(20) Tranqui, D.; Boyer, P.; Vulliet, P. *Acta Crystallogr., Sect. B* **1977**, *33*, 3126–33.
(21) Tranqui, D.; Tissier, A.; Langier, J.; Boyer, P. *Acta Crystallogr., Sect. B* **1977**, *33*, 392–7.
(22) Titze, H. *Acta Chem. Scand., Ser. A* **1974**, *28*, 1079–88.
(23) Sadikov, G. G.; Kukina, G. A.; Porai-Koshits, M. A. *J. Struct. Chem. (Engl. Trans.)* **1971**, *12*, 787–92.
(24) Meites, L. "Polarographic Techniques"; Wiley: New York, 1965; p 279.
(25) Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748–56.
(26) Hoard, J. L.; Silverton, J. V. *Inorg. Chem.* **1963**, *2*, 235–43.
(27) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751–67.
(28) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, N.Y., 1960; p 260.

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Synthesis, Structure, and Properties of the Oxygen-Deficient Bis(3,5-di-*tert*-butylcatecholato)oxomolybdenum(VI) Dimer, $[MoO(O_2C_6H_2(t\text{-}Bu)_2)_2]_2$

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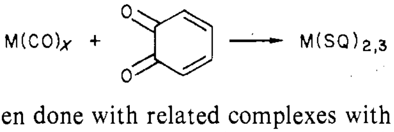
The reaction between $Mo(CO)_6$ and 3,5-di-*tert*-butyl-1,2-benzoquinone in toluene produces a complex of empirical formula $MoO(O_2C_6H_2(t\text{-}Bu)_2)_2$ as a toluene solvate. The results of a crystallographic molecular structure determination show that the complex is a centrosymmetric dimer with oxygen atoms of two catecholate ligands linking adjacent metal centers. Molybdenum–oxygen lengths within the bridge are quite unsymmetrical with the longest length occurring within the chelate ring to an oxygen which is trans to a strongly bound oxo ligand. The ligands have C–O lengths which are consistent with a fully reduced catecholate structure. Accordingly, the metal centers are rare examples of octahedral Mo(VI) having a single oxo ligand. The electronic spectrum of the complex is found to be nearly identical with that of a complex previously characterized as $Mo(O_2C_6H_2(t\text{-}Bu)_2)_3$. A band in the infrared region at 990 cm^{-1} appears attributable to the Mo=O stretch and the proton NMR is consistent with the structural result. Electrochemically, the complex is not observed to undergo oxidation but does undergo two irreversible reductions, likely to Mo(V) species.

Introduction

Much of the coordination chemistry of higher oxidation state molybdenum is centered about classes of complexes containing terminal and bridging oxo ligands. Species containing a single oxo ligand, $Mo{=}O^{n+}$, are commonly found in the chemistry of Mo(IV) and Mo(V) but rarely found with Mo(VI).[1] Examples of cases where the MoO^{4+} unit is found include seven-coordinate peroxo and persulfido complexes, $MoO(X_2)L_4^{2+}$ (X = O, S),[2,3] seven-coordinate dithiocarbamate complexes,[4] $MoO(dtc)_3^+$, and five-coordinate oxyhalides, $MoOX_4$.[5] We have been interested for some time in complexes prepared with *o*-quinone ligands for their unique magnetic, structural, and electrochemical properties. A convenient route to neutral bis and tris complexes with metals of the first transition series involves simple reaction between the neutral *o*-quinone and an appropriate metal carbonyl. Characterization of complexes formed by this method with metals ranging from vanadium to nickel has indicated that the ligands bond as partially reduced semiquinones (eq 1).[6–8] While relatively



(1)

little has been done with related complexes with second- or third-row metals, reactions carried out with $Mo(CO)_6$ suggest rather different chemistry. The reaction with tetrachloro-1,2-benzoquinone gave a dimer, $[Mo(O_2C_6Cl_4)_3]_2$, with fully reduced ligands and Mo(VI) centers.[9] The same reaction carried out with 9,10-phenanthrenequinone under similar conditions was found to be photochemical and produced the *cis*-dioxomolybdenum(VI) complex $Mo_2O_5(O_2C_{14}H_8)_2$ with semiquinone ligands.[10] Razuvaev and co-workers have reported the synthesis of the 3,5-di-*tert*-butylbenzoquinone complex of Mo, $Mo(O_2C_6H_2(t\text{-}Bu)_2)_3$, by the method above and by reaction between $MoCl_3$ and the semiquinone form of the ligand.[11] In view of the interesting structural features of $[Mo(O_2C_6Cl_4)_3]_2$ and $Mo(O_2C_{14}H_8)_3$, we have sought to repeat this synthesis but have obtained results from the hexacarbonylmolybdenum–3,5-di-*tert*-butylbenzoquinone reaction which differ considerably from those reported by Razuvaev. Our characterization of the dimeric oxomolybdenum(VI) product obtained from this reaction is the subject of this paper.

