Bridging and Terminal *o*-Benzoquinone Coordination. The Crystal and Molecular Structure of Hexakis(tetrachloro-1,2-benzoquinone)dimolybdenum

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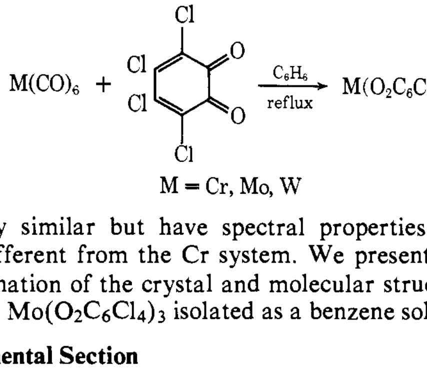
Abstract: The complex $Mo_2(O_2C_6Cl_4)_6$ may be synthesized by reaction of $Mo(CO)_6$ with tetrachloro-1,2-benzoquinone. Crystals of the complex isolated from a benzene solution are monoclinic, space group $C2/c$, with a = 22.417 (4) Å, b = 11.592 (3) Å, c = 27.307 (4) Å, β = 106.44 (4)°, V = 6873 Å^3, d(obsd) = 1.836 (5), and d(calcd) = 1.837 g cm^{-3} for eight formula weights of composition $Mo(O_2C_6Cl_4)_3 \cdot 1.5C_6H_6$ per unit cell. The structure was solved by conventional Patterson, Fourier, and least-squares refinement techniques using X-ray data complete to 2θ = 50° (Mo Kα radiation). Refinement of the complete structure converged with final discrepancy indices of R_1 = 0.065 and R_2 = 0.067 for 2891 independent, observed reflections. The dimeric complex molecule is centered along the crystallographic twofold axis of the space group and has approximate D_2 overall symmetry. The two Mo atoms are separated by 4.608 (2) Å, bridged by two reduced quinone ligands with each metal chelated by two additional ligands. The coordination geometry about the metals is octahedral. Bonding parameters of the bridging and chelating ligands are different. The Mo-O distances of the bridging ligands (1.853 (7), 1.869 (6) Å) are significantly shorter than distances of 1.938 (6) to 1.959 (6) Å for the chelated ligands. While the metals are contained within the chelate rings of these ligands, they are disposed above and below the planes of the bridging ligands resulting in a severely puckered $Mo_2O_4C_4$ ring. The dihedral angle between planes of the two bridging ligands is 70.6 (4)°. Intraligand O-O separations are unusually short (2.424 (8), 2.435 (9) Å) for the chelating ligands (2.756 (8) Å for bridging ligands). Selected interligand O-O separations are also short (2.418 (8), 2.445 (9) Å) suggesting weak interdonor bonding interactions. The benzene solvate molecules are located approximately parallel to the planes of chelating ligands and sandwiched between ligands with interplanar separations of 3.5 Å.

Steric and electrochemical properties of complexes containing ligands capable of forming unsaturated five-membered chelate rings have long been of interest. Complexes of the 1,2-dithiolene ligands have been among the most widely studied systems of this type. Single bis complexes of these ligands exist with charges ranging from neutral to −2 while tris(1,2-dithiolene) complexes are commonly found with charges of 0 to −3.[1] Extensive charge delocalization over the chelate ring appears responsible for the electrochemical diversity of these systems.[2] An intriguing stereochemical aspect of this work is the observed trigonal prismatic coordination of the more highly oxidized tris(1,2-dithiolene) complexes.[3] Extension of these studies to selenium analogs has indicated little change in ligand character with the larger chalcogen.[4,5] However, the change in donor atom from sulfur to oxygen might be expected to yield more drastic differences in both structural and chemical properties.

Synthetic approaches to the synthesis of oxygen donor complexes resembling the neutral bis- and tris(benzene-1,2-dithiolene) systems fall into two classes. Before the significance of the dithiolene work was understood, it was found that catechol reacted with various W(VI) species to form $W(O_2C_6H_4)_3$.[6] More recent work has extended this to other hydroquinones, and similar techniques have been used to generate such compounds as hexakis(phenolate)tungsten(VI).[7] A second approach which appears of more general utility for a variety of metals involves direct reaction of the *o*-benzoquinone form of the ligand with an appropriate metal carbonyl. Neutral binary complexes of Ni, Co, and Fe with tetrachloro-1,2-benzoquinone[8] and 9,10-phenanthrenequinone[9] have been formed by this procedure. We have recently reported the synthesis of neutral, tris(tetrachlorobenzoquinone) complexes of group 6 metals (eq 1).[10] The Cr complex of this series appears to be a simple monomeric molecule and undergoes three reversible oxidation steps to complexes with charges of +1, +2, and +3. These results suggest a stronger similarity to $Cr(dipy)_3$ reported by Herzog[11] than to related 1,2-dithiolene complexes where reduction would be expected. The Mo and W complexes are mutually similar but have spectral properties which are quite different from the Cr system. We present herein the determination of the crystal and molecular structure of the complex $Mo(O_2C_6Cl_4)_3$ isolated as a benzene solvate.



