(44) Several heme proteins such as metmyoglobin hydroxide and methemo-
globin hydroxide (and other derivatives) contain spin equilibrium Fe(III), but
it is not certain whether or not a change in coordination number from six
to five is also involved. See for example: J. K. Beattie and R. J. West, *J.
Am. Chem. Soc.*, **96**, 1933 (1974). In this work, the high-spin and low-spin

"states" of a metmyoglobin hydroxide are reported to have spin lifetimes
of <5 μs.
(45) M. J. Tricker, *J. Nucl. Chem.*, **36**, 1543 (1974).
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for publication.

Coordination Properties of o-Benzoquinones. Structure and Bonding in Tris(tetrachloro-1,2-benzoquinone)chromium(0)

Cortlandt G. Pierpont*[1] and Hartley H. Downs

Contribution from the Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506. Received August 28, 1975

Abstract: Addition of tetrachloro-1,2-benzoquinone to $Cr(CO)_6$ leads to formation of tris(tetrachloro-1,2-benzoquinone)chromium. Crystals of the complex prepared in benzene and recrystallized from CS_2 are isolated as the mixed solvate $Cr(O_2C_6Cl_4)_3 \cdot CS_2 \cdot \frac{1}{2}C_6H_6$. They crystallize in a triclinic cell, space group $P\bar{1}$ with $a = 7.904$ (3) Å, $b = 16.192$ (4) Å, $c = 13.848$ (4) Å, $\alpha = 101.27$ (4)°, $\beta = 82.78$ (4)°, and $\gamma = 126.68$ (4)°. There are two formula weights per unit cell. The structure was solved by conventional Patterson, Fourier, and least-squares procedures using x-ray data complete to $2\theta = 50°$ (Mo $K\alpha$ radiation). Refinement of the structure converged with final discrepancy indices of $R = 0.045$ and $R_w = 0.044$ for 2237 observed reflections. The coordination geometry of $Cr(O_2C_6Cl_4)_3$ is octahedral. Structural features of the ligands indicate that they remain unreduced on coordination, bonding to the Cr(0) metal center as benzoquinones. The cationic Cr(I) complex $Cr(O_2C_6Cl_4)_3^+$ exhibits an ESR spectrum with an unusually low g value of 1.969 (1) and strong ^{53}Cr coupling of 27.5 (5) G. The properties of these complexes suggest a highly localized electronic structure with little contribution from quinone π^* levels.

The 1,2-benzoquinones appear to be an unusually diverse series of ligands. Investigations carried out on molybdenum–quinone complexes have provided examples where the ligands bond in various electronic forms, formally as catecholates, semiquinone radical-anions, or as unreduced benzoquinones. While charge delocalization over the chelate ring is possible, similar to the related 1,2-dithiolene ligands, specific structural features have provided information regarding metal and ligand oxidation states. In the coordination chemistry of molybdenum, cis-dioxo ligands are characteristic of Mo(VI). Thus 9,10-phenanthrenequinone ligands in $Mo_2O_5(O_2C_{14}H_8)_2^2$ and $MoO_2Cl_2(O_2C_{14}H_8)^3$ bond as semiquinone and benzoquinone ligands, respectively. Bridging tetrachloro-1,2-benzoquinone ligands in $[Mo(O_2C_6Cl_4)_3]_2$ possess features consistent with catecholate coordination.[4] The electronic diversity of the molybdenum–quinone system relates to the natural selection of Mo in specific biological electron transfer systems involving the quinoid flavins.[5]

Synthetically, complexes of 1,2-benzoquinones may be formed by addition of the ligand to a complex containing the desired metal in a low oxidation state. Oxidative addition reactions have been used to synthesize catecholate adducts of group 8 metal systems.[6] Others have examined the direct reaction of quinones with metal carbonyls as a means of preparing binary quinone complexes.[7] We have reported the addition of tetrachloro-1,2-benzoquinone to the carbonyls of group 6a metals yielding tris complexes (eq 1).[8] The Mo and

W complexes of this series have been found to be dimeric with bridging and chelating quinone ligands.[4] The geometries are octahedral, and ligand reduction occurs on coordination. The Cr complex is considerably different. From spectral and electrochemical data the complex appears monomeric, undergoing three reversible oxidation reactions to complexes with charges of +1, +2, and +3. Recent results obtained from the addition of tetrachlorocatecholate to Cr(III) salts suggest an analogous series of anionic compounds, as well.[9] In view of the unusual molecular geometry of $[Mo(O_2C_6Cl_4)_3]_2$, the apparent differences between this complex and its Cr analogue, and the trigonal prismatic structure of the 9,10-phenanthrenequinone complex $Mo(O_2C_{14}H_8)_3$,[10] we have undertaken a crystallographic molecular structure determination on $Cr(O_2C_6Cl_4)_3$. We wish to report the results of that investigation with some pertinent paramagnetic resonance data on the related cationic complex $Cr(O_2C_6Cl_4)_3^+$ generated synthetically.