Table I. Crystal Data for $[MoO(O_2C_6H_2(t\text{-}Bu)_2)_2]_2 \cdot C_6H_5CH_3$

space group $P\bar{1}$	$V = 1595.9\ (5)\ \text{Å}^3$
$a = 11.521\ (3)\ \text{Å}$	fw 1197.27
$b = 13.125\ (3)\ \text{Å}$	$\rho(\text{obsd}) = 1.239\ (5)\ \text{g cm}^{-3}$
$c = 11.515\ (3)\ \text{Å}$	$\rho(\text{calcd}) = 1.242\ \text{g cm}^{-3}$
$\alpha = 108.11\ (2)°$	$Z = 1$
$\beta = 97.48\ (2)°$	imposed symmetry $\bar{1}$
$\gamma = 100.29\ (2)°$	$\mu = 4.42\ \text{cm}^{-1}$

Experimental Section

Compound Preparation. The reaction between $Mo(CO)_6$ and 3,5-di-*tert*-butyl-1,2-benzoquinone was carried out in 50 mL of refluxing toluene by combining 0.53 g (2 mmol) of carbonyl with 1.00 g (6 mmol) of quinone. Over the period of a few hours the solution turned from the dark green color of the quinone to the dark purple color of the complex. It is pertinent to point out that both $[Mo(O_2C_6Cl_4)_3]_2$ and $Mo(O_2C_{14}H_8)_3$ are *purple* while $Mo_2O_5(O_2C_{14}H_8)_2$ is *green*. Other reports have appeared describing the synthesis of "green $Mo(O_2C_{14}H_8)_3$" from the reaction of 9,10-phenanthrenequinone and $Mo(CO)_6$.[12] Initially the reaction was carried out under nitrogen; however, efforts were not made to assure a scrupulously oxygen-free system. The complex must form by reaction with trace quantities of oxygen similar to the 9,10-phenanthrenequinone reaction. The complex itself is air stable and may be isolated from toluene solution as $MoO(O_2C_6H_2(t\text{-}Bu)_2)_2 \cdot {}^1/_2C_6H_5CH_3$. The loosely held toluene solvate molecule is easily displaced from the crystal structure at room temperature resulting in decay of crystal quality and erratic chemical analyses for the compound.

Physical Measurements. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer 337 grating spectrophotometer. Visible spectra were recorded on a Cary 17 recording spectrophotometer. A Varian 390 spectrometer was used for NMR spectra. Electrochemical

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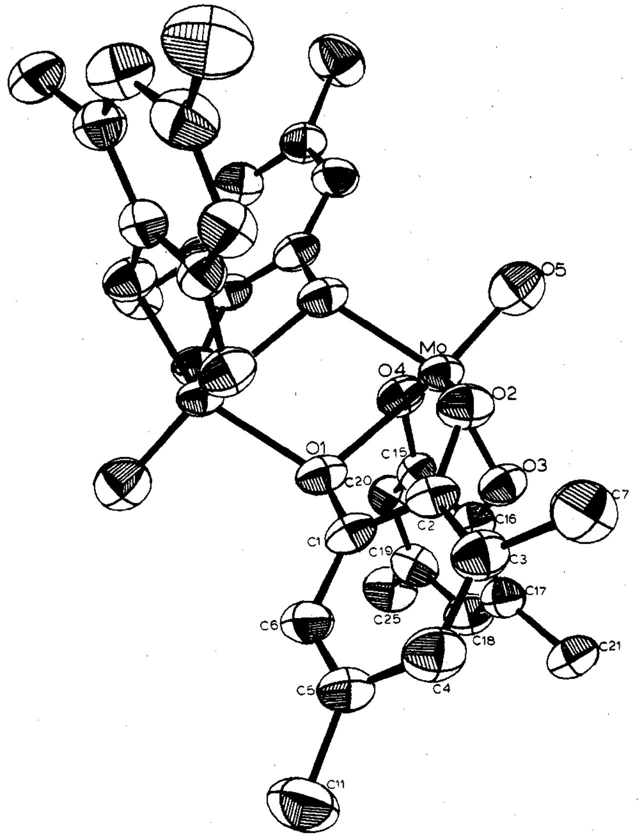


Figure 1. Perspective view of the $[MoO(O_2C_6H_2(t\text{-}Bu)_2)_2]_2$ molecule showing the atom labeling scheme. Methyl carbon atoms of the tertiary butyl groups have been omitted for clarity.

studies were carried out under a nitrogen atmosphere by using a PAR Model 174A polarographic analyzer. Platinum working and auxiliary electrodes were used with a saturated calomel reference electrode. Measurements were carried out in a methylene chloride solution which was approximately 10^{-3} M in complex and 0.1 M in tetra-*n*-butylammonium perchlorate electrolyte.

Structure Determination. A crystal of the complex obtained from toluene solution and coated with an amorphous resin to retard the loss of the solvate was mounted and aligned on a Syntex $P\bar{1}$ automated diffractometer equipped with a graphite crystal monochromator. Preliminary photographs indicated triclinic symmetry. The centered settings of 15 reflections with 2θ values greater than 20° (Mo Kα radiation) were refined by least-squares procedures to give the cell constants contained in Table I. A complete set of intensity data was collected within the angular range $3° \leq 2\theta \leq 50°$ by the θ–2θ scan technique. A symmetrical scan range of ±0.7° was used with a scan rate of 4°/min. Four standard reflections monitored after every 100 reflections measured showed a linear 18% decay over the time required to collect data, presumably due to toluene loss. Data were scaled to compensate for this decay and corrected for Lorentz and polarization effects. Of the 5653 reflections measured 4434 were found to have $F_o^2 > 3\sigma(F_o^2)$ and were used in the refinement.