(1)

M = Cr, Mo, W

Experimental Section

Collection and Reduction of the X-Ray Data. A sample of the complex $Mo_2(O_2C_6Cl_4)_6$ was prepared by reflux of 12.3 g of tetrachloro-1,2-benzoquinone with 2.6 g of $Mo(CO)_6$ in benzene for 24 hr under an atmosphere of N_2. Crystals of the dark violet complex suitable for X-ray analysis were grown directly from the reaction mixture by slow evaporation of a portion of the solvent. Precession and Weissenberg photographs revealed monoclinic symmetry and contained extinctions of hkl, $h + k = 2n + 1$, and $h0l$, $l = 2n + 1$, consistent with space groups $C2/c$ and Cc.[12] A crystal of regular dimensions (0.23 × 0.21 × 0.33 mm) was mounted and aligned along the monoclinic axis on a Picker four-circle automated diffractometer. The angular settings of 18 strong, independent reflections centered using Mo Kα radiation (λ 0.7107 Å) were used to give refined lattice constants of a = 22.417 (4) Å, b = 11.592 (3) Å, c = 27.307 (4) Å, β = 106.44 (4)°, and V = 6873 Å^3. An experimental density of 1.836 (5) g cm^{-3} agrees with a calculated density of 1.837 g cm^{-3} for four dimeric molecules per unit cell. Thus, either twofold or $\bar{1}$ crystallographic symmetry is imposed on the dimer in $C2/c$. The mosaic spread of the crystal was determined using the narrow-source open-counter ω-scan technique[13] and was found acceptable at 0.06°. An independent set of intensity data was collected by the θ-2θ scan technique using the Mo Kα peak with a Zr filter and allowances for the Kα_1 − Kα_2 separation at higher 2θ values. The data set was collected within the angular range 4.5 ≤ 2θ ≤ 50°. Attenuators were inserted automatically if the count rate of the diffracted beam exceeded 9000 counts/sec during the scan. During data collection, the intensities of five standard reflections in different regions of reciprocal space were moni-