Experimental Section

Preparation of $Cr(O_2C_6Cl_4)_3$. The complex was prepared by refluxing 6.1 g of tetrachloro-1,2-benzoquinone (25 mmol) with 1.1 g of $Cr(CO)_6$ (5 mmol) in benzene for 12 h. The dark red complex was filtered from the mixture and washed with cold benzene. It is air stable and when isolated from benzene solution contains four solvent molecules per molecule of complex, $Cr(O_2C_6Cl_4)_3 \cdot 4C_6H_6$. Crystals of $Cr(O_2C_6Cl_4)_3$ suitable for crystallographic work were grown by recrystallization from a saturated carbon disulfide solution. By this procedure solvated samples of stoichiometry $Cr(O_2C_6Cl_4)_3 \cdot CS_2 \cdot \frac{1}{2}C_6H_6$ were obtained and used in the x-ray investigation.

The cationic complex $[Cr(O_2C_6Cl_4)_3](SbF_6)$ was prepared by addition of a slight molar excess of $AgSbF_6$ in methylene chloride to a similar solution of $Cr(O_2C_6Cl_4)_3$. After a few minutes a gray precipitate of silver metal formed and was separated from the solution by filtration. The complex is lighter in color than the neutral species (orange-red). The ESR spectra of $[Cr(O_2C_6Cl_4)_3](SbF_6)$ were recorded on a Varian E-3 spectrometer. Room temperature spectra were
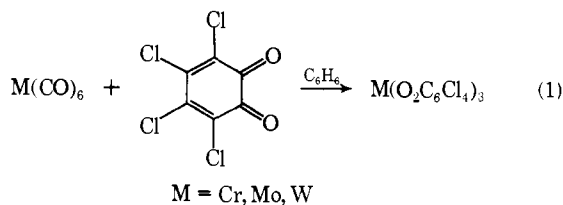

$$M(CO)_6 + \text{(tetrachloro-1,2-benzoquinone)} \xrightarrow{C_6H_6} M(O_2C_6Cl_4)_3 \quad (1)$$

M = Cr, Mo, W

Table I. Final Structural Parameters for $Cr(O_2C_6Cl_4)_3 \cdot CS_2 \cdot \frac{1}{2}C_6H_6$.

