ratio, Cp/Dq = 5.4, as found for V(dtpa)₄ the sequences obtained are as follows: V(1), $d_{x^2-y^2} < d_{xz,yz} < d_{z^2} < d_{xy}$; V(2), $d_{x^2-y^2} < d_{z^2} < d_{xy} < d_{xz,yz}$.

Room-temperature Nujol mull spectra of V(dta)₄ show only two very broad shoulders at ~12 and ~19 kK. Better resolved single-crystal spectra show numerous shoulders in the region in which d–d transitions are expected, giving an at least qualitative agreement with the above scheme. Single-crystal polarized spectra and epr spectra are planned in order to give a more detailed description of the electronic structure of the complexes described.

Transition Metal Eight-Coordination. IV.
Tetrakis(5,7-disubstituted-8-quinolinolato)tungsten(V) Salts[1]

BY RONALD D. ARCHER,* WESLEY D. BONDS, JR., AND ROBERT A. PRIBUSH

Violet, paramagnetic [WQ₄]⁺ ions have been synthesized by a variety of methods and appear to be the first complexes of tungsten(V) possessing four chelate ligands. The 5,7-dichloro-8-quinolinol derivative has been synthesized by the reaction of either K₃W₂Cl₉ or W(CO)₆ with excess ligand at elevated temperatures for extended time periods or by treating the corresponding tungsten(IV) inner complex with Cl₂, Br₂, or HClO₄ at room temperature or with additional ligand at elevated temperatures. The 7-bromo-5-methyl-8-quinolinol–tungsten(V) species is rapidly produced in the melt reaction of the ligand with W(CO)₆. The [WQ₄]X salts, where X⁻ = Cl⁻, Br⁻, ClO₄⁻, or Q⁻, disproportionate in alcoholic or aqueous KOH to WQ₄ and tungsten(VI). Electronic transitions of the [WQ₄] species consist of several bands in the near-infrared and visible region in addition to the normal ligand spectral transitions. A magnetic moment of 1.7 BM, a ⟨g⟩ value of 1.872, and a ¹⁸³W hyperfine splitting of 85 G were observed for the dichloro derivative at room temperature. Low-temperature electron spin resonance spectra exhibit three anisotropic g values indicative of isomerization from the D_{2d}-mmmm isomer found for a related 5-bromo-8-quinolinol–tungsten(IV) chelate.[1a]
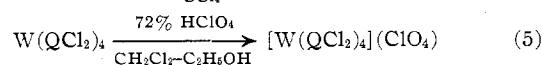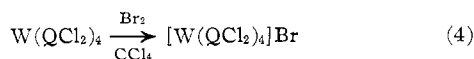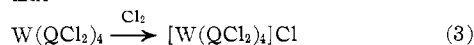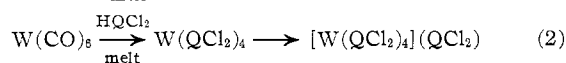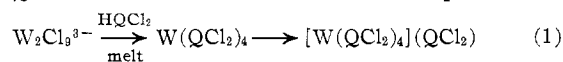
Introduction

Well-defined, eight-coordinate complexes of the transition elements in which the same element occurs in two oxidation states are indeed rare.[2] Eight-coordinate cations are also relatively scarce.[2,3] We have previously isolated WQ₄-type species, where Q⁻ is the anion of an 8-quinolinol derivative.[4] We wish to report the isolation of [WQ₄]X salts, where X⁻ is Cl⁻, Br⁻, or ClO₄⁻. The molybdenum(V) and -(IV) and tungsten(V) and -(IV) octacyano series are the only other eight-coordinate d¹ and d² pairs known.[5] Whereas the octacyanomolybdenum(IV) complex appears more stable than the molybdenum(V) species, the octacyanotungsten(V) complex is of comparable stability with the tungsten(IV) complex.[6] Further-more, recent X-ray results[7] with the octacyano complexes show that dodecahedral and antiprismatic configurations are both accessible for identical ML_8^{n-} species. Whether this is true of complexes with different ligands or chelates with unequal donors, such as the WQ₄ and [WQ₄]⁺ complexes, is unknown. The dodecahedral configuration has been found for tetrakis(5-bromo-8-quinolinolato)tungsten(IV)–benzene,[1a] the only chelate of these series for which suitable, untwinned crystals have been obtained to date.