Table I. Final Structural Parameters for $Mo_2(O_2C_6Cl_4)_6 \cdot 3C_6H_6$

				Atomic Positional and Thermal Parameters					
Atom	x^a	y	z	$\beta_{11}{}^b$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	0.04443 (4)	0.23187 (8)	−0.16430 (3)	0.00177 (3)	0.00735 (9)	0.00139 (1)	−0.00063 (4)	0.00016 (1)	0.00010 (3)
O(1)	−0.0676 (3)	0.1914 (6)	−0.2774 (2)	0.0015 (2)	0.0078 (7)	0.0017 (1)	0.006 (3)	−0.0002 (1)	−0.0012 (3)
O(2)	−0.0221 (3)	0.3273 (5)	−0.1936 (2)	0.0020 (2)	0.0051 (6)	0.0014 (1)	−0.0003 (3)	0.0003 (1)	0.0003 (2)
C(1)	−0.1054 (4)	0.2344 (8)	−0.2498 (3)	0.0018 (3)	0.0064 (10)	0.0016 (2)	0.0000 (5)	0.0003 (2)	0.0006 (4)
C(2)	−0.1691 (5)	0.2055 (10)	−0.2633 (4)	0.0026 (4)	0.0101 (14)	0.0017 (2)	0.0005 (6)	0.0001 (2)	0.0006 (4)
C(3)	−0.2074 (4)	0.2513 (10)	−0.2357 (4)	0.0015 (3)	0.0145 (17)	0.0019 (2)	0.0000 (6)	0.0004 (2)	0.0012 (5)
C(4)	−0.1851 (5)	0.3140 (10)	−0.1951 (4)	0.0031 (4)	0.0118 (15)	0.0017 (2)	0.0023 (7)	0.0012 (3)	0.0011 (5)
C(5)	−0.1223 (5)	0.3446 (9)	−0.1805 (4)	0.0027 (4)	0.0105 (14)	0.0014 (2)	0.0003 (6)	0.0006 (2)	0.0001 (4)
C(6)	−0.0839 (5)	0.3035 (8)	−0.2090 (3)	0.0023 (3)	0.0056 (11)	0.0013 (2)	0.0009 (5)	0.0003 (2)	0.0006 (4)
Cl(1)	−0.1944 (1)	0.1167 (3)	−0.3137 (1)	0.0026 (1)	0.0187 (5)	0.0026 (1)	−0.0022 (2)	−0.0000 (1)	−0.0012 (2)
Cl(2)	−0.2843 (1)	0.2141 (4)	−0.2535 (1)	0.0017 (1)	0.0285 (7)	0.0031 (1)	0.0003 (2)	0.0004 (1)	0.0020 (2)
Cl(3)	−0.2324 (2)	0.3591 (4)	−0.1570 (1)	0.0036 (1)	0.0228 (6)	0.0033 (1)	0.0033 (2)	0.0017 (1)	0.0007 (2)
Cl(4)	−0.0920 (2)	0.4231 (3)	−0.1273 (1)	0.0045 (1)	0.0128 (4)	0.0029 (1)	0.0002 (2)	0.0013 (1)	−0.0016 (1)
O(3)	−0.0245 (3)	0.1308 (5)	−0.1646 (2)	0.0012 (2)	0.0045 (6)	0.0017 (1)	−0.0005 (3)	0.0001 (1)	0.0003 (2)
O(4)	0.0843 (3)	0.0939 (6)	−0.1299 (2)	0.0018 (2)	0.0077 (7)	0.0018 (1)	0.0001 (3)	0.0001 (1)	0.0005 (3)
C(7)	−0.0133 (4)	0.0249 (8)	−0.1458 (3)	0.0017 (3)	0.0061 (11)	0.0015 (2)	−0.0004 (5)	0.0004 (2)	0.0004 (4)
C(8)	−0.0547 (4)	−0.0599 (9)	−0.1455 (4)	0.0013 (3)	0.0066 (11)	0.0022 (2)	0.0003 (5)	0.0001 (2)	0.0010 (4)
C(9)	−0.0354 (5)	−0.1649 (9)	−0.1257 (4)	0.0019 (3)	0.0080 (12)	0.0021 (2)	−0.0012 (5)	0.0003 (2)	0.0008 (4)
C(10)	0.271 (5)	−0.1872 (9)	−0.1064 (4)	0.0030 (4)	0.0052 (11)	0.0021 (2)	0.0008 (5)	0.0005 (2)	0.0010 (4)
C(11)	0.0694 (5)	−0.1021 (9)	−0.1074 (4)	0.0021 (3)	0.0064 (11)	0.0018 (2)	0.0019 (5)	−0.0001 (2)	0.0012 (4)
C(12)	0.0503 (4)	0.0013 (9)	−0.1263 (3)	0.0018 (3)	0.0086 (12)	0.0014 (2)	−0.0003 (6)	0.0004 (2)	0.0002 (4)
Cl(5)	−0.1319 (1)	−0.0269 (3)	−0.1688 (1)	0.0017 (1)	0.0130 (4)	0.0043 (1)	−0.0006 (1)	0.0000 (1)	0.0025 (1)
Cl(6)	−0.0885 (2)	−0.2694 (3)	−0.1256 (1)	0.0036 (1)	0.0105 (3)	0.0036 (1)	−0.0018 (2)	0.0002 (1)	0.0022 (1)
Cl(7)	0.0503 (2)	−0.3180 (3)	−0.0828 (1)	0.0047 (1)	0.0085 (3)	0.0039 (1)	0.0019 (2)	0.0004 (1)	0.0022 (1)
Cl(8)	0.1472 (1)	−0.1253 (3)	−0.0836 (1)	0.0022 (1)	0.0156 (4)	0.0032 (1)	0.0017 (2)	0.0000 (1)	0.0017 (1)
O(5)	0.1127 (3)	0.3396 (5)	−0.1607 (2)	0.0019 (2)	0.0077 (7)	0.0013 (1)	−0.0010 (3)	0.0003 (1)	−0.0004 (2)
O(6)	0.0549 (3)	0.3009 (6)	−0.0979 (2)	0.0022 (2)	0.0087 (7)	0.0015 (1)	−0.0006 (3)	0.0006 (1)	0.0002 (2)
C(13)	0.1306 (4)	0.4009 (9)	−0.1193 (3)	0.0017 (3)	0.0081 (10)	0.0011 (2)	0.0011 (5)	0.0001 (2)	0.0001 (4)
C(14)	0.1788 (4)	0.4810 (9)	−0.1097 (4)	0.0015 (3)	0.0077 (11)	0.0018 (2)	−0.0004 (5)	0.0003 (2)	−0.0007 (4)
C(15)	0.1929 (4)	0.5321 (9)	−0.0641 (4)	0.0015 (3)	0.0072 (11)	0.0022 (2)	−0.0004 (5)	−0.0001 (2)	−0.0007 (4)
C(16)	0.1600 (5)	0.5134 (9)	−0.0271 (4)	0.0020 (3)	0.0083 (11)	0.0015 (2)	0.0003 (5)	−0.0003 (2)	−0.0005 (4)
C(17)	0.1134 (5)	0.4342 (9)	−0.0374 (3)	0.0020 (3)	0.0090 (11)	0.0012 (2)	0.0007 (5)	0.0002 (2)	0.0002 (4)
C(18)	0.0994 (4)	0.3817 (8)	−0.0832 (3)	0.0017 (3)	0.0065 (10)	0.0013 (2)	−0.0005 (4)	0.002 (2)	−0.0002 (4)
Cl(9)	0.2172 (1)	0.5022 (3)	−0.1559 (1)	0.0030 (1)	0.0167 (4)	0.0029 (1)	−0.0027 (2)	0.0014 (1)	−0.0009 (1)
Cl(10)	0.2537 (1)	0.6300 (3)	−0.0508 (1)	0.0024 (1)	0.0117 (3)	0.0033 (1)	−0.0022 (1)	−0.0001 (1)	−0.0011 (1)
Cl(11)	0.1793 (1)	0.5835 (3)	0.0292 (1)	0.0036 (1)	0.0141 (4)	0.0021 (1)	−0.0011 (2)	−0.0001 (1)	−0.0018 (1)
Cl(12)	0.0705 (1)	0.4091 (3)	0.0060 (1)	0.0036 (1)	0.0135 (4)	0.0017 (1)	−0.0006 (2)	0.0009 (1)	−0.0004 (1)

