) are available from the authors on request.

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