Results

Synthesis.—Reactions which lead to the tetrakis-(5,7-dichloro-8-quinolinolato)tungsten(V) ion include (where QCl₂⁻ = the anion of 5,7-dichloro-8-quinolinol)

$$W_2Cl_9{}^{3-} \xrightarrow[\text{melt}]{\text{HQCl}_2} W(QCl_2)_4 \longrightarrow [W(QCl_2)_4](QCl_2) \qquad (1)$$

$$W(CO)_6 \xrightarrow[\text{melt}]{\text{HQCl}_2} W(QCl_2)_4 \longrightarrow [W(QCl_2)_4](QCl_2) \qquad (2)$$

$$W(QCl_2)_4 \xrightarrow[\text{CCl}_4]{\text{Cl}_2} [W(QCl_2)_4]Cl \qquad (3)$$

$$W(QCl_2)_4 \xrightarrow[\text{CCl}_4]{\text{Br}_2} [W(QCl_2)_4]Br \qquad (4)$$

$$W(QCl_2)_4 \xrightarrow[\text{CH}_2\text{Cl}_2-\text{C}_2\text{H}_5\text{OH}]{72\% \text{ HClO}_4} [W(QCl_2)_4](ClO_4) \qquad (5)$$

(1) (a) Part III: W. D. Bonds, Jr., R. D. Archer, and W. C. Hamilton, *Inorg. Chem.*, **10**, 1764 (1971). (b) Abbreviations: HQCl₂ = 5,7-dichloro-8-quinolinol; HQBrMe = 7-bromo-5-methyl-8-quinolinol; HQAc = 5-acetyl-8-quinolinol; HQBr = 5-bromo-8-quinolinol; HQClNO₂ = 7-chloro-5-nitro-8-quinolinol, etc.; HQ = 8-quinolinol and its derivatives in general. (c) Abstracted in part from the Ph.D. dissertation of W. D. B., University of Massachussetts, 1970.

(2) S. J. Lippard, *Progr. Inorg. Chem.*, **8**, 109 (1967).

(3) (a) D. G. Hendricker and R. L. Bodner, *Inorg. Nucl. Chem. Lett.*, **6**, 187 (1970), and (b) R. L. Bodner and D. G. Hendricker, *ibid.*, **6**, 421 (1970), have recently synthesized an extensive series of labile complexes with 1,8-naphthyridine which are eight-coordinate: (c) A. Clearfield, P. Singh, and I. Bernal, *J. Chem. Soc. D*, 389 (1970).

(4) (a) R. D. Archer and W. D. Bonds, Jr., *J. Amer. Chem. Soc.*, **89**, 2236 (1967); (b) W. D. Bonds, Jr., and R. D. Archer, *Inorg. Chem.*, **10**, 2057 (1971).

(5) In addition to ref 2, reviews considering eight-coordinate complexes include (a) J. L. Hoard and J. V. Silverton, *ibid.*, **2**, 235 (1963); (b) E. L. Muetterties and C. M. Wright, *Quart. Rev., Chem. Soc.*, **21**, 109 (1967); (c) R. V. Parish, *Coord. Chem. Rev.*, **1**, 439 (1966); (d) J. S. Wood, *ibid.*, **2**, 403 (1967); and earlier references such as (e) L. E. Marchi, W. C. Fernelius, and J. P. McReynolds, *J. Amer. Chem. Soc.*, **65**, 329 (1943).

(6) (a) A. Samotus and B. Kosowicz, *Proc. Int. Conf. Coord. Chem., 12th*, 211 (1969); (b) A. Samotus, *Proc. Int. Conf. Coord. Chem., 13th*, **2**, 287 (1970).

