

Synthesis, Structures, and Properties of the Tris(catecholato)rhenium(VI) Complexes $\text{Re}(\text{O}_2\text{C}_6\text{H}_2(t\text{-Bu})_2)_3$ and $\text{Re}(\text{O}_2\text{C}_6\text{Cl}_4)_3$

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Catecholate complexes of rhenium have been prepared with 3,5-di-*tert*-butyl-1,2-benzoquinone and tetrachloro-1,2-benzoquinone ligands. $\text{Re}(\text{O}_2\text{C}_6\text{H}_2)_3$ crystallizes in the monoclinic space group $P2_1/n$ with $a = 15.880$ (3) Å, $b = 15.897$ (3) Å, $c = 16.450$ (3) Å, $\beta = 93.53$ (2)°, and $Z = 4$. The anisole solvate of $\text{Re}(\text{O}_2\text{C}_6\text{Cl}_4)_3$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 8.610$ (1) Å, $b = 25.518$ (11) Å, $c = 14.731$ (3) Å, $\beta = 98.38$ (2)°, and $Z = 4$. Both complexes are tris-chelated with distorted octahedral coordination geometries for the rhenium atoms. The twist angles between triangular faces of the D_3 coordination polyhedra were determined to be 37.9° for the di-*tert*-butylcatecholate complex and 40.0° for the tetrachlorocatecholate complex. EPR and IR spectral analyses agree with the crystallographic characterization in indicating that the charge distribution in these complexes is of the type $\text{Re}^{\text{VI}}(\text{Cat})_3$. Their EPR spectra appear to be unique for Re(VI) compounds due to the well-resolved rhenium hyperfine coupling, which is usually not observed in solution at room temperature. As would be expected with third-row transition-metal complexes, the EPR spectra show evidence of strong second-order effects, and the solid-state magnetic moments differ significantly from spin-only values due to spin-orbit coupling. The electrochemistry of these complexes shows both chemically reversible one-electron-reduction and -oxidation couples.

Introduction

Catecholate ligands have been found to stabilize high-oxidation-state metals ions in the absence of oxo ligands. Examples include the molybdenum(VI) complex $\text{Mo}_2(\text{O}_2\text{C}_6\text{Cl}_4)_6$,¹ the vanadium(V) complexes $\text{Na}[\text{V}(\text{O}_2\text{C}_6\text{Cl}_4)_3]$ and $\text{Na}[\text{V}(\text{O}_2\text{C}_6\text{H}_2(t\text{-Bu})_2)_3]$,² and the osmium(VI) complex $\text{Os}(\text{O}_2\text{C}_6\text{H}_2(t\text{-Bu})_2)_3$.³ Catecholate and oxo ligands both bond as strong σ and π donors and can stabilize electron-deficient metal ions through donation of electron density into vacant metal electronic levels.

The charge distribution within metal quinone complexes is determined by the relative energy of the metal d orbitals and quinone ligand π orbitals. Studies carried out on neutral bis- and tris(quinone) complexes containing first-row transition metals have indicated that the metal ions are in the +2 or +3 oxidation state and that the quinone ligands are bonded in the partially reduced semiquinone form. Few studies have been carried out on analogous complexes prepared with larger metal ions, but the results obtained with Mo, W, and Os appear to indicate that the ligands are in the catecholate form and that the metals have been oxidized to the +6 oxidation state.⁴ Information on charge distribution within these complexes can be obtained through a number of experimental techniques including X-ray crystallography and EPR spectroscopy. Metal-oxygen and carbon-oxygen bond lengths often provide information on both metal and quinone charge. Spin-orbit coupling effects and nuclear hyperfine interactions are sensitive to the location of the paramagnetic center.⁵ Pertinent to the investigation described in this report, neutral complexes prepared with the 1,2-dithiolene and 1,2-thioamide ligands show significant charge delocalization within the chelate ring. Formal assignment of charge for ligand and metal is inappropriate for these complexes, unlike their localized quinone analogues.⁶

A convenient general synthetic route to the neutral metal quinone complexes involves treating a neutral metal carbonyl complex with the benzoquinone form of the ligand.⁴ In studies on the photodissociation of metal carbonyl complexes, Wan has reported that the photolysis at 310 nm of rhenium carbonyl with 3,5-di-*tert*-butyl-1,2-benzoquinone (DBBQ) led to formation of a chelated rhenium(I) semiquinone complex, $\text{Re}(\text{CO})_4(\text{DBSQ})$.⁷ Using similar procedures involving photolysis with a polychromatic

light source, we were able to isolate the tris-chelated rhenium(VI) catecholate complex $\text{Re}(\text{DBCat})_3$.⁸ Examples of rhenium(VI) compounds not containing oxo or nitrido ligands are rare and include the air- and moisture-sensitive hexamethylrhenium(VI) and hexafluororhenium(VI) complexes.^{9,10} In this paper we report details of the synthesis and physical characterization of the remarkably stable tris-chelated rhenium(VI) 3,5-di-*tert*-butylcatecholate complex, $\text{Re}(\text{DBCat})_3$, as well as the analogous compound containing the tetrachlorocatecholate ligand, $\text{Re}(\text{Cl}_4\text{Cat})_3$.

Experimental Section

$\text{Re}_2(\text{CO})_{10}$ was obtained from Strem Chemical Co. and was used as received. Tetrachloro-1,2-benzoquinone and 3,5-di-*tert*-butyl-1,2-benzoquinone were obtained from Aldrich Chemical Co. and were used as received. All reactions were carried out in freshly distilled solvents by standard Schlenk line techniques.