			Group Positional Parameters			
Group^c	x_c	y_c	z_c	ϕ	θ	φ
R1	0.2500	0.2500	0.0000	−0.890 (6)	2.703 (5)	1.768 (6)
R2	0.0000	0.0000	0.0000	−1.224 (7)	−3.173 (6)	0.394 (5)
R3	0.0000	0.2631 (9)	0.2500	−3.159 (9)	−3.187 (9)	2.918 (8)

[a] Estimated standard deviations of the least significant figures are given in parentheses here and in succeeding tables. [b] Anisotropic thermal parameters are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. [c] x_c, y_c, z_c are the fractional coordinates of the rigid group centers. The angles ϕ, θ, φ, are in radians and have previously been defined by R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 4, 773 (1965).

tored after every 100 reflections measured. None of the standards deviated from its mean value by more than 3% during the time required to collect the data. Data were processed in the usual way with values of I and $\sigma(I)$ corrected for Lorentz and polarization effects. Since the crystal was approximately equidimensional in shape and the linear absorption coefficient small (μ = 13.4 cm^{-1}), no correction was made for absorption effects. The intensities of a total of 6517 reflections were measured of which 2891 were observed to greater than 2σ and have been included in the refinement.

Solution and Refinement of the Structure. In initial stages of the refinement $C2/c$ was chosen as the space group. The position of the Mo atom was determined from a three-dimensional Patterson map and found to be near the twofold axis of the space group. Phases derived from the Mo atom were used to locate the chlorine atoms of the ligands and the Mo and Cl atoms together were used to determine the positions of all other atoms of the structure. The benzene solvate molecules were found centered at two $\bar{1}$ sites of the space group with a third located on the twofold axis. Isotropic refinement of all atoms with benzene solvate molecules treated as rigid groups (d(C–C) = 1.392 Å) with a single group thermal parameter gave discrepancy indices

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$$

and

$$R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2)^{1/2}$$

of 0.133 and 0.154, respectively. Further refinement with anisotropic thermal parameters for nongroup atoms and individual isotropic thermal parameters for atoms of the groups converged to R_1 = 0.065 and R_2 = 0.067. At the completion of the refinement, the standard deviation of an observation of unit weight was 1.74. During all cycles of refinement the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ and the weights, w, were taken as $4F_o^2/\sigma^2(F_o^2)$. The standard deviations $\sigma(F^2)$ were estimated from counting statistics described previously.[14] In all calculations the atomic scattering factors for the atoms were those of Cromer and Waber[15] with values of $\Delta f'$ and $\Delta f''$ for the Mo and Cl atoms taken from the report by Cromer and Liberman.[16] The final positional and thermal parameters of the structure are given in Table I. Derived positional and isotropic thermal parameters of the solvate atoms are given in Table II. Table III contains root-means-square vibrational amplitudes of atoms refined anisotropically. A table of the final F_o and $|F_c|$ values for the 2891 reflections used in the refinement is available.[17]

Discussion of the Structure

While related molybdenum complexes of sulfur and selenium donor ligands have been shown to possess monomeric, trigonal prismatic coordination geometries, $Mo(O_2C_6Cl_4)_3$ is dimeric. The molecule contains both chelating and bridging quinone ligands with octahedral coordination geometries for the metal atoms. A full stereoview of the molecule

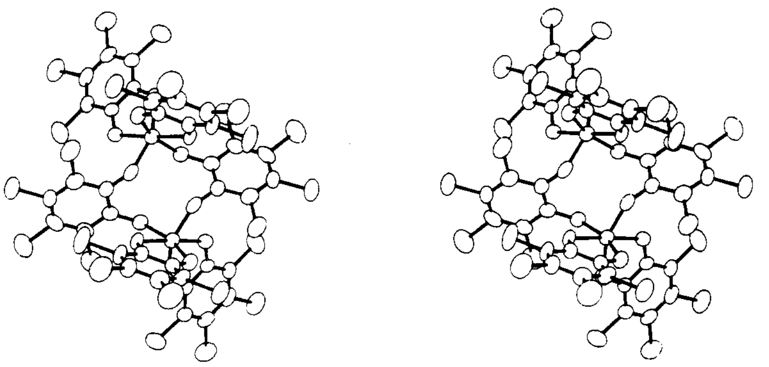


Figure 1. Stereoview of the $Mo_2(O_2C_6Cl_4)_6$ dimer. The view is approximately down the crystallographic twofold axis of the molecule.