(7) (a) B. J. Corden, J. A. Cunningham, and R. Eisenberg, *Inorg. Chem.*, **9**, 356 (1970). (b) L. D. C. Bok, J. G. Leipoldt, and S. S. Basson, *Acta Crystallogr., Sect. B*, **26**, 684 (1970), present distorted dodecahedral and antiprismatic structures for the [W(CN)₈]³⁻ ion. Antiprismatic coordination for the corresponding d² ions has also been observed [(c) J. Chojnacki, J. Grochowski, L. Lebioda, B. Oleksyn, and K. Stadnicka, *Rocz. Chem.*, **43**, 273 (1969); (d) S. S. Basson, L. D. C. Bok, and J. G. Leipoldt, *Acta Crystallogr. Sect. B*, **26**, 1209 (1970)] even though the classical structure is known to be dodecahedral: (e) J. L. Hoard and H. H. Nordsieck, *J. Amer. Chem. Soc.*, **61**, 2853 (1939); *cf.* (f) J. L. Hoard, T. A. Hamor, and M. D. Glick, *ibid.*, **90**, 3177 (1968).
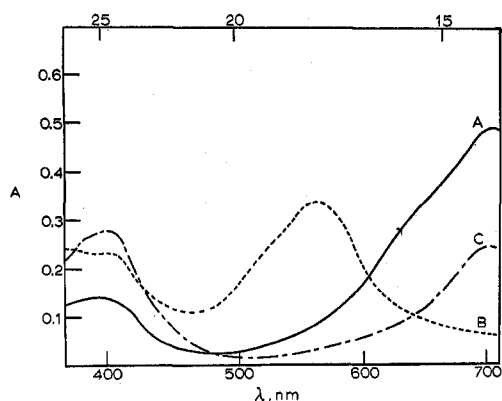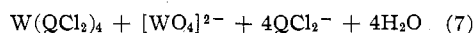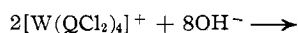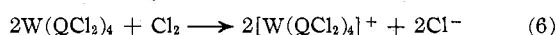
Figure 1.—Visible and near-ultraviolet spectra of $W(QCl_2)_4$ (A), the $[W(QCl_2)_4]Cl$ produced by Cl_2 oxidation (B), and the disproportionation products produced after addition of concentrated aqueous KOH (C).

The $[W(QCl_2)_4]^+$ salts are more soluble in solvents of moderate polarity such at CH_2Cl_2 than in nonpolar or highly polar solvents. Although either Cl_2 or Br_2 will oxidize the neutral $W(QCl_2)_4$ chelate, iodine does not oxidize this species. Perchloric acid is also a suitable oxidant for the tungsten(IV) to -(V) chelate oxidation.

Electrophoresis experiments have shown the cationic nature of the violet species. That is, the violet complex migrates in the same direction as other cationic species.

The $[W(QCl_2)_4]Cl$ species, prepared from $W(QCl_2)_4$ and chlorine, undergoes a novel 1:1 disproportionation on treatment with excess potassium hydroxide, as demonstrated by the visible spectra in Figure 1. Spectrum C is consistent with a mixture of $W(QCl_2)_4$, $[WO_4]^{2-}$, and QCl_2^-, suggesting the Figure 1 spectra are a result of the sequence

$$2W(QCl_2)_4 + Cl_2 \longrightarrow 2[W(QCl_2)_4]^+ + 2Cl^- \qquad (6)$$

$$2[W(QCl_2)_4]^+ + 8OH^- \longrightarrow$$
$$W(QCl_2)_4 + [WO_4]^{2-} + 4QCl_2^- + 4H_2O \qquad (7)$$

Evidence for this reaction includes the following: (1) the 700-nm peak intensity is only one-half that of the original $W(QCl_2)_4$ peak; (2) the increased intensity at *ca.* 385 nm over that of the original $W(QCl_2)_4$ complex is consistent with the spectrum of the QCl_2^- ion;[8] and (3) infrared spectra of the products show absorptions at the same energies exhibited by $Na_2WO_4 \cdot 2H_2O$. Dissolution of the tungsten(V) species in reagent grade organic solvents (without the removal of oxygen or water) also yields some of the tungsten(IV) chelate. Quantitative experiments again suggest disproportionation.