$\text{Re}(\text{O}_2\text{C}_6\text{H}_2(t\text{-Bu})_2)_3$. 3,5-Di-*tert*-butyl-1,2-benzoquinone (1.07 g; 4.86 mmol) in 30 mL of anisole was freeze-thaw-degassed for three cycles prior to addition to a similarly degassed solution of $\text{Re}_2(\text{CO})_{10}$ (0.52 g; 0.80 mmol) in 50 mL of anisole. The resulting solution was photolyzed at room temperature for 24 h by using a General Electric 275-W sunlamp. The crystalline product was isolated from the solution in nearly quantitative yield after slow evaporation of the solvent.

$\text{Re}(\text{O}_2\text{C}_6\text{Cl}_4)_3 \cdot \text{C}_6\text{H}_5(\text{OCH}_3)$. Tetrachloro-1,2-benzoquinone (1.43 g; 5.80 mmol) in 40 mL of anisole was freeze-thaw-degassed for three cycles prior to addition to a similarly degassed solution of $\text{Re}_2(\text{CO})_{10}$ (0.47 g; 0.73 mmol) in 40 mL of anisole. The resulting solution was refluxed for 24 h. The crystalline product was isolated from the solution in nearly quantitative yield after slow evaporation of the solvent at room temperature.

Physical Measurements. Infrared spectra were recorded on a Beckman IR 4250 spectrometer and on an IBM IR/30 series FTIR spectrometer with samples prepared as KBr pellets. UV-vis spectra were recorded on a Hewlett Packard 8451A diode array spectrophotometer. Magnetic susceptibility measurements were made by the Faraday technique on a Sartorius 4433 microbalance, and electron paramagnetic resonance spectra were obtained on a Varian E-109 spectrometer with DPPH used as the g value standard. Mass spectra were recorded on a VG Analytical 7070 EQ mass spectrometer, and the FAB solvent was a glycerol-pump oil mixture. Cyclic voltammograms were obtained with a BAS-100 electrochemical analyzer. A platinum-disk working electrode and a platinum wire counter electrode were used. The reference electrode was based on the Ag/Ag^+ couple and consisted of a silver acetate solution in contact with a silver wire placed in glass tubing with a Vycor frit at one end and to allow ion transport. Tetrabutylammonium hexafluorophosphate was used as the supporting electrolyte, and the ferrocene/

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Table I. Crystal Data and Details of the Structure Determinations and Refinements

	Re(DBCat) ₃	Re(Cl ₄ Cat) ₃ · C ₆ H ₅ (OCH ₃)
formula	ReO ₆ C ₄₂ H ₆₀	ReO ₆ C ₂₅ H ₅ Cl ₁₂
mol wt	847.14	1031.98
space group ^a	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
cryst syst	monoclinic	monoclinic
<i>a</i> , Å	15.880 (3)	8.610 (1)
<i>b</i> , Å	15.897 (3)	25.518 (11)
<i>c</i> , Å	16.450 (3)	14.731 (3)
β, deg	93.53 (2)	98.38 (2)
vol, Å ³	4145 (1)	3202 (2)
Z	4	4
<i>d</i> _{calcd} , g cm ⁻³	1.358	2.11
<i>d</i> _{exptl} , g cm ⁻³	1.34 (2)	2.13 (2)
<i>F</i> (000)	1740	1972
μ, cm ⁻¹	31.38	50.66
cryst dimens, mm	0.44 × 0.16 × 0.12	0.54 × 0.19 × 0.15
diffractometer	Nicolet P3F	
data collected	+ <i>h</i> , + <i>k</i> , ± <i>l</i>	
radiation (λ, Å)	Mo Kα (0.710 69)	
monochromator angle, deg	12.2	
temp, K	294–296	
scan technique	θ–2θ	
scan range (2θ), min–max, deg	3.0–58.0	3.0–55.0
scan speed, deg/min	4.0–30.0	
scan range, deg	0.7 below Kα ₁ and 0.7 above Kα ₂	
bkgd	stationary crystal–stationary counter; bkgd time = 0.5(scan time)	
no. of unique reflns measd	10906	7385
no. of obsd reflns	5711	4200
criterion	<i>F</i> > 6(σ(<i>F</i>))	
abs cor	empirical	
transmission factors	0.904–0.807	0.978–0.847
programs used	SHELXLT ^c	
scattering factors	neutral atoms ^d	
<i>R</i> ₁ , <i>R</i> ₂ ^e	0.0389, 0.0416	0.0378, 0.0417
goodness of fit ^f	1.092	1.120
weight	1/(σ(<i>F</i>) ² + 0.0005 <i>F</i> ²)	
no. of params	442	399
ratio of observns to params	12.92	10.53
max shift/error (non-hydrogen)	0.028	0.029
residual electron density, e/Å ³	0.88	0.66

^a *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1965; Vol. 1. ^b Cell dimensions were determined by least-squares fit of the setting angles of 20 reflections with 2θ in the range 20–30°. ^c Sheldrick, G. M. "SHELXLT, a Program for Crystal Structure Determination"; Nicolet Instrument Corp., Madison, WI 53711-0508. ^d *International Tables for X-ray Crystallography*; Knoch: Birmingham, England, 1974; Vol. 4, pp 55–60, 99–101, 149–150. ^e The quantity minimized in the least-squares procedures is $\sum w(|F_o| - |F_c|)^2$. $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$. ^f GOF = $[\sum w(|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2}$, where *N*_o are the number of observed reflections and *N*_v are the number of variables refined.

ferrocenium couple was used as the internal standard. The Fe/Fe⁺ couple was found to occur at 0.23 V in this experimental arrangement.