Atomic Positional and Thermal Parameters

Atom	x^a	y	z	$\beta_{11}{}^b$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr	0.0049 (2)	0.2148 (1)	−0.2218 (1)	0.0198 (2)	0.0040 (1)	0.0046 (1)	0.0039 (1)	−0.0013 (1)	0.0001 (1)
O(1)	0.1854 (7)	0.1782 (4)	−0.1809 (4)	0.0180 (6)	0.0040 (5)	0.0052 (4)	0.0046 (5)	−0.0025 (6)	0.0000 (4)
O(2)	−0.1641 (7)	0.0834 (4)	−0.2179 (4)	0.0182 (7)	0.0034 (5)	0.0044 (5)	0.0037 (5)	−0.0023 (5)	0.0001 (4)
C(1)	0.1069 (12)	0.0931 (6)	−0.1633 (5)	0.0223 (10)	0.0034 (6)	0.0029 (7)	0.0047 (6)	−0.0016 (7)	0.0001 (6)
C(2)	0.2046 (12)	0.0518 (6)	−0.1267 (6)	0.0189 (11)	0.0054 (6)	0.0033 (6)	0.0051 (7)	0.0019 (5)	0.0001 (6)
C(3)	0.1085 (13)	−0.0381 (6)	−0.1066 (6)	0.0253 (11)	0.0041 (7)	0.0039 (6)	0.0055 (6)	0.0009 (5)	0.0003 (5)
C(4)	−0.0866 (13)	−0.0919 (6)	−0.1291 (6)	0.0207 (13)	0.0033 (6)	0.0049 (7)	0.0023 (6)	0.0030 (7)	0.0000 (5)
C(5)	−0.1803 (12)	−0.0522 (6)	−0.1694 (6)	0.0141 (11)	0.0045 (7)	0.0046 (6)	0.0030 (7)	−0.0001 (5)	−0.0008 (5)
C(6)	−0.0867 (11)	0.0405 (6)	−0.1855 (5)	0.0155 (12)	0.0036 (5)	0.0024 (6)	0.0017 (6)	0.0005 (6)	−0.0002 (5)
Cl(1)	0.4429 (3)	0.1188 (2)	−0.1033 (2)	0.0203 (5)	0.0058 (4)	0.0080 (3)	0.0051 (4)	−0.0017 (4)	0.0006 (5)
Cl(2)	0.2181 (4)	−0.0864 (2)	−0.0540 (2)	0.0378 (5)	0.0071 (4)	0.0063 (4)	0.0113 (4)	0.0004 (3)	0.0013 (3)
Cl(3)	−0.2003 (4)	−0.2044 (2)	−0.1071 (2)	0.0348 (4)	0.0042 (3)	0.0085 (4)	0.0048 (4)	0.0040 (3)	0.0018 (4)
Cl(4)	−0.4116 (3)	−0.1169 (2)	−0.2004 (2)	0.0208 (5)	0.0048 (4)	0.0093 (4)	0.0021 (3)	−0.0007 (3)	−0.0002 (3)
O(3)	0.0594 (8)	0.1921 (4)	−0.3638 (4)	0.0193 (7)	0.0042 (6)	0.0045 (4)	0.0045 (5)	−0.0003 (5)	0.0003 (4)
O(4)	−0.1800 (7)	0.2443 (4)	−0.2677 (4)	0.0203 (7)	0.0035 (5)	0.0037 (4)	0.0036 (5)	−0.0016 (6)	0.0000 (5)
C(7)	−0.0404 (11)	0.2084 (6)	−0.4159 (6)	0.0138 (11)	0.0037 (7)	0.0057 (5)	0.0034 (6)	−0.0008 (6)	0.0001 (5)
C(8)	−0.0309 (12)	0.1985 (6)	−0.5203 (6)	0.0201 (10)	0.0053 (6)	0.0040 (6)	0.0052 (7)	−0.0000 (5)	−0.0002 (5)
C(9)	−0.1377 (12)	0.2208 (6)	−0.5671 (6)	0.0203 (10)	0.0054 (6)	0.0038 (6)	0.0038 (7)	−0.0019 (5)	0.0004 (4)
C(10)	−0.2643 (12)	0.2562 (6)	−0.5126 (7)	0.0202 (12)	0.0058 (7)	0.0057 (5)	0.0048 (8)	−0.0039 (7)	0.0006 (5)
C(11)	−0.2859 (11)	0.2617 (6)	−0.4122 (6)	0.0146 (11)	0.0043 (7)	0.0047 (4)	0.0031 (6)	−0.0006 (6)	−0.0005 (6)
C(12)	−0.1752 (11)	0.2398 (6)	−0.3602 (6)	0.0124 (11)	0.0039 (7)	0.0046 (4)	0.0032 (7)	−0.0020 (6)	0.0003 (5)
Cl(5)	0.1227 (4)	0.1559 (2)	−0.5820 (2)	0.0365 (56)	0.0143 (5)	0.0063 (4)	0.0160 (3)	0.0009 (4)	−0.0009 (4)
Cl(6)	−0.1282 (4)	0.2091 (2)	−0.6919 (2)	0.0427 (5)	0.0134 (4)	0.0043 (3)	0.0125 (4)	−0.0011 (5)	0.0010 (4)
Cl(7)	−0.3938 (4)	0.2877 (2)	−0.5756 (2)	0.0366 (5)	0.0099 (4)	0.0072 (4)	0.0100 (3)	−0.0057 (5)	0.0008 (4)
Cl(8)	−0.4504 (3)	0.2950 (2)	−0.3455 (2)	0.0247 (5)	0.0078 (4)	0.0069 (4)	0.0084 (4)	−0.0019 (4)	−0.0003 (4)
O(5)	0.1944 (7)	0.3451 (4)	−0.2049 (4)	0.0185 (7)	0.0035 (5)	0.0047 (5)	0.0024 (6)	−0.0008 (5)	0.0007 (5)
O(6)	−0.0670 (7)	0.2512 (4)	−0.0857 (4)	0.0204 (8)	0.0034 (5)	0.0039 (4)	0.0026 (4)	−0.0008 (5)	0.0004 (4)
C(13)	0.1836 (12)	0.3890 (6)	−0.1175 (6)	0.0193 (11)	0.0034 (6)	0.0056 (8)	0.0039 (6)	−0.0029 (6)	0.0000 (5)
C(14)	0.3112 (12)	0.4844 (6)	−0.0853 (7)	0.0199 (13)	0.0035 (7)	0.0072 (7)	0.0025 (6)	−0.0036 (8)	0.0008 (6)
C(15)	0.2814 (12)	0.5243 (6)	0.0098 (7)	0.0226 (12)	0.0030 (7)	0.0069 (6)	0.0025 (6)	−0.0065 (7)	−0.0004 (6)
C(16)	0.1282 (13)	0.4731 (6)	0.0731 (6)	0.0248 (12)	0.0039 (6)	0.0051 (7)	0.0057 (7)	−0.0035 (6)	−0.0005 (5)
C(17)	0.0080 (12)	0.3825 (6)	0.0450 (6)	0.0224 (11)	0.0040 (8)	0.0040 (7)	0.0056 (6)	−0.0010 (6)	0.0003 (7)
C(18)	0.0358 (11)	0.3374 (6)	−0.0509 (6)	0.0162 (12)	0.0037 (7)	0.0046 (6)	0.0032 (7)	−0.0008 (7)	0.0013 (5)
Cl(9)	0.4882 (3)	0.5431 (2)	−0.1639 (2)	0.0238 (5)	0.0053 (9)	0.0087 (5)	0.0022 (4)	−0.0009 (5)	0.0019 (4)
Cl(10)	0.4326 (4)	0.6385 (2)	0.0521 (2)	0.0330 (6)	0.0038 (4)	0.0099 (4)	0.0032 (4)	−0.0079 (4)	−0.0015 (4)
Cl(11)	0.0988 (4)	0.5284 (2)	0.1878 (2)	0.0400 (5)	0.0069 (4)	0.0064 (4)	0.0097 (5)	−0.0048 (5)	−0.0024 (5)
Cl(12)	−0.1763 (4)	0.3185 (2)	0.1174 (2)	0.0336 (5)	0.0058 (5)	0.0055 (4)	0.0072 (5)	0.0013 (4)	0.0009 (4)