Reaction of $W(CO)_6$ with 8-quinolinol derivatives first produces tungsten(IV) chelates and then the tungsten(V) chelates. The ease of conversion to tungsten(V) appears to follow the ligand order: 8-quinolinol < 5,7-dihalo-8-quinolinol < 7-bromo-5-methyl-8-quinolinol. Whereas the 8-quinolinol shows very little tendency to give the tungsten(V) complex in the melt reaction, the 5,7-dichloro and 5,7-dibromo derivatives form the tungsten(V) species under com-
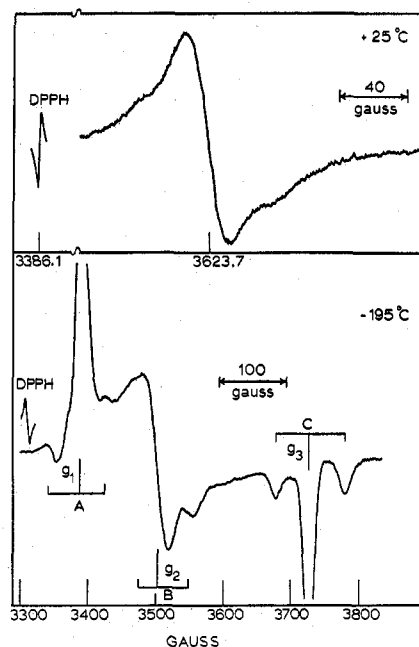

Figure 2.—Electron spin resonance spectra of $[W(QCl_2)_4]Cl$ in dichloromethane at room and liquid nitrogen temperatures.

parable conditions. With 7-bromo-5-methyl-8-quinolinol reaction to tungsten(V) proceeds very rapidly under comparable conditions; in fact, stopping at tungsten(IV) appears virtually impossible using a melt reaction.

Mossy tin or copper turnings reduce the $[WQ_4]X$ species in dichloromethane. The reaction quantitatively reduces the tungsten(V) complexes but has not been studied in detail.

Physical Studies.—The magnetic susceptibility of $[W(QCl_2)_4]Cl$ at room temperature is 600 (± 100) $\times$ 10^{-6} cgs unit, which is 1200 (± 150) $\times$ 10^{-6} cgs unit when corrected for the diamagnetism of the ligand and the tungsten core. Therefore, a magnetic moment of about 1.7 BM is indicated, near the spin-only value for a d^1 species, such as tungsten(V).

The electron spin resonance spectra of $[W(QCl_2)_4]Cl$ in CH_2Cl_2 at 25° at several concentrations indicate an isotropic g tensor of 1.872 $\pm$ 0.001. An isotropic hyperfine splitting of 85 $\pm$ 5 G for ^{183}W (14% abundance) is indicated by shoulders observed on the main resonance. See Figure 2 and Table I. The spectra indicate that the unpaired electron is primarily on the tungsten nucleus. The isotropic g tensor and hyperfine splitting are in the range observed for tungsten(V).[9]

To further elucidate structural information, frozen CH_2Cl_2 glasses of $[W(QCl_2)_4]Cl$ were prepared and their anisotropic electron spin resonance spectra were measured. The spectra (Figure 2 and Table I) exhibit a broadness typical of tungsten(V).[9] Using line-shape analysis,[10] anisotropic g values of 1.956, 1.893, and 1.775

(8) Methanolic solutions of 5,7-dichloro-8-quinolinol plus aqueous hydroxide give a solution with a maximum about 385 nm. Therefore, the shoulder below 400 nm in curve C of Figure 1 is logically assigned to the 5,7-dichloro-8-quinolinolate ion. Quantitative evaluation of the near-ultraviolet region was not possible owing to the use of a mixed solvent system which was necessary due to the solubility of the species involved.