Crystallographic Structure Determinations on Re(O₂C₆H₄(*t*-Bu))₃ and Re(O₂C₆H₄)₃·C₆H₅(OCH₃). Both crystals were mounted on glass fibers and aligned on a Nicolet P3F automated diffractometer. Axial and rotational photographs indicated monoclinic symmetry for both crystals. Unit cell dimensions given in Tables I were calculated from the centered positions of 25 intense reflections with 2θ values greater than 25°. Details of procedures used for data collection and structure determination for Re(DBCat)₃ and Re(Cl₄Cat)₃·C₆H₅(OCH₃) are given in Table I.

For both structures the position of the Re atom was determined from a three-dimensional Patterson map. Phases derived from the Re position were used to locate all other non-hydrogen atoms of the structures. Final cycles of refinement converged with discrepancy indices of *R* = 0.0389 and *R*_w = 0.0416 for Re(DBCat)₃ and *R* = 0.0378 and *R*_w = 0.0417 for Re(Cl₄Cat)₃. In both structures the maximum residual electron density (0.88 e/Å³ for Re(DBCat)₃; 0.66 e/Å³ for Re(Cl₄Cat)₃) was in the vicinity of the Re atoms. Final positional and isotropic thermal parameters for all atoms in Re(DBCat)₃ are listed in Table II, and the corresponding data for Re(Cl₄Cat)₃ are listed in Table III. Tables containing anisotropic thermal parameters and structure factors for both structures are available as supplementary material.

Table II. Atom Coordinates (×10⁴) and Temperature Factors (Å² × 10³) for Re(DBCat)₃

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ^a
Re1	2018 (1)	1745 (1)	-1771 (1)	36 (1)
O1	1996 (2)	2961 (2)	-1818 (2)	43 (1)
O2	836 (2)	1966 (2)	-1653 (2)	40 (1)
O3	2100 (2)	1602 (2)	-2937 (2)	40 (1)
O4	1704 (2)	580 (2)	-1907 (2)	39 (1)
O5	3228 (2)	1759 (3)	-1607 (2)	41 (1)
O6	2161 (2)	1547 (2)	-612 (2)	39 (1)
C1	1249 (3)	3337 (4)	-1689 (3)	38 (2)
C2	602 (4)	2779 (3)	-1574 (3)	36 (2)
C3	-206 (4)	3045 (3)	-1402 (3)	38 (2)
C4	-321 (4)	3905 (4)	-1396 (3)	41 (2)
C5	321 (4)	4495 (4)	-1524 (3)	40 (2)
C6	1127 (4)	4191 (4)	-1673 (3)	41 (2)
C7	-900 (4)	2408 (4)	-1249 (4)	48 (2)
C8	-1722 (4)	2841 (5)	-1022 (5)	71 (3)
C9	-595 (5)	1838 (4)	-531 (4)	72 (3)
C10	-1090 (4)	1867 (4)	-2008 (4)	62 (3)
C11	149 (4)	5443 (4)	-1536 (4)	48 (2)
C12	-654 (7)	5676 (6)	-1179 (8)	162 (7)
C13	825 (6)	5924 (5)	-1089 (7)	136 (5)
C14	82 (8)	5728 (5)	-2400 (5)	135 (6)
C15	1838 (3)	853 (3)	-3249 (3)	36 (2)
C16	1579 (3)	294 (4)	-2677 (3)	36 (2)
C17	1222 (3)	-479 (3)	-2885 (4)	39 (2)
C18	1225 (4)	-687 (4)	-3711 (4)	45 (2)
C19	1535 (4)	-146 (4)	-4301 (4)	43 (2)
C20	1823 (3)	641 (4)	-4069 (3)	40 (2)
C21	859 (4)	-1043 (4)	-2250 (4)	47 (2)
C22	228 (4)	-547 (4)	-1767 (4)	63 (3)
C23	1578 (5)	-1369 (5)	-1660 (4)	67 (3)
C24	394 (5)	-1793 (4)	-2621 (4)	70 (3)
C25	1560 (4)	-451 (4)	-5181 (4)	53 (2)
C26	1667 (9)	248 (6)	-5769 (5)	176 (7)
C27	2278 (7)	-1060 (8)	-5213 (5)	156 (6)
C28	772 (6)	-925 (7)	-5468 (5)	121 (5)
C29	3561 (3)	1640 (3)	-839 (3)	36 (2)
C30	2961 (4)	1490 (4)	-276 (3)	38 (2)
C31	3180 (4)	1280 (4)	525 (3)	41 (2)
C32	4039 (4)	1305 (4)	734 (3)	45 (2)
C33	4662 (4)	1502 (3)	192 (4)	40 (2)
C34	4414 (3)	1664 (3)	-611 (3)	38 (2)
C35	2510 (4)	1052 (4)	1120 (4)	53 (2)
C36	1954 (5)	1812 (5)	1249 (5)	76 (3)
C37	2911 (5)	763 (7)	1931 (4)	95 (4)
C38	1960 (5)	330 (5)	761 (4)	75 (3)
C39	5600 (4)	1516 (4)	489 (4)	50 (2)
C40	5721 (5)	2096 (7)	1219 (6)	131 (5)
C41	5868 (6)	660 (5)	775 (8)	145 (6)
C42	6153 (5)	1815 (9)	-135 (6)	197 (9)

^a Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized *U*_{ij} tensor.