CS$_2$ Solvate

Atom	x^a	y	z	$\beta_{11}{}^b$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(19)	0.2315 (24)	0.4545 (11)	−0.5021 (9)	0.1192 (25)	0.0125 (16)	0.0087 (14)	0.0052 (17)	−0.0223 (13)	0.0056 (10)
S(1)	0.2666 (7)	0.4470 (3)	−0.4041 (3)	0.0865 (8)	0.0142 (8)	0.0161 (7)	0.0044 (8)	−0.0098 (9)	0.0040 (7)
S(2)	0.1728 (9)	0.4577 (5)	−0.6004 (4)	0.1056 (10)	0.0200 (8)	0.0217 (8)	−0.0019 (9)	−0.0161 (10)	0.0090 (8)

Hemibenzene Solvate

Atom	x^a	y	z	$\beta_{11}{}^b$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(20)	0.3901 (20)	0.0153 (9)	−0.5608 (12)	0.0447 (24)	0.0076 (14)	0.0126 (11)	0.0008 (12)	−0.0076 (13)	0.0014 (11)
C(21)	0.4857 (22)	0.0185 (9)	−0.3973 (10)	0.0482 (26)	0.0066 (16)	0.0135 (13)	0.0030 (14)	−0.0057 (11)	−0.0005 (10)
C(22)	0.3711 (18)	0.0368 (9)	−0.4536 (14)	0.0382 (21)	0.0066 (17)	0.0222 (13)	0.0013 (11)	−0.0052 (11)	0.0025 (11)

^{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 $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

obtained in methylene chloride solution; glass spectra recorded at liquid nitrogen temperature were taken in CH_2Cl_2-ethylene glycol and CH_2Cl_2-1-propanol solutions.

Collection of X-Ray Data. Precession and Weissenberg photographs taken on crystals of $Cr(O_2C_6Cl_4)_3 \cdot CS_2 \cdot \frac{1}{2}C_6H_6$ indicated triclinic symmetry. A crystal of dimensions 0.23 × 0.21 × 0.33 mm was mounted along the a^* axis and aligned on a Picker four-circle automated diffractometer. The angular settings of 18 strong, independent reflections, centered using Mo $K\alpha$ radiation (λ 0.7107 Å), gave a cell of refined lattice parameters $a = 7.904$ (3) Å, $b = 16.192$ (4) Å, $c = 13.848$ (4) Å, $\alpha = 101.27$ (4)°, $\beta = 82.78$ (4)°, $\gamma = 126.68$ (4)°, and $V = 1552$ Å^3. An experimental density of 1.95 (1) g/cm^3 agrees with a calculated value of 1.937 g/cm^3 for two formula weights of $Cr(O_2C_6Cl_4)_3 \cdot CS_2 \cdot \frac{1}{2}C_6H_6$ per unit cell. Space group $P\bar{1}$ was chosen for the refinement. The mosaic spread of the crystal was determined using the narrow-source open-counter ω-scan technique[11] and found acceptable at 0.06°. An independent set of intensity data was collected by the θ-2θ scan technique using the Zr filtered Mo $K\alpha$ peak with allowances made for the $K\alpha_1$-$K\alpha_2$ separation at higher 2θ values. The

data set was collected within the angular range $4.5 \leq 2\theta \leq 50°$. Attenuators were inserted automatically if the count rate of the diffracted beam exceeded 9000 counts/s during scan. The intensities of five standard reflections in different regions of reciprocal space were monitored during data collection after every 100 reflections measured. None of these standards deviated from its mean value by more than 3% during the time required to collect data. Data were processed in the usual way with values of I and $\sigma(I)$ corrected for Lorentz and polarization effects. No correction was applied for absorption effects since the linear absorption coefficient is small ($\mu = 15.6$ cm^{-1}) and rotation of the crystal at $\chi = 90.00°$ produced no significant variation in intensity of a reflection coincident with the ϕ axis of the instrument. The intensities of 5481 reflections were measured of which 2237 were observed to be greater than 2σ and have been included in the refinement.