The position of the Mo atom was determined from a three-dimensional Patterson map. Phases derived from the Mo position were used to locate all other nonhydrogen atoms of the structure. Isotropic refinement of all nonhydrogen atoms converged with $R = 0.104$ and $R_w = 0.129$. Further refinement with anisotropic thermal parameters for all nonhydrogen atoms gave discrepancy indices of $R = 0.058$ and $R_w = 0.072$. One *tert*-butyl group of the structure, consisting of carbon atoms C(12), C(13), and C(14), was found to suffer from twofold disorder with approximate occupancy factors of 0.33 and 0.66 for the two sets of methyl carbon atoms. Also, the toluene solvate was found to be located about a crystallographic inversion center requiring an occupancy factor of 0.5 for the disordered methyl carbon atom. Hydrogen atom positions for all carbon atoms but the disordered *tert*-butyl and toluene methyl groups were obtained from a final difference Fourier map. Their fixed contributions were included in a final cycle of refinement which converged with discrepancy indices of $R = 0.056$ and $R_w = 0.068$. The error in an observation of unit weight was 1.89. Computer programs, calculational procedures, and sources of scattering factors have been noted previously.[13] Final positional and thermal parameters for all atoms are presented in Table II. A table of $|F_o|$ and $|F_c|$ is available.

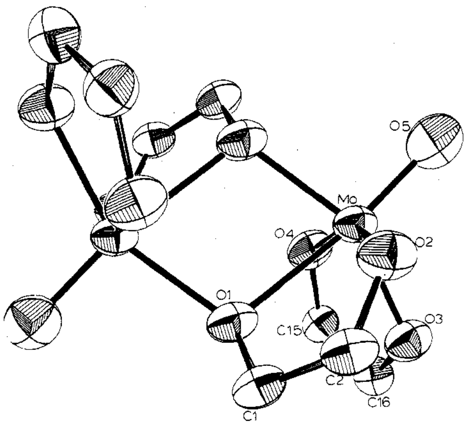


Figure 2. A view of the inner coordination geometry of $[MoO(O_2C_6H_2(t\text{-}Bu)_2)_2]_2$.

Description of the Structure

The results of the structure determination show that the complex molecule is a centrosymmetric dimer, $[MoO(O_2C_6H_2(t\text{-}Bu)_2)_2]_2$. A view of the molecule is shown in Figure 1 with a view of the inner coordination geometry in Figure 2. Intramolecular bond distances and angles are contained in Table III. Each metal has a distorted octahedral geometry with a long Mo–O(1) length at the position trans to the strongly bound oxo ligand, O(5). Bridging the two metal atoms are oxygen atoms of two fully reduced di-*tert*-*t*-butylcatecholate ligands. The Mo–O(1) lengths of the bridge are unsymmetrical with the shorter length to the outer molybdenum, 2.039 (3) Å, and the longer length within the chelate ring, 2.325 (3) Å. This pattern of Mo–O lengths serves to stabilize the dimeric structure, for, had the two strongest Mo–O bonds been within the chelate ring, the complex would readily dissociate to $MoO(O_2C_6H_2(t\text{-}Bu)_2)_2$, a five-coordinate monomer similar to $MoOCl_4$. The single oxo ligand bound to each metal has a Mo–O(5) bond length of 1.668 (3) Å, comparable to a value of 1.658 (5) Å reported for $MoOCl_4$[5] and within the range of values associated with oxo ligands multiply bonded to Mo(VI). Within the dimer, oxo ligands have a trans orientation. Other Mo–O lengths of the structure are normal. The second oxygen of the bridging ligand has a Mo–O(2) length of 1.927 (3) Å. The other unique ligand of the structure has Mo–O lengths of 1.945 (3) and 1.948 (3) Å for O(3) and O(4). As expected, the repulsive influence of the oxo ligand is reflected in the bond angles to the cis oxygen atoms with all four angles exceeding 98°. This distortion, with the large difference in Mo–O(1) and Mo–O(1)′ lengths, results in a O(1)–Mo–O(1)′ angle of 73.5 (2)° and brings O(1) to within 2.626 (6) Å of O(1)′.

Quinone ligand C–O lengths are diagnostic of formal ligand charge. Fully reduced catecholate ligands have C–O lengths which are 1.35 Å with little variation.[7,9] Chelated semiquinone ligands have lengths of 1.29 Å,[7] also with little variation, and unreduced *o*-quinones, lengths of 1.23 Å.[14] Furthermore, quinone complexes generally exhibit other structural features or magnetic and spectral properties consistent with formal ligand change.[6,7] In none of the quinone complexes characterized to date has there been the ambiguity of ligand charge associated with the neutral 1,2-dithiolene complexes. The ligands in $[MoO(O_2C_6H_2(t\text{-}Bu)_2)_2]_2$ are clearly fully reduced catecholates and the metal ions, Mo(VI). The C–O lengths for the chelated oxygens are all within a standard deviation

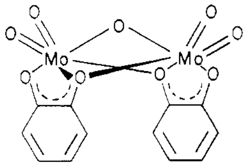
Table II. Final Positional and Thermal Parameters for $[MoO(O_2C_6H_2(t\text{-}Bu)_2)_2]_2 \cdot C_6H_5CH_3$