Experimental Results

The Re(DBCat)₃ complex was prepared by irradiation of a toluene or anisole solution containing Re₂(CO)₁₀ and 3,5-di-*tert*-butyl-1,2-benzoquinone using a polychromatic light source. A dark purple crystalline product was obtained in nearly quantitative yield after slow evaporation of the solvent under nitrogen. The Re(Cl₄Cat)₃ complex was prepared by refluxing a toluene or anisole solution containing Re₂(CO)₁₀ and tetrachloro-1,2-benzoquinone. The solid product was obtained as above and was found to crystallize from solution with one anisole solvent molecule per molecule of complex. Both compounds were found to be air-stable and showed no unusual moisture sensitivity. An attempt was made to synthesize Re(DBCat)₃ thermally. Re₂(CO)₁₀ and the quinone were boiled together in mesitylene. A quantity of the complex was formed, but this route is less efficient than the procedure using photolysis. Photolysis of a toluene solution containing Re₂(CO)₁₀ and tetrachlorobenzoquinone failed to produce Re(Cl₄Cat)₃.

Spectroscopic Properties of the Re(DBCat)₃ and Re(Cl₄Cat)₃ Complexes. Infrared spectra on both complexes appear diagnostic of charge distribution. The spectrum of Re(DBCat)₃ shows

Table III. Atomic Coordinates ($\times 10^4$) and Temperature Factors ($\text{\AA}^2 \times 10^3$) for $\text{Re}(\text{Cl}_4\text{Cat})_3 \cdot \text{C}_6\text{H}_5(\text{OCH}_3)$

atom	x	y	z	U^a
Re1	-1868 (1)	1117 (1)	2393 (1)	38 (1)
O1	-3945 (5)	1432 (2)	2200 (3)	41 (2)
O2	-1331 (5)	1851 (2)	2510 (3)	42 (2)
O3	-2132 (5)	948 (2)	3643 (3)	43 (2)
O4	265 (5)	942 (2)	2904 (3)	40 (2)
O5	-2733 (5)	445 (2)	1950 (3)	40 (2)
O6	-1289 (5)	1108 (2)	1167 (3)	39 (2)
C1	-3998 (8)	1957 (3)	2268 (4)	37 (2)
C2	-2536 (8)	2190 (3)	2416 (5)	39 (2)
C3	-2369 (8)	2729 (3)	2465 (4)	37 (2)
C4	-3724 (9)	3028 (3)	2391 (4)	37 (2)
C5	-5207 (8)	2797 (3)	2237 (5)	43 (3)
C6	-5361 (8)	2251 (3)	2170 (5)	41 (2)
C7	-810 (8)	832 (3)	4217 (4)	37 (2)
C8	545 (8)	832 (3)	3802 (4)	36 (2)
C9	2006 (8)	732 (3)	4297 (5)	37 (2)
C10	2074 (8)	623 (3)	5232 (5)	43 (3)
C11	709 (8)	628 (3)	5646 (5)	43 (3)
C12	-740 (8)	721 (3)	5141 (5)	41 (2)
C13	-2546 (8)	313 (3)	1091 (4)	36 (2)
C14	-1725 (8)	681 (3)	665 (4)	35 (2)
C15	-1380 (8)	594 (3)	-206 (5)	39 (2)
C16	-1948 (9)	144 (3)	-671 (5)	46 (3)
C17	-2814 (8)	-226 (3)	-235 (5)	41 (2)
C18	-3110 (8)	-140 (3)	661 (5)	41 (2)
C19	-533 (2)	2994 (1)	2632 (2)	58 (1)
C12	-3578 (3)	3696 (1)	2507 (2)	57 (1)
C13	-6860 (2)	3180 (1)	2125 (2)	66 (1)
C14	-7154 (2)	1947 (1)	2019 (2)	62 (1)
C15	3626 (2)	733 (1)	3755 (1)	57 (1)
C16	3830 (3)	468 (1)	5870 (2)	72 (1)
C17	839 (3)	505 (1)	6795 (1)	67 (1)
C18	-2446 (2)	708 (1)	5609 (1)	63 (1)
C19	-276 (3)	1043 (1)	-707 (1)	58 (1)
C110	-1624 (3)	36 (1)	-1771 (1)	68 (1)
C111	-3506 (3)	-775 (1)	-814 (2)	67 (1)
C112	-4078 (3)	-590 (1)	1227 (1)	57 (1)
C19	7095	2287	4847	67 (4)
C20	5693 (9)	2006 (2)	4674 (5)	80 (4)
C21	4259	2270	4581	95 (5)
C22	4227	2815	4661	96 (5)
C23	5629	3095	4835	104 (6)
C24	7063	2831	4928	76 (4)
C25	9862 (13)	2255 (5)	5084 (9)	120 (6)
O7	8424 (9)	1996 (3)	4903 (6)	102 (3)

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

features similar to the spectra of $[\text{MoO}(\text{DBCat})_2]_2^{11}$ and $\text{Na}[\text{V}(\text{DBCat})_3]_2^{12}$ which have been characterized crystallographically and were shown to contain catecholate ligands. The major features of this spectrum above 900 cm^{-1} include *tert*-butyl stretching frequencies at 2958 , 2907 , and 2870 cm^{-1} , intense bands at 1590 , 1363 , 1200 , and 985 cm^{-1} , and bands of medium intensity at 1465 , 1303 , 1262 , 1176 , and 1027 cm^{-1} . Most of these bands correlate well with bands in the spectra of the molybdenum dimer and the vanadium monomer.