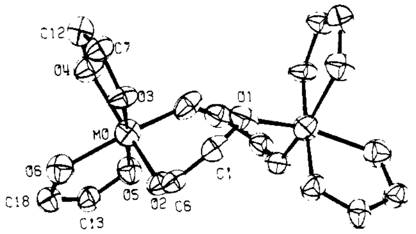


Figure 2. View of the inner coordination geometry of the $Mo_2(C_2C_6Cl_4)_6$ molecule. The dihedral angle between planes of bridging ligands is 70.6 (4)°.

Table II. Derived Positional and Isotropic Thermal Parameters for Group Carbon Atoms

Atom	x	y	z	B, Å^2
		Ring R1		
C1	0.2622 (9)	0.2973 (13)	0.0475 (8)	8.7 (5)
C2	0.2168 (8)	0.2132 (13)	0.0343 (8)	10.1 (6)
C3	0.2949 (8)	0.3317 (13)	0.0128 (9)	8.3 (5)
		Ring R2		
C1	0.0238 (8)	−0.1038 (13)	0.0229 (9)	11.0 (6)
C2	−0.0388 (9)	−0.0872 (14)	0.0017 (9)	8.9 (5)
C3	0.0655 (9)	−0.0166 (13)	0.0203 (9)	10.8 (6)
		Ring R3		
C1	0.0617 (9)	0.2599 (14)	0.2730 (9)	11.8 (6)
C2	0.0314 (10)	0.3653 (14)	0.2631 (10)	16.3 (7)
C3	0.0295 (9)	0.1577 (14)	0.2587 (9)	12.2 (7)

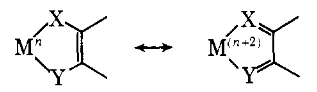
Table III. Root-Mean-Square Amplitudes of Vibration for $Mo_2(O_2C_6Cl_4)_6$

Atom	Min, Å	Intermed, Å	Max, Å
Mo	0.191 (1)	0.219 (1)	0.246 (1)
O(1)	0.172 (10)	0.199 (10)	0.300 (11)
O(2)	0.181 (10)	0.211 (11)	0.239 (10)
C(1)	0.194 (14)	0.208 (15)	0.252 (16)
C(2)	0.218 (13)	0.269 (16)	0.276 (16)
C(3)	0.188 (14)	0.242 (16)	0.329 (18)
C(4)	0.196 (14)	0.230 (15)	0.336 (17)
C(5)	0.219 (13)	0.252 (15)	0.271 (16)
C(6)	0.169 (14)	0.225 (15)	0.248 (16)
Cl(1)	0.212 (4)	0.330 (5)	0.373 (6)
Cl(2)	0.204 (4)	0.320 (5)	0.453 (6)
Cl(3)	0.230 (4)	0.340 (5)	0.421 (6)
Cl(4)	0.248 (5)	0.327 (4)	0.346 (5)
O(3)	0.154 (10)	0.186 (10)	0.260 (11)
O(4)	0.200 (10)	0.226 (11)	0.268 (11)
C(7)	0.186 (13)	0.210 (15)	0.240 (16)
C(8)	0.167 (13)	0.206 (14)	0.303 (17)
C(9)	0.181 (14)	0.237 (15)	0.299 (16)
C(10)	0.169 (14)	0.271 (15)	0.282 (16)
C(11)	0.122 (14)	0.264 (16)	0.288 (16)
C(12)	0.205 (14)	0.218 (14)	0.247 (16)
Cl(5)	0.197 (4)	0.265 (5)	0.429 (6)
Cl(6)	0.215 (5)	0.292 (5)	0.407 (6)
Cl(7)	0.197 (5)	0.346 (6)	0.401 (6)
Cl(8)	0.199 (4)	0.322 (5)	0.372 (5)
O(5)	0.187 (10)	0.217 (11)	0.249 (11)
O(6)	0.209 (10)	0.237 (11)	0.255 (11)
C(13)	0.171 (14)	0.208 (14)	0.254 (16)
C(14)	0.183 (14)	0.222 (15)	0.268 (16)
C(15)	0.174 (13)	0.224 (15)	0.301 (16)
C(16)	0.182 (14)	0.232 (15)	0.287 (16)
C(17)	0.198 (14)	0.227 (15)	0.258 (16)
C(18)	0.184 (14)	0.219 (15)	0.225 (15)
Cl(9)	0.213 (4)	0.307 (5)	0.375 (6)
Cl(10)	0.184 (4)	0.313 (5)	0.366 (6)
Cl(11)	0.215 (4)	0.323 (6)	0.346 (6)
Cl(12)	0.236 (5)	0.284 (5)	0.314 (6)

is shown in Figure 1 with a view of the inner coordination geometry in Figure 2. Pertinent bond distances and angles are presented in Table IV.