atom	x	y	z	B_{11}[a]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
				Complex Molecule					
Mo	0.08372 (4)	0.00866 (3)	0.14216 (4)	2.76 (3)	2.12 (2)	3.13 (2)	0.65 (2)	0.86 (2)	0.51 (2)
O(1)	−0.0646 (3)	0.0704 (2)	0.0445 (3)	3.5 (1)	2.6 (1)	3.5 (1)	0.9 (1)	1.2 (1)	0.4 (1)
O(2)	0.1546 (3)	0.1580 (2)	0.1576 (3)	3.5 (1)	2.6 (1)	4.4 (1)	0.6 (1)	1.3 (1)	1.0 (1)
C(1)	−0.0355 (5)	0.1844 (4)	0.0948 (4)	3.8 (1)	2.5 (1)	3.1 (1)	0.9 (1)	1.2 (1)	1.5 (1)
C(2)	0.0838 (5)	0.2301 (4)	0.1568 (5)	3.6 (2)	2.7 (2)	3.3 (2)	0.9 (2)	1.4 (2)	1.0 (2)
C(3)	0.1251 (5)	0.3450 (4)	0.2142 (5)	3.9 (2)	2.8 (2)	3.9 (2)	0.8 (2)	1.1 (2)	0.9 (2)
C(4)	0.0402 (6)	0.4046 (4)	0.2048 (5)	4.9 (3)	2.4 (2)	5.0 (2)	0.8 (2)	1.0 (2)	0.9 (2)
C(5)	−0.0806 (5)	0.3604 (4)	0.1420 (5)	4.7 (3)	3.0 (2)	4.0 (3)	1.7 (2)	1.0 (2)	0.8 (2)
C(6)	−0.1166 (5)	0.2466 (4)	0.0846 (5)	3.8 (2)	3.3 (2)	3.9 (2)	1.3 (2)	0.9 (2)	0.6 (2)
C(7)	0.2565 (5)	0.3965 (4)	0.2816 (6)	4.2 (3)	2.7 (2)	5.9 (3)	0.2 (2)	0.3 (2)	0.8 (2)
C(8)	0.3390 (6)	0.3719 (5)	0.1863 (7)	4.7 (3)	4.6 (3)	8.1 (4)	0.0 (2)	2.2 (3)	1.0 (3)
C(9)	0.2795 (6)	0.5231 (5)	0.3407 (7)	4.9 (3)	3.2 (3)	9.2 (4)	0.3 (3)	0.7 (3)	0.2 (3)
C(10)	0.2888 (6)	0.3491 (5)	0.3836 (7)	5.9 (4)	5.5 (4)	6.0 (4)	0.2 (3)	−0.6 (3)	1.7 (3)
C(11)	−0.1703 (7)	0.4347 (5)	0.1434 (7)	5.9 (4)	4.4 (3)	7.4 (4)	2.6 (3)	0.5 (3)	1.6 (3)
C(12)[b]	−0.2927 (11)	0.3762 (10)	0.0662 (15)	6.9 (9)	5.3 (7)	15.2 (14)	2.9 (6)	−4.5 (9)	−1.2 (9)
C(13)[b]	−0.1867 (12)	0.4840 (9)	0.2849 (11)	10.9 (9)	7.6 (7)	6.8 (6)	6.6 (7)	3.7 (7)	2.2 (6)
C(14)[b]	−0.1185 (11)	0.5397 (9)	0.1118 (11)	7.9 (9)	5.9 (8)	9.2 (9)	1.8 (7)	0.9 (8)	4.4 (8)
C(12)[c]	−0.2758 (12)	0.3893 (12)	0.1936 (18)	9.4 (11)	11.9 (10)	23.6 (13)	9.2 (8)	11.9 (10)	9.9 (10)
C(13)[c]	−0.2133 (13)	0.4099 (12)	−0.0116 (9)	10.1 (10)	11.9 (10)	8.8 (10)	7.2 (8)	−0.5 (9)	4.2 (9)
C(14)[c]	−0.0996 (11)	0.5536 (12)	0.1803 (10)	11.9 (9)	2.5 (8)	17.3 (10)	4.7 (8)	7.5 (8)	−0.7 (9)
O(3)	0.0178 (3)	0.0758 (2)	0.2867 (3)	3.6 (1)	2.8 (1)	3.5 (1)	0.5 (1)	1.2 (1)	0.3 (1)
O(4)	−0.0494 (3)	−0.1109 (2)	0.1311 (3)	3.9 (1)	2.7 (1)	3.8 (1)	0.4 (1)	1.2 (1)	0.7 (1)
C(15)	−0.1287 (5)	−0.0839 (4)	0.2049 (4)	3.4 (2)	2.9 (2)	2.9 (2)	0.6 (2)	0.6 (2)	0.9 (2)
C(16)	−0.0907 (5)	0.0216 (4)	0.2947 (4)	3.4 (2)	2.9 (2)	3.2 (2)	0.6 (2)	0.7 (2)	1.2 (2)
C(17)	−0.1572 (5)	0.0580 (4)	0.3864 (5)	3.9 (2)	3.5 (2)	3.5 (2)	1.3 (2)	1.0 (2)	1.4 (2)
C(18)	−0.2625 (5)	−0.0139 (5)	0.3790 (5)	4.5 (3)	4.1 (2)	4.6 (3)	1.2 (2)	1.9 (3)	1.6 (2)
C(19)	−0.3038 (5)	−0.1206 (5)	0.2881 (5)	3.5 (2)	4.2 (3)	5.1 (3)	0.9 (2)	1.4 (2)	2.5 (3)
C(20)	−0.2350 (5)	−0.1546 (4)	0.2004 (5)	3.7 (2)	4.8 (2)	4.0 (3)	0.4 (2)	0.5 (2)	0.9 (2)
C(21)	−0.1116 (5)	0.1718 (4)	0.4885 (5)	4.9 (3)	3.7 (2)	3.5 (2)	1.5 (2)	1.6 (2)	0.8 (2)
C(22)	−0.1992 (7)	0.1907 (5)	0.5806 (6)	10.4 (5)	4.4 (3)	5.5 (4)	2.0 (3)	4.8 (4)	0.9 (2)
C(23)	−0.1038 (6)	0.2604 (5)	0.4301 (6)	6.4 (4)	3.8 (2)	4.6 (3)	1.4 (3)	1.6 (2)	1.0 (4)
C(24)	0.0127 (7)	0.1763 (5)	0.5583 (6)	8.9 (5)	5.5 (4)	3.5 (3)	2.8 (3)	−0.9 (3)	−0.6 (3)
C(25)	−0.4227 (6)	−0.1951 (5)	0.2914 (7)	4.1 (3)	4.8 (3)	7.4 (4)	0.4 (3)	2.1 (3)	2.6 (3)
C(26)	−0.5273 (7)	−0.1416 (8)	0.2665 (8)	3.4 (3)	12.4 (5)	13.8 (7)	0.6 (4)	2.5 (4)	5.7 (6)
C(27)	−0.4189 (9)	−0.2038 (9)	0.4192 (9)	9.8 (6)	12.3 (5)	9.2 (6)	−4.2 (5)	0.9 (5)	7.8 (6)
C(28)	−0.4478 (7)	−0.3095 (6)	0.1911 (10)	5.4 (4)	5.8 (4)	15.2 (8)	−0.4 (3)	4.5 (4)	2.4 (4)
O(5)	−0.0494 (3)	−0.1109 (2)	0.1311 (3)	4.9 (2)	3.8 (2)	5.1 (2)	1.1 (2)	1.1 (1)	1.6 (1)
				Toluene Solvate					
C(29)	−0.4060 (6)	−0.0488 (6)	−0.0255 (6)	6.4 (5)	11.8 (8)	11.5 (7)	4.2 (5)	4.7 (4)	7.8 (5)
C(30)	−0.3927 (6)	0.0286 (6)	−0.0854 (6)	5.9 (5)	10.6 (6)	12.0 (7)	3.2 (5)	2.9 (6)	6.8 (5)
C(31)	−0.4866 (6)	0.0793 (6)	−0.1123 (6)	10.9 (8)	9.4 (5)	8.6 (6)	3.0 (5)	3.9 (7)	5.2 (5)
C(32)[d]	−0.4706 (7)	0.1414 (7)	0.2149 (8)	10.9 (10)	14.1 (20)	12.4 (17)	3.6 (15)	2.1 (15)	8.3 (16)