The spectrum of $\text{Re}(\text{Cl}_4\text{Cat})_3$ also shows strong similarities to the spectra of other metal tetrachlorocatecholate complexes, including $\text{Mo}_2(\text{Cl}_4\text{Cat})_6$ and $\text{Na}[\text{V}(\text{Cl}_4\text{Cat})_3]$, which have previously been shown to contain catecholate ligands.^{1,2} The major features of this spectrum above 800 cm^{-1} include bands of strong intensity at 1400 , 1243 , 1220 , 1005 , and 955 cm^{-1} and bands of medium intensity at 1540 , 1263 , 820 , and 800 cm^{-1} . All of these bands must arise from stretching and bending modes within the ligands because the energies of these bands are virtually identical in the rhenium, molybdenum, and vanadium complexes.

Optical spectra of both complexes show strong bands in the 500 – 600 -nm region, resulting in the intense purple color for the

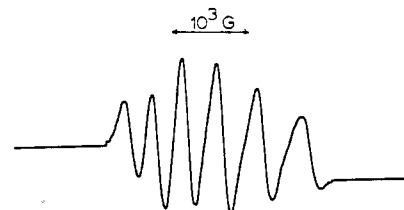


Figure 1. EPR spectrum recorded on $\text{Re}(\text{DBCat})_3$ in methylene chloride. The spectrum is centered at a $\langle g \rangle$ value of 2.040 and shows an average Re hyperfine coupling constant of 474 G .

compounds. In methylene chloride solution $\text{Re}(\text{DBCat})_3$ has bands at 273 nm ($\epsilon 16000$) and 492 nm ($\epsilon 20000$) and a shoulder near 590 nm . The tetrachloro analogue has bands at 286 nm ($\epsilon 15000$) and 508 nm ($\epsilon 23000$) and a shoulder near 640 nm . The slight red-shift of the bands in $\text{Re}(\text{Cl}_4\text{Cat})_3$ relative to the bands in $\text{Re}(\text{DBCat})_3$ gives the compound a more blue-violet color. Both compounds were also characterized by mass spectral analysis. A simple electron-impact spectrum of $\text{Re}(\text{DBCat})_3$ gave two parent ion peaks at m/e 846 and 848 , corresponding to complex molecules containing the ^{185}Re and ^{187}Re isotopes. The tetrachloro complex was less volatile, and simple electron-impact mass spectrometry failed to yield a clear spectrum. However, the fast-atom bombardment (FAB) technique gave a spectrum consistent with the expected isotope pattern that would arise from the rhenium and chlorine isotopes, giving major parent ion peaks at m/e 923 and 925 .

As d^1 -Re(VI) complexes, $\text{Re}(\text{DBCat})_3$ has a solid-state magnetic moment of $1.18 (1) \mu_B$ and $\text{Re}(\text{Cl}_4\text{Cat})_3$ has a magnetic moment of $1.26 (1) \mu_B$. Both values differ significantly from the expected spin-only value and reflect the effect of strong spin-orbit coupling.

The solution EPR spectra of these two complexes appear to be unique for Re(VI) compounds, where usually metal hyperfine coupling remains unresolved at room temperature. The complexes ReMe_6 ,^{9b} ReOMe_4 ,¹³ tris(*o*-aminobenzenethiolato)rhenium,¹⁴ and the tris(1,2-dithiolene)rhenium⁶ complexes all show weak, broad, featureless EPR signals at room temperature. In contrast, both spectra of the Re^{VI} catecholate complexes consist of six well-resolved lines due to the $I = 5/2$ ^{185}Re and ^{187}Re isotopes. The spectrum of $\text{Re}(\text{DBCat})_3$ shown in Figure 1 is centered about a $\langle g \rangle$ value of 2.040 , and the analogous spectrum of the tetrachloro complex is centered about a $\langle g \rangle$ value of 2.004 . Spacings between the rhenium hyperfine lines are not equal and increase with field strength. For both complexes the low-field separation is 350 G and the high-field separation is 600 G . Spin density is clearly concentrated on the metal.

Frozen-solution EPR spectra recorded on the trigonal-prismatic tris(aminobenzenethiolato)rhenium complex were interpreted to show evidence of extensive spin delocalization onto the ligand.¹² The magnetic moment of the complex, $1.47 \mu_B$, was viewed as resulting from an intermolecular exchange mechanism between complex molecules with Re ions separated by approximately 9 \AA . The distance between Re ions in both catecholate structures is also 9 \AA , and strong intermolecular exchange between the metal-localized spins seems unlikely. A strong spin-orbit coupling effect appears responsible for both the second-order effects observed in the EPR spectra and the anomalously low magnetic moments measured at room temperature for the catecholate complexes.