(9) (a) B. R. McGarvey, *Inorg. Chem.*, **5**, 476 (1966); (b) R. G. Hayes, *J. Chem. Phys.*, **44**, 2210 (1966); (c) D. P. Rillema and C. H. Brubaker, Jr., *Inorg. Chem.*, **9**, 397 (1970). The implication in ref 7a that the esr results in ref 9a and 9b are not useful for stereochemical predictions is incorrect. The esr spectra of the tetraalkylammonium salt in which the octacyano complex has D_2 symmetry are *not* the same as the esr spectra of corresponding D_{4d} species (R. A. Pribush and R. D. Archer, to be published elsewhere). The evaluations made by McGarvey and Hayes are both reasonable and useful.

(10) F. K. Kneubühl, *J. Chem. Phys.*, **33**, 1074 (1960).

TABLE I
ELECTRON SPIN RESONANCE PARAMETERS FOR TUNGSTEN(V) 8-QUINOLINOL COMPLEXES[a]

Complex	Temp, °K	⟨g⟩	g_1	g_2	g_3	⟨A⟩	A^e	B^e	C^e
[W(QCl₂)₄]Cl	298	1.872					85		
	77	(1.875)[c]	1.956	1.893	1.775	(89)	88	76	104
	77	(1.875)	1.954[d]	1.892[d]	1.779[d]				
[W(QBr₂)₄]Cl	77	(1.875)	1.955	1.892	1.778	[g]	81	f	113
[W(QI₂)₄]Cl[b]	77	(1.871)	1.953	1.881	1.779		f	f	f
[W(QBrMe)₄](QBrMe)[b]	77	(1.874)	1.957	1.893	1.774	(80)	76	61	104
[W(QBr)₄]Cl[b]	77	(1.872)	1.955	1.886	1.774		91	f	103
[W(QAc)₄]Cl[b]	77	(1.875)	1.955	1.890	1.784		77[g]	f	102

[a] Solvent and glass matrices of CH_2Cl_2; g values ±0.001 and hyperfine values in gauss (±5 G).   [b] Not a completely pure sample.   [c] Calcd values given in parentheses; ⟨g⟩ = (g_1 + g_2 + g_3)/3; calcd ⟨A⟩ = (A + B + C)/3.   [d] Powdered solid, not in solvent matrix.   [e] Gauss.   [f] Unobserved, obscured by peak broadness or solubility limitations.   [g] Based on only one hyperfine line observation.

TABLE II
ELECTRONIC ABSORPTION SPECTRA OF TUNGSTEN(V) 8-QUINOLINOL COMPLEXES[a]

[W(QCl₂)₄]Cl	[W(QBr₂)₄]Cl	[W(QI₂)₄]Cl[d]	[W(QBrMe)₄]-(QBrMe)[d]	[W(QBr)₄]Cl[d]	[W(QAc)₄]Cl[d]	Tentative assignments
12.2(sh; 1400)	12.2(sh; 500)	12.3(sh; 1300)	12.2(sh; 1000)	12.3(sh; 380)	13.1(sh; 130)	d ← d
13.5(sh; 1950)	13.6(sh; 800)	13.7(sh; 1630)	13.9(sh; 1500)	c	c	d ← d
18.3(19,700)[b]	18.5(10,200)	18.3(20,000)	18.3(12,400)	18.9(9600)	19.2(24,000)	d ← π(n)[e,f]
19.5(sh; 13,200)	19.5(sh; 8500)	c	19.4(sh; 10,300)	c	20.8(sh; 10,000)	d ← π(n)[f]
21.2(sh; 5200)	c	c	20.9(sh; 6600)	21.7(sh; 6400)	21.9(sh; 5600)	d ← π(n)
25.0(sp; 10,500)	25.3(sh; 9500)	c	25.4(sh; 10,000)	26.2(sh; 11,000)	27.0(sh; 17,000)	¹Lₐ[f]
27.4(sp; 11,000)	27.7(sh; 12,100)	27.2(sp; 15,000)	27.9(sp; 12,200)	28.4(sh; 13,500)	29.0(sh; 15,000)	¹L_b[f]