[a] The anisotropic thermal parameters (Å^2) are of the form $\exp[-0.25(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$. [b] Occupancy factor of 0.6667. [c] Occupancy factor of 0.3333. [d] Occupancy factor of 0.50.

of the 1.35 Å value, while the length to the bridging oxygen is still longer, 1.385 (5) Å. Carbon–carbon bond lengths within both independent ligands are of normal values and are consistent with this formulation.

The bridged oxygen mode of coordination found in this structure was found for the 9,10-phenanthrenesemiquinone ligands in $Mo_2O_5(O_2C_{14}H_8)_2$ (I)[10] and the catecholate ligands in $Mo_2O_5(O_2C_6H_4)_2^{2-}$.[15] It has also been found for the bis(3,5-di-*tert*-butylsemiquinone)cobalt(II) tetramer[8] and may prove to be a general structural feature of many complexes containing reduced quinone ligands. Structural features of the chelate ring associated with the second set of catecholate ligands compare quite favorably with the chelated ligands in $[Mo(O_2C_6Cl_4)_3]_2$[9] and $Mo(O_2C_{14}H_8)_3$.[16] Mo–O lengths in these two structures are approximately 1.95 Å, while the lengths to O(3) and O(4) in the present structure are 1.945 (3) and 1.948 (3) Å. Bite angles at the metal are 75–77° in the two previous structures and $MoO_2(O_2C_6H_4)_2^{2-}$,[17] and in $[MoO(O_2C_6H_2(t\text{-}Bu)_2)_2]_2$ the value is 73.5 (2)°. The C–O lengths and angles about the interior of the chelate ring compare well with values found in $[Mo(O_2C_6Cl_4)_3]_2$ and $Mo(O_2C_{14}H_8)_3$.



The crystal structure consists of well-separated complex molecules and a toluene solvate molecule also located about an inversion center. Intermolecular stacking found commonly in complexes formed with the planar 9,10-phenanthrenequinone and tetrachloro-1,2-benzoquinone ligand reduces complex solubility and often inhibits solution characterization. The bulky *tert*-butyl substituents present a minor crystallographic problem in terms of potential rotational disorder but contribute to greater complex solubility.

Spectral Properties of $[MoO(O_2C_6H_2(t\text{-}Bu)_2)_2]_2$

Razuvaev and co-workers recently reported $Mo(O_2C_6H_2(t\text{-}Bu)_2)_3$ prepared by the reaction of the quinone with $Mo(CO)_6$.[11] While their analytical data and molecular weight are consistent with the tris formulation, their electronic spectrum is nearly identical with that of $[MoO(O_2C_6H_2(t\text{-}Bu)_2)_2]_2$ (Table V). In an attempt to assign the oxygen-to-molybdenum charge-transfer band, the spectrum of $[MoO(O_2C_6H_2(t\text{-}Bu)_2)_2]_2$ has been compared with the spectrum of $MoOCl_4$.[18] Both have bands at 37 000 cm^{-1} which may correspond to the $Mo{=}O^{4+}$ chromophore. Spectra run

Table III. Intramolecular Bond Distances (Å) and Angles (deg) for $[MoO(O_2C_6H_2(t\text{-}Bu)_2)_2]_2$[a]