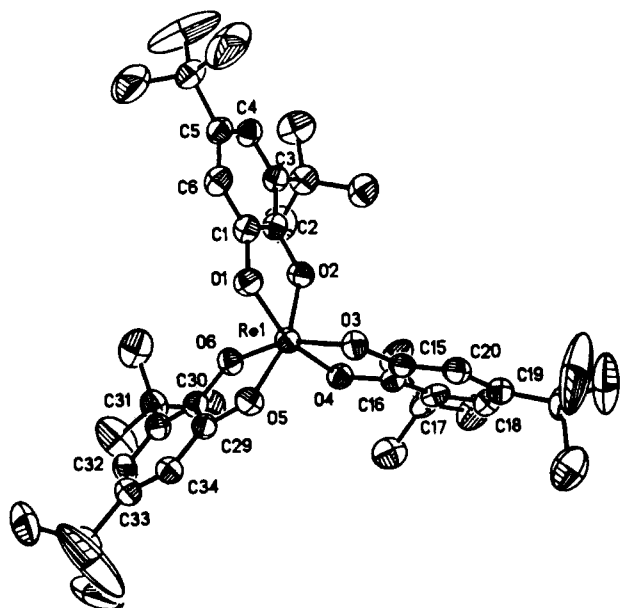
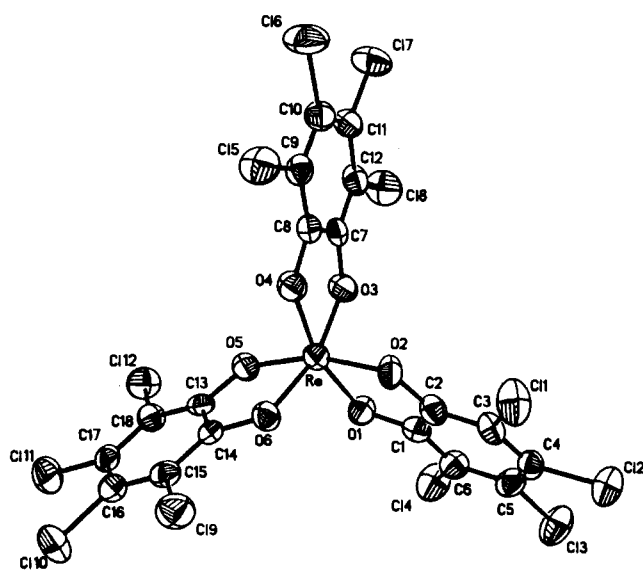
Crystallographic Characterization of $\text{Re}(\text{DBCat})_3$ and $\text{Re}(\text{Cl}_4\text{Cat})_3$. Crystal suitable for study were isolated from the reaction mixtures of both rhenium compounds. The crystals of $\text{Re}(\text{Cl}_4\text{Cat})_3$ was coated with an amorphous resin to prevent loss of solvent and crystal deterioration.

A structural feature common to both complexes is the distorted octahedral coordination geometry of the rhenium atoms shown

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Figure 2. ORTEP plot showing the molecular geometry of $\text{Re}(\text{DBCat})_3$.Figure 3. ORTEP plot showing the molecular geometry of $\text{Re}(\text{Cl}_4\text{Cat})_3$.

in Figures 2 and 3. This differs from the case of other tris-chelated rhenium complexes, such as the 1,2-dithiolene¹⁵ and 1,2-aminobenzenethiolato compounds,^{12,14} where the rhenium atoms have trigonal-prismatic coordination geometries. A measure of the prismatic-antiprismatic distortion of the octahedron is the twist angle between triangular faces of the D_3 coordination polyhedron. This angle is 0° for a regular trigonal prism and 60° for an octahedron. Values calculated for the rhenium-catecholate structures were 37.9° for the di-*tert*-butylcatecholate complex and 40.0° for the tetrachlorocatecholate complex. Stiefel and Brown have correlated values of twist angle with the ligand-bite to metal-ligand bond distance ratio for six-coordinate tris-chelated complexes.¹⁶ The ratio of bite to bond distance is 1.27 for $\text{Re}(\text{DBCat})_3$ and 1.28 for $\text{Re}(\text{Cl}_4\text{Cat})_3$. Both values are smaller than the ideal value of 1.41 for an octahedron, suggesting that the trigonal distortions result from chelation constraints of the catecholate ligands.

An important feature of both complexes is the extremely short rhenium-oxygen bond lengths. Bond distances and angles for $\text{Re}(\text{DBCat})_3$ are given in Table IV, and corresponding values for

Table IV. Selected Bond Lengths and Angles for $\text{Re}(\text{DBCat})_3$

Bond Lengths (Å)			
Rhenium-Oxygen			
Re-O1	1.935 (4)	Re-O4	1.926 (4)
Re-O2	1.931 (4)	Re-O5	1.925 (3)
Re-O3	1.943 (4)	Re-O6	1.933 (4)
Ligand 1			
O1-C1	1.358 (7)	C4-C5	1.410 (8)
O2-C2	1.353 (6)	C5-C6	1.404 (8)
C1-C2	1.378 (8)	C6-C1	1.373 (8)
C2-C3	1.397 (8)	C3-C7	1.528 (8)
C3-C4	1.380 (8)	C5-C11	1.530 (8)
Ligand 2			
O3-C15	1.351 (6)	C18-C19	1.408 (8)
O4-C16	1.350 (6)	C19-C20	1.377 (8)
C15-C16	1.375 (8)	C20-C15	1.390 (8)
C16-C17	1.387 (8)	C17-C21	1.517 (8)
C17-C18	1.398 (8)	C19-C25	1.529 (8)
Ligand 3			
O5-C29	1.352 (6)	C32-C33	1.407 (8)
O6-C30	1.356 (6)	C33-C34	1.379 (8)
C29-C30	1.389 (8)	C34-C29	1.384 (7)
C30-C31	1.383 (8)	C31-C35	1.533 (9)
C31-C32	1.386 (8)	C33-C39	1.539 (8)
Bond Angles (deg)			
O1-Re-O2	78.8 (2)	O2-C2-C1	112.9 (5)
O3-Re-O4	78.8 (1)	Re-O3-C15	116.1 (3)
O5-Re-O6	78.9 (1)	Re-O4-C16	117.0 (3)
O1-Re-O3	94.6 (2)	O3-C15-C16	114.0 (5)
O2-Re-O5	162.2 (2)	O4-C16-C15	113.0 (5)
O4-Re-O6	88.3 (1)	Re-O5-C29	117.3 (3)
Re-O1-C1	116.6 (3)	Re-O6-C30	117.6 (3)
Re-O2-C2	117.3 (3)	O5-C29-C30	113.7 (5)
O-C1-C2	113.8 (5)	O6-C30-C29	112.4 (5)