Solution and Refinement of the Structure. The position of the Cr atom was determined from a sharpened three-dimensional Patterson map. Phases derived from the Cr were used to locate the 12 Cl atoms which, in turn, gave positions of all other atoms of the structure. The
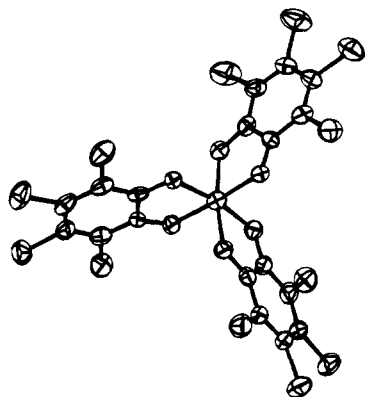
Figure 1. View of the $Cr(O_2C_6Cl_4)_3$ molecule approximately down the C_3 axis.

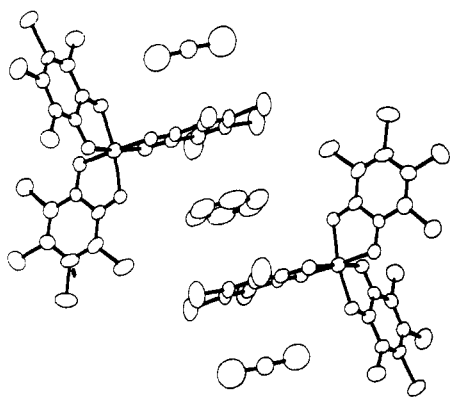**Figure 2.** The contents of one unit cell of $Cr(O_2C_6Cl_4)_3 \cdot CS_2 \cdot \frac{1}{2}C_6H_6$. The benzene ring at the center is located about a crystallographic center of inversion.

benzene molecule was found to be centered about a crystallographic center of inversion. Complete isotropic refinement of the structure gave discrepancy indices $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$ of 0.125 and 0.137, respectively. Further refinement with anisotropic thermal parameters for all atoms converged to $R = 0.045$ and $R_w = 0.044$. At completion of the refinement the standard deviation of an observation of unit weight was 1.06. During all cycles of refinement the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ and the weights w were determined as $4F_o^2/\sigma^2(F_o^2)$. The standard deviations $\sigma(F^2)$ were estimated by procedures described previously.[12] In all calculations the atomic scattering factors for the atoms were those of Cromer and Waber[13] with values of $\Delta f'$ and $\Delta f''$ for the Cr, Cl, and S atoms taken from Cromer and Liberman.[14] The final positional and thermal parameters of all atoms appear in Table I. Root-mean-square vibrational amplitudes of atoms refined anisotropically and a table of the final F_o and $|F_c|$ values for the 2237 reflections used in the refinement are available.[15]

Description of the Structure

While related 1,2-dithiolene[16] complexes and the quinone complex tris(9,10-phenanthrenequinone)molybdenum[10] have trigonal prismatic geometries the structure of tris(tetra-chloro-1,2-benzoquinone)chromium is octahedral. The molecule possesses approximate D_3 symmetry with a twist angle of 51.1 (10)° between points on trigonal faces perpendicular to the C_3 axis. A view of the complex molecule is presented in Figure 1 with intramolecular distances and angles in Table II. The contents of one unit cell are shown in Figure 2. At the center of this view is the benzene solvate molecule located about a crystallographic center of inversion. One ligand of each complex molecule is sandwiched between a CS_2 and the benzene forming a five-membered stack. Retention of the benzene from $Cr(O_2C_6Cl_4) \cdot 4C_6H_6$ appears to arise from formation of a relatively strong charge-transfer interaction. The separation

Table II. Principal Intramolecular Bonding Parameters for $Cr(O_2C_6Cl_4)_3$

Ligand I
Distances (Å)

Cr-O(1)	1.950 (5)	C(4)-C(5)	1.37 (1)
Cr-O(2)	1.946 (5)	C(5)-C(6)	1.39 (1)
O(1)-C(1)	1.282 (8)	C(6)-C(1)	1.42 (1)
O(2)-C(6)	1.277 (9)	Cl(1)-C(2)	1.74 (1)
C(1)-C(2)	1.41 (1)	Cl(2)-C(3)	1.70 (1)
C(2)-C(3)	1.37 (1)	Cl(3)-C(4)	1.70 (1)
C(3)-C(4)	1.43 (1)	Cl(4)-C(5)	1.71 (1)

Angles (deg)