Distances from the Mo Atom			
Mo–Mo′	3.4968 (9)	Mo–O(3)	1.945 (3)
Mo–O(1)	2.325 (3)	Mo–O(4)	1.948 (3)
Mo–O(1)′	2.039 (3)	Mo–O(5)	1.668 (3)
Mo–O(2)	1.927 (3)		
Angles about the Mo Atom			
O(1)–Mo–O(1)′	73.5 (2)	O(3)–Mo–O(4)	78.3 (1)
O(1)–Mo–O(2)	73.4 (2)	O(3)–Mo–O(5)	108.3 (2)
O(1)–Mo–O(3)	81.5 (1)	O(3)–Mo–O(1)′	151.1 (1)
O(1)–Mo–O(4)	84.1 (1)	O(4)–Mo–O(5)	108.3 (2)
O(2)–Mo–O(3)	85.1 (1)	O(4)–Mo–O(1)	84.6 (1)
O(2)–Mo–O(4)	153.9 (1)	O(5)–Mo–O(1)	166.9 (1)
O(2)–Mo–O(5)	98.3 (2)	O(5)–Mo–O(1)	98.6 (2)
O(2)–Mo–O(1)′	101.3 (1)		
Distances within the Bridging 3,5-Di-*tert*-butylcatecholate Ligand			
O(1)–C(1)	1.385 (5)	C(3)–C(4)	1.370 (8)
O(2)–C(2)	1.357 (6)	C(3)–C(7)	1.534 (8)
C(1)–C(2)	1.394 (7)	C(4)–C(5)	1.409 (8)
C(1)–C(6)	1.362 (7)	C(5)–C(6)	1.391 (7)
C(2)–C(3)	1.407 (7)	C(5)–C(11)	1.540 (8)
Angles within the Bridging 3,5-Di-*tert*-butylcatecholate Ligand			
Mo–O(1)–Mo′	106.5 (1)	C(2)–C(1)–C(6)	122.9 (5)
Mo–O(1)–C(1)	121.0 (3)	O(2)–C(2)–C(1)	116.3 (4)
Mo–O(2)–C(2)	120.0 (3)	O(2)–C(2)–C(3)	123.4 (5)
O(1)–C(1)–C(2)	114.2 (4)	C(1)–C(2)–C(3)	120.3 (5)
O(1)–C(1)–C(6)	122.9 (5)		
Distances within the Chelated 3,5-Di-*tert*-butylcatecholate Ligand			
O(3)–C(16)	1.352 (6)	C(17)–C(21)	1.535 (7)
O(4)–C(15)	1.346 (6)	C(18)–C(19)	1.415 (8)
C(15)–C(16)	1.398 (6)	C(19)–C(20)	1.379 (7)
C(16)–C(17)	1.399 (7)	C(19)–C(25)	1.547 (8)
C(17)–C(18)	1.373 (7)	C(20)–C(15)	1.382 (7)
Angles within the Chelated 3,5-Di-*tert*-butylcatecholate Ligand			
Mo–O(3)–C(16)	117.1 (3)	C(15)–C(16)–C(17)	120.9 (5)
Mo–O(4)–C(15)	116.3 (3)	O(4)–C(15)–C(16)	113.9 (4)
O(3)–C(16)–C(15)	112.4 (4)	O(4)–C(15)–C(20)	124.5 (4)
O(3)–C(16)–C(17)	126.4 (5)	C(16)–C(15)–C(20)	121.5 (5)

[a] Prime symbol refers to atoms generated by the inversion symmetry operation.

Table IV. Dihedral Angles and Least-Squares Planes for $[MoO(O_2C_6H_2(t\text{-}Bu)_2)_2]_2$

Dihedral Angles

plane 1	plane 2	angle, deg
O(1)–Mo–O(2)	bridging ligand	25.4 (2)
O(3)–Mo–O(4)	chelating ligand	9.2 (2)

Least-Squares Planes

atom	deviation, Å	atom	deviation, Å
Bridging Ligand			
$5.47x + 1.46y - 1.07z = 1.04$			
Mo	−0.719	C(3)	−0.003 (5)
O(1)	−0.011 (3)	C(4)	−0.019 (6)
O(2)	0.005 (3)	C(5)	−0.005 (5)
C(1)	0.008 (5)	C(6)	0.028 (6)
C(2)	0.002 (5)		
Chelating Ligand			
$6.21x - 8.98y + 7.89z = -1.57$			
Mo	−0.227	C(17)	0.021 (5)
O(3)	0.001 (4)	C(18)	0.029 (6)
O(4)	0.029 (3)	C(19)	0.012 (6)
C(15)	−0.042 (5)	C(20)	−0.027 (5)
C(16)	−0.042 (5)		

over a number of different concentrations show no evidence of complex dissociation in cyclohexane or dichloromethane solution.

The infrared spectrum of $[MoO(O_2C_6H_2(t\text{-}Bu)_2)_2]_2$ is quite complex, consisting mainly of catecholate ligand bands. There are several bands in the region between 950 and 1050 cm^{-1} where the M=O stretching vibration should occur. A band at 990 cm^{-1} appears in the spectrum of the complex but not in the spectrum of the free catechol and may be assigned as this vibration. The Mo=O vibration of $MoOCl_4$ occurs at a slightly higher value, 1015 cm^{-1}, but in this structure there are no donor ligands trans to the oxo ligand.[5,19]

Table V. Electronic Spectra of Oxomolybdenum(VI) Complexes

compound	medium	spectra, cm^{-1}	log ε
$[MoO(O_2C_6H_2(t\text{-}Bu)_2)_2]_2$	CH_2Cl_2	11 300	3.7
		18 940	4.3
		31 746	4.1
		37 175	4.3
"$Mo(O_2C_6H_2(t\text{-}Bu)_2)_3$"	*a*	11 364	3.6
		19 231	4.0
		31 746	3.8
		37 040	4.0
$MoOCl_4$	CCl_4	14 430[b]	2.5
		20 750	3.5
		37 170	3.5

[a] Medium not given. See ref 11. [b] Band probably due to Mo(V) impurity. See ref 18.