Table V. Selected Bond Lengths and Angles for $\text{Re}(\text{Cl}_4\text{Cat})_3 \cdot \text{C}_6\text{H}_6(\text{OCH}_3)$

Bond Lengths (Å)			
Rhenium-Oxygen			
Re-O1	1.942 (4)	Re-O4	1.933 (4)
Re-O2	1.930 (5)	Re-O5	1.944 (4)
Re-O3	1.937 (5)	Re-O6	1.942 (5)
Ligand 1			
O1-C1	1.345 (8)	C3-C4	1.384 (10)
O2-C2	1.342 (8)	C4-C5	1.395 (10)
C1-C2	1.381 (10)	C5-C6	1.400 (11)
C2-C3	1.384 (10)	C6-C1	1.384 (10)
Ligand 2			
O3-C7	1.347 (8)	C9-C10	1.398 (10)
O4-C8	1.340 (8)	C10-C11	1.402 (11)
C7-C8	1.393 (10)	C11-C12	1.377 (9)
C8-C9	1.383 (9)	C12-C7	1.382 (10)
Ligand 3			
O5-C13	1.343 (8)	C15-C16	1.390 (10)
O6-C14	1.341 (8)	C16-C17	1.412 (11)
C13-C14	1.380 (10)	C17-C18	1.398 (10)
C14-C15	1.377 (10)	C18-C13	1.372 (9)
Bond Angles (deg)			
O1-Re-O2	79.4 (2)	O2-C2-C1	114.3 (6)
O3-Re-O4	79.3 (2)	Re-O3-C7	116.1 (4)
O5-Re-O6	79.4 (2)	Re-O4-C8	117.2 (4)
O1-Re-O3	89.9 (2)	O3-C7-C8	114.2 (6)
O2-Re-O5	163.9 (2)	O4-C8-C7	113.1 (6)
O4-Re-O6	90.1 (2)	Re-O5-C13	116.5 (4)
Re-O1-C1	116.1 (4)	Re-O6-C14	115.6 (4)
Re-O2-C2	116.4 (4)	O5-C13-C14	113.3 (6)
O1-C1-C2	113.7 (6)	O6-C14-C13	115.2 (6)

$\text{Re}(\text{Cl}_4\text{Cat})_3$ are given in Table V. The average rhenium-oxygen bond length is 1.932 (4) Å for the di-*tert*-butylcatecholate complex and 1.938 (5) Å for the tetrachlorocatecholate complex. These values appear shorter than other Re-O lengths to all but oxo

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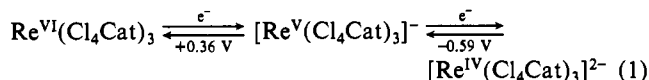
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ligands. In a related complex, Herrmann and co-workers have reported an average Re–O length of 1.99 (1) Å for the tetrachlorocatecholate ligands of $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{Cl}_4\text{Cat})_2$.¹⁷ The extremely short Re–O bond lengths in the two tris-chelated catecholate complexes reflect strong interactions between the π -donor orbitals of the catecholate oxygen atoms and the vacant metal orbitals of the Re(VI) ions.

The results of crystallographic characterization on both complexes are also indicative of the charge distribution within the complexes. Previous structural characterization of metal–quinone complexes has shown that the carbon–oxygen bond lengths within the ligands are diagnostic of formal ligand charge.⁴ Fully reduced catecholate ligands have C–O lengths that vary little from 1.35 Å while partially reduced semiquinone ligands have C–O lengths close to 1.29 Å. The carbon–oxygen bond lengths of the quinone ligands in these compounds averaged to 1.353 (6) Å for Re(DBCat)₃ and 1.343 (8) Å for Re(Cl₄Cat)₃, values that are typical of localized catecholate ligands. The carbon–carbon bond lengths in the ligands are also indicative of localized catecholate ligands. The average C–C bond lengths were 1.389 (8) Å in Re(DBCat)₃ and 1.388 (10) Å in Re(Cl₄Cat)₃, values that are consistent with C–C lengths in aromatic rings.

Electrochemistry on Re(DBCat)₃ and Re(Cl₄Cat)₃. Solutions prepared with Re(DBCat)₃ and Re(Cl₄Cat)₃ in methylene chloride were studied by using cyclic voltammetry. The di-*tert*-butylcatecholate complex was found to undergo chemically reversible one-electron oxidation and reduction reactions. Reduction occurs at –0.62 V (vs. Fc/Fc⁺) with a peak separation varying from 110 to 530 mV as scan rate was increased from 100 mV/s to 10 V/s. At all scan rates the i_c/i_a ratio was close to 1. Oxidation occurs reversibly at +0.63 V, but the i_c/i_a ratio varies from 0.2 to 1.0 as scan rate is increased from 100 mV/s to 10 V/s. The tetrachlorocatecholate complex undergoes two quasireversible one-electron reductions and a reversible one-electron oxidation. The first reduction occurs at +0.36 V with a peak separation of 81 mV at a scan rate of 10 mV/s; the second occurs at –0.59 V with a peak separation of 127 mV at a scan rate of 100 mV/s. For both, the i_c/i_a ratio was approximately 1. The oxidation couple was observed at +0.94 V vs. Fc/Fc⁺.