The dimer is centered on the crystallographic twofold axis of the space group and is required to have C_2 symmetry. Molybdenum atoms are 4.608 (2) Å apart and are located well above and below the least-squares planes of the bridging ligands (Table V). The result is a severely puckered $Mo_2O_4C_4$ ring and approximate D_2 symmetry for the dimer.

Bridging and Terminal Quinone Ligands. Studies on a large number of complexes with ligands which form symmetrical five-membered chelate rings have indicated significant change delocalization over both ligand and metal. Systems studied most extensively are those with either sulfur or nitrogen as the donor atom (I).[1,2] Metal–ligand delocalization results in strong ligand bonding to the metal and, structurally, short metal-donor distances.[3] This is particularly true of the more highly oxidized complexes where distances are significantly shorter than those of ligands which form even-membered chelate rings. It is, therefore, surprising that the Mo–O distances of the *bridging* ligands in $Mo_2(O_2C_6Cl_4)_6$ are significantly shorter (1.86 (1) Å) than those of the chelated ligands (1.95 (1) Å) and are among the shortest Mo–O distances reported for a polyatomic ligand.[18] Generally Mo–O distances for oxygen donor ligands are greater than 2.00 Å for Mo(VI) complexes.[19]



(X or Y = NH, S)

I

Bonding parameters within the bridging and chelating ligands are quite different. Intraligand oxygen–oxygen separations vary significantly for the two. Bites of the chelating ligands are 2.428 (8) and 2.435 (9) Å while the O–O separation of the bridging ligand is 2.756 (8) Å on the order of values found for 1,3-diketonate ligands. Angles about the carbonyl ring carbon atoms indicate apparent contraction

Table IV. Principle Intramolecular Bonding Parameters for $Mo_2(O_2C_6Cl_4)_6$

	Bridging Ligand Distances (Å)		
Mo–O(1)	1.853 (7)[a]	C(4)–C(5)	1.41 (1)
Mo–O(2)	1.869 (6)	C(5)–C(6)	1.38 (1)
O(1)–C(1)	1.36 (1)	C(6)–C(1)	1.36 (1)
O(2)–C(6)	1.37 (1)	Cl(1)–C(2)	1.70 (1)
C(1)–C(2)	1.42 (1)	Cl(2)–C(3)	1.73 (1)
C(2)–C(3)	1.38 (1)	Cl(3)–C(4)	1.74 (1)
C(3)–C(4)	1.32 (1)	Cl(4)–C(5)	1.71 (1)
	Angles (deg)		
Mo'–O(1)–C(1)	136.8 (6)	O(1)–C(1)–C(6)	121.9 (9)
Mo–O(2)–C(6)	130.4 (6)	O(2)–C(6)–C(5)	118.9 (9)
O(1)–C(1)–C(2)	119.6 (9)	O(2)–C(6)–C(1)	119.5 (9)
	Chelated Ligand I Distances (Å)		
Mo–O(3)	1.938 (6)	C(10)–C(11)	1.37 (1)
Mo–O(4)	1.955 (6)	C(11)–C(12)	1.33 (1)
O(3)–C(7)	1.33 (1)	C(12)–C(7)	1.42 (1)
O(4)–C(12)	1.33 (1)	Cl(5)–C(8)	1.73 (1)
C(7)–C(8)	1.35 (1)	Cl(6)–C(9)	1.70 (1)
C(8)–C(9)	1.36 (1)	Cl(7)–C(10)	1.68 (1)
C(9)–C(10)	1.39 (1)	Cl(8)–C(11)	1.72 (1)
	Angles (deg)		
Mo–O(3)–C(7)	118.8 (6)	O(3)–C(7)–C(12)	113.5 (8)
Mo–O(4)–C(12)	119.5 (6)	O(4)–C(12)–C(11)	128.1 (9)
O(3)–C(7)–C(8)	127.4 (9)	O(4)–C(12)–C(7)	111.0 (9)
	Chelated Ligand II Distances (Å)		
Mo–O(5)	1.959 (6)	C(16)–C(17)	1.37 (1)
Mo–O(6)	1.942 (6)	C(17)–C(18)	1.36 (1)
O(5)–C(13)	1.32 (1)	C(18)–C(13)	1.36 (1)
O(6)–C(18)	1.34 (1)	Cl(9)–C(14)	1.71 (1)
C(13)–C(14)	1.40 (1)	Cl(10)–C(15)	1.74 (1)
C(14)–C(15)	1.34 (1)	Cl(11)–C(16)	1.70 (1)
C(15)–C(16)	1.41 (1)	Cl(12)–C(17)	1.73 (1)
	Angles (deg)		
Mo–O(5)–C(13)	117.2 (6)	O(5)–C(13)–C(18)	115.6 (9)
Mo–O(6)–C(18)	118.0 (6)	O(6)–C(18)–C(17)	124.6 (9)
O(5)–C(13)–C(14)	125.3 (9)	O(6)–C(18)–C(13)	111.9 (8)
	Interdonor Contacts and Angles about Mo Atom Distances (Å)		
O(1)' ··· O(2)	2.756 (8)	O(3) ··· O(4)	2.424 (8)
O(1)' ··· O(3)	2.982 (9)	O(3) ··· O(6)	2.959 (8)
O(1)' ··· O(4)	2.712 (8)	O(4) ··· O(5)	3.082 (9)
O(1)' ··· O(5)	2.445 (9)	O(4) ··· O(6)	2.692 (9)
O(2) ··· O(3)	2.418 (8)	O(5) ··· O(6)	2.435 (9)
O(2) ··· O(5)	2.932 (8)	Mo ··· Mo'	4.608 (2)
O(2) ··· O(6)	2.767 (8)		
	Angles (deg)		
O(1)–Mo–O(2)	98.4 (3)	O(2)–Mo–O(6)	93.1 (3)
O(1)–Mo–O(3)	103.7 (3)	O(3)–Mo–O(4)	77.0 (3)
O(1)–Mo–O(4)	90.8 (3)	O(3)–Mo–O(5)	176.4 (3)
O(1)–Mo–O(5)	79.7 (3)	O(3)–Mo–O(6)	99.4 (3)
O(1)–Mo–O(6)	155.7 (3)	O(4)–Mo–O(5)	103.9 (2)
O(2)–Mo–O(3)	78.8 (3)	O(4)–Mo–O(6)	87.4 (3)
O(2)–Mo–O(4)	155.6 (3)	O(5)–Mo–O(6)	77.2 (3)
O(2)–Mo–O(5)	100.0 (3)		