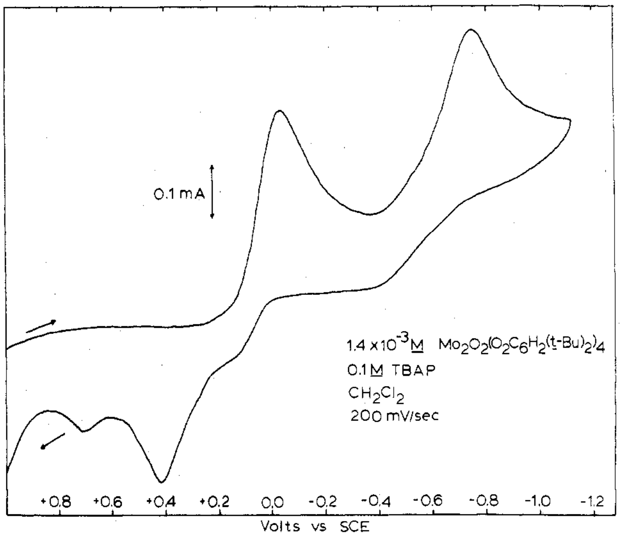


Figure 3. The cyclic voltammogram of $[MoO(O_2C_6H_2(t\text{-}Bu)_2)_2]_2$.

The diamagnetic $[MoO(O_2C_6H_2(t\text{-}Bu)_2)_2]_2$ molecule gives a sharp NMR spectrum consisting of four singlets for the nonequivalent *tert*-butyl groups at 0.95, 1.27, 1.28, and 1.57 ppm and resonances at 6.81, 6.83, 7.08 and 7.11 ppm for the four unique ring protons. While there is no evidence of complex dissociation in $CDCl_3$, spectra recorded in deuterated acetone show only two *tert*-butyl resonances at 1.25 and 1.42 ppm. This appears to indicate dissociation to a six-coordinate monomer, $MoO(O_2C_6H_2(t\text{-}Bu)_2)_2(sol)$, in coordinating solvents. Furthermore, samples isolated from acetone and redissolved in $CDCl_3$ give resonances associated with the dimer indicating that monomer and dimer are interconvertible.

Electrochemistry of $[MoO(O_2C_6H_2(t\text{-}Bu)_2]_2$

The redox chemistry of the quinone–catecholate complexes has proven to be of interest and there has been a large volume of recent work on the redox properties of binuclear molybdenum complexes.[20] There are a number of potentially electroactive electrons associated with the catecholate ligands of the $[MoO(O_2C_6H_2(t\text{-}Bu)_2)_2]_2$ dimer. Also, the Mo(VI) centers may undergo reduction of Mo(V). Figure 3 shows the cyclic voltammogram of the complex. The neutral dimer does not undergo oxidation but does undergo two irreversible reduction reactions at −0.03 and −0.75 V. Two anodic oxidations are observed at +0.42 and +0.71 V but these are only observed when cathodic scans are extended beyond the first reduction wave. Therefore the species which appears to undergo oxidation is the product of this first reduction not the neutral dimer. It is not known whether the dimeric structure of the complex is retained upon reduction or indeed whether the complex undergoing reduction is the dimer characterized structurally or a monomer which forms in the presence of coordinating electrolyte. It is quite possible that a monomeric Mo(V) species $MoO(O_2C_6H_2(t\text{-}Bu)_2)_2^-$ is the product of the first reduction and a Mo(VI) complex is the product of the second.

Oxygen Atom Transfer Reactions

The molybdo enzymes, nitrate reductase and certain oxidases, catalyze reactions which involve the net transfer of an oxygen atom to or from a Mo center.[21] Interest in developing synthetic analogues for metalloenzymes has led to a number of investigations which involve the reaction of an oxygen atom donor with a partially reduced Mo center, usually Mo(IV) or Mo(V).[22] The product of the reaction is generally a dioxomolybdenum(VI) species. As we had mentioned in the Introduction, the chemistry of the reaction between $Mo(CO)_6$ and an *o*-quinone was found to be quite different for *o*-chloranil and 9,10-phenanthrenequinone, the product in the former case $[Mo(O_2C_6Cl_4)_3]_2$ but a dioxomolybdenum(VI) complex (I) in the latter. The product obtained with 3,5-di-*tert*-butylbenzoquinone has shed some light on this chemistry as it has features common to both reaction products. All three have Mo(VI) centers and dimeric structures. The $[MoO(O_2C_6H_2(t\text{-}Bu)_2)_2]_2$ dimer has an oxomolybdenum structure similar to $Mo_2O_5(O_2C_{14}H_8)_2$, which, of course, has three more oxygen atoms and semiquinone ligands. Relative to $Mo_2O_5(O_2C_{14}H_8)_2$, and in terms of general patterns of Mo(VI) chemistry, the metal centers in $[MoO(O_2C_6H_2(t\text{-}Bu)_2)_2]_2$ can be regarded as oxygen deficient. The *o*-chloranil dimer $[Mo(O_2C_6Cl_4)_3]_2$ has fully reduced catecholate ligands as we find in the present complex. The formal chemical sequence relating these three complexes by the addition of oxygen atoms and the removal of unreduced quinone ligands is presented in eq 2. Through the series the oxidation state of the metal

$$[Mo^{VI}(Cat)_3]_2 \xrightarrow[-2Quin]{+2O} [Mo^{VI}O(Cat)_2]_2 \xrightarrow[-2Quin]{+3O} Mo^{VI}{}_2O_5(SQ)_2 \quad (2)$$

remains fixed with the charge required to formally reduce oxygen atoms to oxo ligands coming from the π^* levels of the reduced catecholate ligands. In this sense the ligands serve as electron storage areas.