Reduction of both complexes must necessarily occur at the metal because quinone ligands in the catecholate form are in their most reduced state. The one-electron reduction of Re^{VI}(DBCat)₃ at –0.62 V produces [Re^V(DBCat)₃][–] with a d² configuration resulting for the rhenium ion. The corresponding reduction of rhenium in the tetrachloro analogue occurs at a much more positive potential of +0.36 V, demonstrating weaker π donation by tetrachlorocatecholate ligands compared that from 3,5-DBCat ligands. Strong π donation is decreased due to the presence of electron-withdrawing chlorine atoms on the catecholate ring. Equation 1 indicates probable Re complexes associated with both



reductions of Re^{VI}(Cl₄Cat)₃. Assignment of the second reduction of Re(Cl₄Cat)₃ to a reaction producing [Re^{IV}(Cl₄Cat)₃]^{2–} is corroborated by Griffith's recent report on the synthesis of [PPh₄]₂[Re^{IV}(Cat)₃][–]·H₂O.¹⁸ This reduction could also be present in the electrochemistry of Re(DBCat)₃, but at potential more negative than 1.5 V.

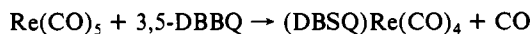
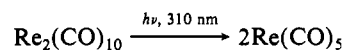
Oxidation of these Re(VI) catecholate complexes could occur either at the metal to produce Re⁷⁺-d⁰ ions or at the ligands to produce mixed-charge-ligand compounds of type [Re(DBCat)₂(DBSQ)]⁺. Both possibilities are feasible because strong π -donor catecholate ligands could shift the oxidation potential of Re(VI)

to a positive value, and ligand oxidations that produce mixed-ligand products are well-known.⁴

Discussion

Crystallographic characterization coupled with electron paramagnetic resonance and solid-state infrared spectral analyses have shown that the two tris-chelated rhenium quinone complexes are of the form Re^{VI}(Cat)₃, where Cat = 3,5-di-*tert*-butylcatecholate or tetrachlorocatecholate. These results differ significantly from those of previous work using manganese carbonyl. In that case, a tetrameric manganese(II) semiquinone product, Mn₄(DBSQ)₈, was observed to form upon the photolysis of Mn₂(CO)₁₀ in the presence of 3,5-di-*tert*-butyl-1,2-benzoquinone.¹⁹ This difference in charge between first- and third-row metals is likely related to the energy difference between the 3d and 5d electronic levels relative to the quinone π level. It appears to occur generally, having been also found for the Cr^{III}(SQ)₃–W^{VI}(Cat)₃ and Fe^{III}(SQ)₃–Os^{VI}(Cat)₃ pairs.^{3,20–22}

The results of this investigation complement results previously obtained by Wan on the photochemical reaction of rhenium carbonyl in the presence of 3,5-di-*tert*-butyl-1,2-benzoquinone.⁷ Wan found that, upon photolysis at 310 nm in toluene, a rhenium(I) semiquinone product, Re(CO)₄(3,5-DBSQ), was formed. This product was characterized on the basis of EPR, UV/vis, and solution IR spectroscopy. The following reaction mechanism was suggested:



Additional work has shown that Re₂(CO)₁₀ undergoes thermal dissociation to form Re(CO)₅. Therefore, initial formation of Re(CO)₄(DBSQ) may occur in both the photochemical and thermal routes to Re(DBCat)₃. The failure of the photochemical synthesis of Re(Cl₄Cat)₃ may be due to insertion of the metal into a carbon–chlorine bond of the quinone. Both reduction to catecholate and insertion are known to occur for tetrachlorobenzoquinone upon treatment with metal carbonyl complexes, and insertion products are obtained exclusively with Mn₂(CO)₁₀ upon photolysis at room temperature. Further reaction of Re(CO)₄(SQ) species with benzoquinone appears to occur by initial carbonyl displacement, and this reaction is under further investigation.

Although other second- and third-row transition metals have been shown to form high-oxidation-state catecholate complexes, the rhenium compounds reported here are among the few Re(VI) complexes not containing oxo ligands that are stable in air. In contrast, both Re(Me)₆ and ReF₆ are relatively unstable and quite reactive. The hexamethyl compound decomposes above –20 °C, and it reacts in air to produce oxo- and peroxorhenium products.^{9a} It seems apparent that in the case of the catecholate complexes strong σ and π donation to the metal stabilizes the unusually high Re(VI) oxidation state.

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Registry No. Re(O₂C₆H₂(*t*-Bu)₂)₃, 106758-96-7; Re(O₂C₆Cl₄)₃·C₆H₅(OCH₃), 106681-93-0; Re₂(CO)₁₀, 14285-68-8; [Re(DBCat)₃][–], 106681-89-4; [Re(Cl₄Cat)₃][–], 106681-90-7; [Re(Cl₄Cat)₃]^{2–}, 106681-91-8; 3,5-di-*tert*-butyl-1,2-benzoquinone, 3383-21-9; tetrachloro-1,2-benzoquinone, 2435-53-2.

Supplementary Material Available: Tables of anisotropic thermal parameters for Re(O₂C₁₄H₂₀)₃ and Re(O₂C₆Cl₄)₃·C₆H₅(OCH₃) (2 pages); listings of observed and calculated structure factors for both compounds (59 pages). Ordering information is given on any current masthead page.

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