[a] Prime symbol refers to atoms of the dimer related to those in Table I by the crystallographic twofold rotation of the space group.

Table V. Dihedral Angles and Least-Squares Planes for $Mo_2(O_2C_6Cl_4)_6$

Plane 1	Dihedral Angles Plane (2)	Angle (deg)
O(1), O(2), C(1)	O(1)', O(2)', C(1)'	70.6 (4)
Mo, O(1), O(2)	Mo', O(1)', O(2)'	121.2 (5)

Atom	Distance (Å)	Atom	Distance (Å)
	Least-Squares Planes[a, b]		
	Bridging Ligand $0.83x - 9.41y + 15.17z = 6.09$		
Mo	−1.45	C(4)	−0.02 (1)
Mo	1.23	C(5)	0.00 (1)
O(1)	−0.02	C(6)	0.01 (1)
O(2)	−0.05	Cl(1)	−0.07
C(1)	0.00 (1)	Cl(2)	0.01
C(2)	−0.02 (1)	Cl(3)	−0.13
C(3)	0.03 (1)	Cl(4)	−0.02
	Chelated Ligand I $6.73x - 3.55y - 25.93z = -3.61$		
Mo	−0.13	C(11)	0.00 (1)
O(3)	−0.03	C(12)	0.00 (1)
O(4)	0.01	Cl(5)	0.02
C(7)	0.01 (1)	Cl(6)	−0.01
C(8)	−0.01 (1)	Cl(7)	0.00
C(9)	0.00 (1)	Cl(8)	0.01
C(10)	0.00 (1)		
	Chelated Ligand II $12.63x - 8.52y + 6.16z = -2.50$		
Mo	−0.08	C(17)	−0.01 (1)
O(5)	−0.04	C(18)	0.00 (1)
O(6)	−0.03	Cl(9)	−0.01
C(13)	0.00 (1)	Cl(10)	−0.03
C(14)	0.01 (1)	Cl(11)	0.02
C(15)	−0.01 (1)	Cl(12)	0.05
C(16)	0.01 (1)		

[a] Least-squares planes calculated according to W. C. Hamilton, *Acta Crystallgr.*, **14**, 185 (1961). Equations are given in monoclinic coordinates. [b] Atoms listed without errors were not included in the calculation of the plane.

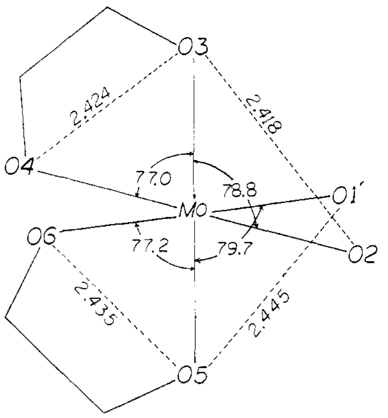
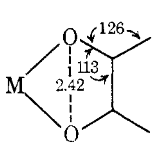


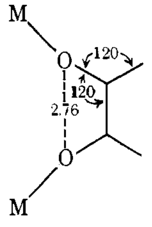
Figure 3. Drawing of the MoO_6 octahedron pointing out short interdonor contacts and contracted O-Mo-O angles.

of the bite of the chelated ligand. The inner and outer O–C–C angles of the bridging ligand show no significant variation from 120° while the outer angles of the chelating ligands are 127.4 (9), 128.1 (9), 125.3 (9), and 124.6 (9)° with interior angles of the chelate ring of 113.5 (8), 111.0 (9), 115.6 (9), and 111.9 (8)°.