We have been interested in examining the interconvertibility of the various members of the series. We have found that $Mo_2O_5(O_2C_{14}H_8)_2$ can be used to synthesize $Mo(O_2C_{14}H_8)_3$ in high yield by reaction with additional phenanthrenequinone, although the conditions of this reaction remain somewhat puzzling.[23] The $[MoO(O_2C_6H_2(t\text{-}Bu)_2)_2]_2$ dimer should prove to be quite useful in this endeavor since it may serve as a precursor either to $Mo(O_2C_6H_2(t\text{-}Bu)_2)_3$ by oxygen abstraction in the presence of excess quinone or to $Mo_2O_5(O_2C_6H_2(t\text{-}Bu)_2)_2$ by oxygen atom addition and benzoquinone displacement.

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Registry No. $[MoO(O_2C_6H_2(t\text{-}Bu)_2)_2]_2 \cdot C_6H_5CH_3$, 69847-08-1; $Mo(CO)_6$, 13939-06-5; 3,5-di-*tert*-butyl-1,2-benzoquinone, 3383-21-9.

Supplementary Material Available: Listing of structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) E. I. Stiefel, *Prog. Inorg. Chem.*, **22**, 1 (1977); (b) B. Spivack and Z. Dori, *Coord. Chem. Rev.*, **17**, 99 (1975).
(2) (a) I. Larking and R. Stromberg, *Acta Chem. Scand.*, **24**, 2043 (1970); (b) J. M. LeCarpentier, R. Schlupp and R. Weiss, *Acta Crystallogr., Sect. B*, **28**, 1278 (1972).
(3) J. Dirand-Colin, M. Schappacher, L. Ricard, and R. Weiss, *J. Less-Common Met.*, **54**, 91 (1977).
(4) J. Dirand, L. Ricard, and R. Weiss, *Transition Met. Chem.*, **1**, 2 (1975).
(5) K. Iijima and S. Shibata, *Bull. Chem. Soc. Jpn.*, **48**, 666 (1975).
(6) R. M. Buchanan, H. H. Downs, W. B. Shorthill, C. G. Pierpont, S. L. Kessel, and D. N. Hendrickson, *J. Am. Chem. Soc.*, **100**, 4318 (1978).
(7) R. M. Buchanan, S. L. Kesel, H. H. Downs, C. G. Pierpont, and D. N. Hendrickson, *J. Am. Chem. Soc.*, **100**, 7894 (1978).
(8) R. M. Buchanan and C. G. Pierpont, submitted for publication.
(9) C. G. Pierpont and H. H. Downs, *J. Am. Chem. Soc.*, **97**, 2123 (1975).
(10) C. G. Pierpont and R. M. Buchanan, *J. Am. Chem. Soc.*, **97**, 6450 (1975).
(11) V. Lobanov, G. A. Abakumov, and G. A. Razuvaev, *Dokl. Akad. Nauk SSSR*, **235**, 441 (1977).
(12) H. Tom Dieck, F. Hohmann, M. Form, T. Mack, and I. Renk, *J. Less-Common Met.*, **54**, 221 (1977).
(13) C. G. Pierpont, *Inorg. Chem.*, **16**, 636 (1977). Values of R and R_w are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. The function minimized during refinement was $\sum w(|F_o| - |F_c|)^2$ with weights calculated by the equation $w = 4F_o^2/\sigma^2(F_o^2)$.
(14) C. G. Pierpont and H. H. Downs, *Inorg. Chem.*, **16**, 2970 (1977).
(15) L. O. Atovmyan, V. V. Tkachev, and T. G. Shishova, *Dokl. Akad. Nauk SSSR*, **205**, 609 (1972).
(16) C. G. Pierpont and R. M. Buchanan, *J. Am. Chem. Soc.*, **97**, 4912 (1975).
(17) V. V. Tkachev and L. O. Atovmyan, *Coord. Chem.* (*USSR*), **1**, 845 (1975).
(18) M. L. Larson and F. W. Moore, *Inorg. Chem.*, **5**, 801 (1966).
(19) C. G. Barraclough and D. J. Kew, *Aust. J. Chem.*, **23**, 2387 (1970).
(20) (a) J. K. Howie and D. T. Sawyer, *Inorg. Chem.*, **15**, 1892 (1976); (b) V. R. Ott, D. S. Swieter, and F. A. Schultz, *ibid.*, **16**, 2538 (1977).
(21) R. C. Bray and J. C. Swann, *Struct. Bonding (Berlin)*, **11**, 107 (1971).
(22) (a) J. T. Spence and R. D. Taylor, *J. Less-Common Met.*, **54**, 449 (1977); (b) R. Durant, C. D. Garner, M. R. Hyde, F. E. Mabbs, J. R. Parsons, and D. Richens, *ibid.*, **54**, 459 (1977); (c) G. J.-J. Chen, J. W. McDonald, and W. E. Newton, *Inorg. Chem.*, **15**, 2612 (1976).
(23) The reaction was first observed upon Soxhlet extraction of crude $Mo_2O_5(O_2C_{14}H_8)_2$ in the presence of excess quinone with benzene. It has been found to occur reproducibly but the details of the reaction remain a mystery.