Cr-O(1)-C(1)	112.6 (5)	O(1)-C(1)-C(6)	115.9 (8)
Cr-O(2)-C(6)	113.1 (5)	O(2)-C(6)-C(5)	124.6 (8)
O(1)-C(1)-C(2)	123.6 (8)	O(2)-C(6)-C(1)	116.3 (8)

Ligand II
Distances (Å)

Cr-O(3)	1.958 (5)	C(10)-C(11)	1.37 (1)
Cr-O(4)	1.935 (6)	C(11)-C(12)	1.40 (1)
O(3)-C(7)	1.272 (8)	C(12)-C(7)	1.45 (1)
O(4)-C(12)	1.265 (8)	Cl(5)-C(8)	1.71 (1)
C(7)-C(8)	1.42 (1)	Cl(6)-C(9)	1.70 (1)
C(8)-C(9)	1.33 (1)	Cl(7)-C(10)	1.71 (1)
C(9)-C(10)	1.43 (1)	Cl(8)-C(11)	1.72 (1)

Angles (deg)

Cr-O(3)-C(7)	113.8 (5)	O(3)-C(7)-C(12)	114.8 (8)
Cr-O(4)-C(12)	114.4 (5)	O(4)-C(12)-C(11)	126.3 (8)
O(3)-C(7)-C(8)	126.1 (8)	O(4)-C(12)-C(7)	115.6 (7)

Chelated Ligand III
Distances (Å)

Cr-O(5)	1.950 (5)	C(16)-C(17)	1.35 (1)
Cr-O(6)	1.955 (5)	C(17)-C(18)	1.43 (1)
O(5)-C(13)	1.293 (9)	C(18)-C(13)	1.44 (1)
O(6)-C(18)	1.288 (9)	Cl(9)-C(14)	1.70 (1)
C(13)-C(14)	1.43 (1)	Cl(10)-C(15)	1.72 (1)
C(14)-C(15)	1.38 (1)	Cl(11)-C(16)	1.71 (1)
C(15)-C(16)	1.43 (1)	Cl(12)-C(17)	1.70 (1)

Angles (deg)

Cr-O(5)-C(13)	112.2 (5)	O(5)-C(13)-C(18)	117.0 (8)
Cr-O(6)-C(18)	113.4 (5)	O(6)-C(18)-C(17)	124.6 (7)
O(5)-C(13)-C(14)	123.1 (8)	O(6)-C(18)-C(13)	115.0 (8)

Interdonor Contacts and Angles about Cr Atom
Distances (Å)

O(1)⋯O(2)	2.547 (8)	O(2)⋯O(4)	2.880 (8)
O(1)⋯O(3)	2.918 (8)	O(2)⋯O(6)	2.803 (7)
O(1)⋯O(5)	2.755 (8)	O(3)⋯O(4)	2.536 (8)
O(1)⋯O(6)	2.822 (7)	O(3)⋯O(5)	2.864 (8)
O(2)⋯O(3)	2.828 (8)	O(4)⋯O(5)	2.816 (8)
O(4)⋯O(6)	2.744 (8)	O(5)⋯O(6)	2.571 (7)

Angles (deg)

O(1)-Cr-O(2)	81.7 (2)	O(2)-Cr-O(5)	169.5 (2)
O(1)-Cr-O(3)	96.6 (2)	O(2)-Cr-O(6)	91.9 (2)
O(1)-Cr-O(4)	176.6 (2)	O(3)-Cr-O(4)	81.3 (2)
O(1)-Cr-O(5)	89.9 (2)	O(3)-Cr-O(5)	94.3 (2)
O(1)-Cr-O(6)	92.6 (2)	O(3)-Cr-O(6)	170.2 (2)
O(2)-Cr-O(3)	92.8 (2)	O(4)-Cr-O(5)	92.9 (2)
O(2)-Cr-O(4)	95.8 (2)	O(4)-Cr-O(6)	89.7 (2)
		O(5)-Cr-O(6)	82.3 (2)

between carbon atoms of the benzene solvate and carbonyl carbons of the adjacent ligands is short (3.36 (1), 3.41 (1) Å, Table IV) with shortest atom-plane separations of 3.28 Å. These values reflect a significantly stronger ligand-benzene-ligand bridge than those of $[Mo(O_2C_6Cl_4)_3]_2 \cdot 3C_6H_6$ with interplanar separations greater than 3.45 Å and where quinone ligands appear more strongly reduced.[4]

The inner coordination geometry of $Cr(O_2C_6Cl_4)_3$ resembles the general structural features of various Cr(III) com-

Table III. Dihedral Angles and Least-Squares Planes for $Cr(O_2C_6Cl_4)_3$

	Dihedral Angles	
Plane (1)	Plane (2)	Angle (deg)
O(1)–Cr–O(2)	O(3)–Cr–O(4)	87.8 (2)
O(1)–Cr–O(2)	O(5)–Cr–O(6)	87.4 (2)
O(3)–Cr–O(4)	O(5)–Cr–O(6)	92.9 (2)