Orientation of the metals 1.23 Å above and 1.45 Å below the bridging ligand plane is consistent with the hydroquinone character of the C–O distances (1.36 (1) Å) with approximate sp^3 hybridization for the oxygens.



chelating



bridging

Intramolecular Oxygen–Oxygen Contacts. Structural studies on neutral tris(1,2-dithiolene) complexes have led to

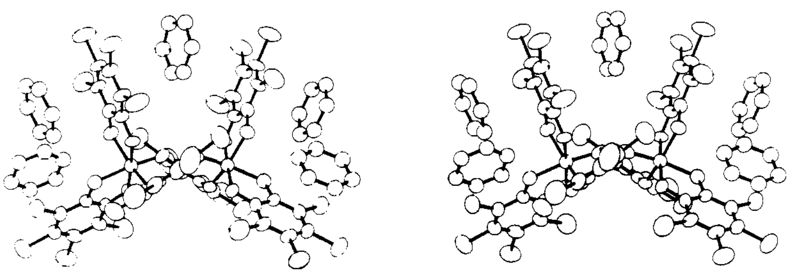
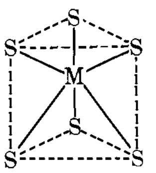


Figure 4. Stereoview of $Mo_2(O_2C_6Cl_4)_6 \cdot 3C_6H_6$ including solvent molecules. Benzenes on the right and left sides of the view are related by crystallographic twofold symmetry. The ring at the upper center is located along the twofold axis with outer C_6H_6 molecules at crystallographic centers of inversion.

the conclusion that interligand S–S bonding, although weak, contributes significantly to the stabilization of the unusual trigonal prismatic geometry.



Intraligand and interligand S–S contacts are roughly equivalent (3.05 Å) and independent of the size of the central metal atom. Thus, complexes of metals with different radii (V, Re) are observed to have equivalent M–S distances (2.33 Å).[3] While the intraligand O–O separations of the chelated ligands are unusually short in $Mo_2(O_2C_6Cl_4)_6$ the shortest interdonor contact on the MoO_6 octahedron (Figure 3) occurs between O(2) and O(3) with a value of 2.418 (8) Å. The related contact between O(1)′ and O(5) is similarly short, 2.445 (9) Å, comparable to the intraligand O–O separations. Oxygens O(3) and O(5) are mutually trans (O(3)-Mo-O(5) = 176.4 (3)°) and may be used to define perpendicular planes O(2), O(3), O(4) and O(1)′, O(5), O(6). In both instances the outer atoms of the plane O(2), O(4) and O(1)′, O(6) are drawn up toward the central atoms O(3) and O(5) forming trans angles of 155.6 (3) and 155.7 (3)°. Angles at the metal formed by the chelating ligands are 77.0 (3) and 77.2 (3)° while O(1)′-Mo-O(5) and O(2)-Mo-O(3) have surprisingly comparable values of 79.7 (3) and 78.8 (3)°. Since there are no intra- or intermolecular restrictions to result in these short interligand contacts, these separations appear to result from bonding between oxygen donor atoms.

Clathrate Solvate Structure. Crystals of $Mo_2(O_2C_6Cl_4)_6$ used in this study were isolated from a benzene solution and were found to contain three independent half C_6H_6 molecules per asymmetric unit or three complete molecules per dimeric complex molecule. Two of the molecules are located at crystallographic centers of inversion with the third along the twofold axis of the space group (Figure 4). The two rings at the centers of inversion are parallel with chelating ligands located 3.47 and 3.54 Å from the ligand planes. Additionally, ligands of adjacent molecules related by the centers of inversion are located on the opposite sides of the solvate rings resulting in a sandwich, clathrate structure for the benzene. Thus, each complex molecule is linked to four adjacent molecules through benzene solvate bridges, resulting in formation of a two-dimensional polymeric array. The solvent molecule along the twofold axis is positioned interstitially between two chelating ligands of the dimer with the closest contact to these ligands of 3.47 Å. Hydroquinones are well known for their ability to form charge-transfer complexes and the benzene-ligand separations observed are within the range of values observed for weak complexes between hydroquinones and quinoid molecules.[20] Compounds of this type, particularly situations where transition metal complexes are linked by such interactions, have long been of interest for their conductive properties.[21]

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th Street, N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number JACS-75-2123.

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