Least-Squares Planes[a,b]
Chelated Ligand I
$2.65x - 4.95y - 11.61z = -1.73$

Atom	Distance (Å)	Atom	Distance (Å)
Cr	0.20	C(4)	0.01 (1)
O(1)	0.02	C(5)	−0.02 (1)
O(2)	0.05	C(6)	0.01 (1)
C(1)	0.01 (1)	Cl(1)	−0.05
C(2)	−0.03 (1)	Cl(2)	0.10
C(3)	0.02 (1)	Cl(3)	0.00
		Cl(4)	−0.09

Chelated Ligand II
$2.58x + 11.26y - 0.53z = -2.44$

Atom	Distance (Å)	Atom	Distance (Å)
Cr	0.10	C(11)	−0.02 (1)
O(3)	0.06	C(12)	−0.01 (1)
O(4)	−0.02	Cl(5)	−0.06
C(7)	0.02 (1)	Cl(6)	−0.05
C(8)	−0.01 (1)	Cl(7)	0.08
C(9)	−0.01 (1)	Cl(8)	−0.10
C(10)	0.03 (1)		

Chelated Ligand III
$6.86x - 11.35y + 7.04z = 3.96$

Atom	Distance (Å)	Atom	Distance (Å)
Cr	0.00	C(17)	−0.01 (1)
O(5)	−0.06	C(18)	0.02 (1)
O(6)	0.05	Cl(9)	0.00
C(13)	−0.02 (1)	Cl(10)	0.05
C(14)	0.00 (1)	Cl(11)	−0.03
C(15)	0.01 (1)	Cl(12)	−0.04
C(16)	−0.01 (1)		

Benzene Solvate
$2.65x + 11.19y = 1.77z = 0.43$

Atom	Distance (Å)	Atom	Distance (Å)
Cr	3.24	C(12)	3.28
O(3)	3.48	Cl(5)	3.53
O(4)	3.16	Cl(6)	3.65
C(7)	3.39	Cl(7)	3.62
C(8)	3.49	Cl(8)	3.15
C(9)	3.54	C(20)	0.00 (1)
C(10)	3.50	C(21)	0.00 (1)
C(11)	3.33	C(22)	0.00 (1)

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

plexes. The Cr–O distances average to 1.949 (5) Å with the stacked quinone ligand (O(3), O(4)) chelating in a slightly unsymmetrical way. This value compares well with distances of 1.942–1.959(7)Å for $Cr(acac)_3$[17] and 1.96 Å for $Cr(C_2O_4)_3{}^{3-}$ [18] and is slightly shorter than a value of 1.965 (2) Å for *fac*-tris(glycinato)chromium(III).[19] It is important to point out, however, that these complexes all contain three more electrons than $Cr(O_2C_6Cl_4)_3$.[20]

Table IV. Shortest Contacts between Solvate Molecules and the Complex

Carbon Disulfide		Hemibenzene	
Atoms	Distances (Å)	Atoms	Distances (Å)
O(5)···S(1)	3.35 (1)	C(7)···C(20)	3.41 (1)
C(7)···S(1)	3.50 (1)	C(12)···C(21)	3.36 (1)
C(12)···S(1)	3.68 (1)	C(8)···C(22)	3.52 (1)
C(9)···S(2)	3.59 (1)	C(11)···C(21)′	3.56 (1)
C(10)···S(2)	3.80 (1)		
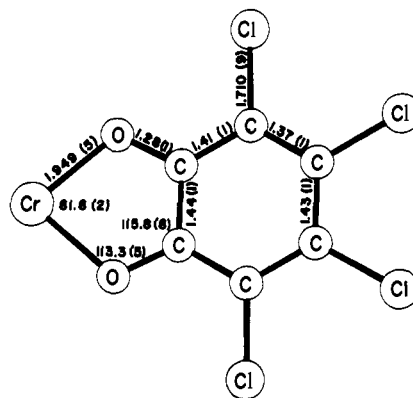
Figure 3. Average bonding parameters for the tetrachloro-1,2-benzoquinone ligands in $Cr(O_2C_6Cl_4)_3$.

Distances within the ligands reflect substantial benzoquinone character. The carbonyl lengths (1.28 (1) Å) are the shortest yet observed for a quinone complex. Semiquinone ligands in $Mo_2O_5(O_2C_{14}H_8)_2$ have C–O values of 1.31 (1) Å. Chelated ligands in $[Mo(O_2C_6Cl_4)_3]_2$ have C–O distances of 1.33 (1) Å with values of 1.36 (1) Å for the bridging ligands. These values seem most consistent with a formulation of Mo(VI) for the metal centers in this complex. Average carbon–carbon distances in the 3–4 and 5–6 positions of the quinone benzene rings are slightly shorter than other C–C distances. Nevertheless, these values, and also the C–O lengths, are not as short as values observed in free benzoquinone molecules,[21] nor are they as short as values reported for the 1,2-benzoquinone diimine ligand in $Fe(CN)_4((NH)_2C_6H_4)^{2-}$, which contains an Fe(II) center of relatively low basicity.[22]

Electron Spin Resonance Spectra of $Cr(O_2C_6Cl_4)_3{}^+$. The paramagnetic resonance spectra of the tris(tetrachloro-1,2-benzoquinone)chromium cation have been examined in both dichloromethane solution at room temperature and in glass matrices at 100 K. Spectra obtained in both cases are isotropic with $\langle g \rangle = 1.9687$ (5) and hyperfine coupling to the ^{53}Cr nucleus of 27.5 (3) G. The isotropic g value is among the lowest observed for Cr compounds while the hyperfine coupling is, by far, the largest.[23]

In assessing the extent to which ligand radical-anion character contributes to chromium–quinone bonding in $Cr(O_2C_6Cl_4)_3{}^+$ it is useful to compare these spectral values with those obtained for complexes with $O_2C_6Cl_4$ coordinating ostensively as a semiquinone ligand. The cationic complexes $M(PPh_3)_2(O_2C_6Cl_4)^+$, M = Pd, Pt; $M(PPh_3)_2(CO)Cl(O_2C_6Cl_4)^+$, M = Rh, Ir; and $Ru(PPh_3)_2(CO)_2(O_2C_6Cl_4)^+$ exhibit similar isotropic ESR spectra with low hyperfine coupling to the phosphorus nuclei, spectra with g values in the range of 2.005 similar to free quinone radical anions.[24] These observations are distinctly different from the spectrum of $Cr(O_2C_6Cl_4)_3{}^+$ which bears greater similarity to spectra of Cr(I) complexes. Isotropic g values of 1.9973 and 1.9865 have been reported for $Cr(dipy)_3{}^+$ and $Cr(C_6H_6)_2{}^+$, respectively.[25,26] Both have substantially smaller $\langle A_{53Cr} \rangle$ values than

$Cr(O_2C_6Cl_4)_3^+$, 21.8 G for $Cr(dipy)_3^+$ and 17.6 G for $Cr(C_6H_6)_2^+$. We, therefore, conclude that $Cr(O_2C_6Cl_4)_3^+$ is best described as a complex of Cr(I) with an unexpectedly localized electronic structure.

Octahedral vs. Trigonal Prismatic Coordination. Factors stabilizing the trigonal prismatic (TP) geometries in oxidized tris(1,2-dithiolene) complexes, the organometallic complexes tris(methyl vinyl ketone)tungsten[27] and tris(1,3-butadiene) molybdenum,[28] and recently tris(9,10-phenanthrenequinone)molybdenum[10] remain unclear. In all cases ligand structural parameters are consistent with partial oxidation of the metal. Both single-crystal and powder x-ray diffraction data on neutral tris(1,2-dithiolene) complexes indicate that TP coordination is common to all known systems of this type. The neutral tris(1,2-benzoquinone) complexes of group 6a metals, isoelectronic with known TP 1,2-dithiolene complexes, offer a more diverse series of coordination geometries. The tris(tetrachloro-1,2-benzoquinone)molybdenum complex is dimeric and octahedral, while its 9,10-phenanthrenequinone analogue has a TP geometry. In both molecules two quinone ligands chelate normally with similar C–O and Mo–O distances. Subtle electronic differences in the metal centers of these two complexes are reflected in the structural parameters of the third quinone ligand. In $[Mo(O_2C_6Cl_4)_3]_2$ this ligand bridges metals with short Mo–O distances, long C–O values, and features characteristic of catecholate coordination. However, the third ligand of $Mo(O_2C_{14}H_8)_3$ has Mo–O distances longer than chelated values and C–O distances comparable to those found for the radical-anion ligands in $Mo_2O_5(O_2C_{14}H_8)_2$. Thus, in these similar systems structural differences appear related to the formal charge associated with one ligand with an octahedral geometry resulting in the case where complete reduction of this ligand occurs.

The structural properties of $Cr(O_2C_6Cl_4)_3$ are quite pertinent to consideration of electronic factors stabilizing the TP geometry since it presents a situation where charge is essentially localized on the metal. Short C–O distances with trends observed for the ring C–C values suggest only slight contributions from ligand π^* levels. The metal center in $Cr(O_2C_6Cl_4)_3$ is, therefore, best described as Cr(0) similar to $Cr(dipy)_3$. Electron paramagnetic resonance spectra of $Cr(O_2C_6Cl_4)_3^+$ are most consistent with a low-spin Cr(I) complex possessing a highly localized electronic structure. It, therefore, appears that the TP geometry results from a delicate balance of metal and ligand contributions. In the situation where an imbalance is created by the electronic properties of either ligand or metal an octahedral geometry results.

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