[a] The values given are in kK, where 1 kK = 1000 cm⁻¹; the numbers in parentheses are ε values; sh = shoulder; sp = satellite peak.   [b] This peak appears at *ca.* 17.7 kK in a hexachlorobutadiene mull.   [c] Unobserved.   [d] Sample only about 95–99% pure.   [e] [W-(QClNO₂)₄]Cl has a maximum at 18.7 kK.   [f] The π* ← d transition may be combined with one of these transitions.

have been assigned with corresponding hyperfine values of 88, 76, and 104 G. These values yield ⟨g⟩ = 1.875 and ⟨A⟩ = 89 G. Because of the broad lines and the uncertainty in assigning absolute values under broadening conditions, these values are within experimental (and interpretational) error of the room-temperature isotropic values. A powder spectrum gave equivalent g values (Table I). Broadness makes g_1 and g_2 overlap sufficiently that interpretation as $g_\perp$ would be logical if the CH_2Cl_2 glasses had not been studied.

The possibility of stereochemical nonrigidity for eight-coordinate systems[5a,11] suggests that the observed spectra could be the result of two isomers or minima in the stereochemical nonrigidity potential energy surface in which one isomeric form has $g_{\parallel}$ = 1.775 and another has $g_{\parallel}$ = 1.956, with both isomers possessing $g_\perp$ values near 1.90.[11d] This interpretation appears improbable because all six tungsten(V) derivatives exhibit very similar electron spin resonance spectra with no detectable changes in relative intensities from one derivative to another. The possibility that all six derivatives have almost equal amounts of two configurations appears unlikely. Several other possible interpretations of the low-temperature spectra have been considered and ruled out on probability or hyperfine coupling considerations.

The electronic absorption spectrum of [W(QCl₂)₄]Cl in dichloromethane is shown in Figure 3. The spectrum is characterized by two low-energy transitions in the near-infrared region as well as an intense (ε >10⁴) peak near 18,200 cm⁻¹. The detailed spectra of six of the tungsten(V) species are given in Table II.

The infrared vibrational spectrum of [W(QCl₂)₄]Cl

(11) (a) E. L. Muetterties, *Inorg. Chem.*, **4**, 569 (1965); (b) E. L. Muetterties, *Rec. Chem. Progr.*, **31**, 51 (1970); (c) D. G. Blight and D. L. Kepert, *Theor. Chim. Acta*, **11**, 51 (1968). (d) Two isomers could be frozen into the glass matrices if two isomeric minima occur in the solution stereochemical nonrigidity potential energy surface, even though (as noted by a reviewer) no intramolecular rearrangement is anticipated in the solid state.
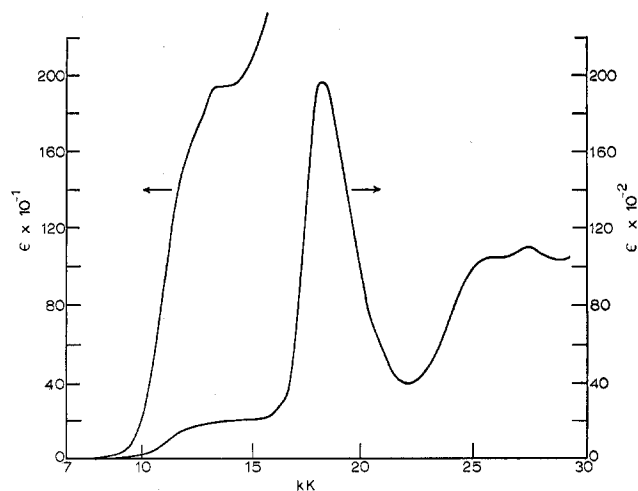

Figure 3.—Electronic absorption spectra of [W(QCl₂)₄]Cl in dichloromethane at room temperature, where 1 kK = 1000 cm⁻¹.

is typical of complexed 8-quinolinolates;[12] *e.g.*, an absorption at or just above 1100 cm⁻¹ indicative of coordinated 8-quinolinol[12] was found at 1115 cm⁻¹. No attempt has been made to assign metal–ligand stretches. A copy of a typical spectrum is available from the authors upon request.
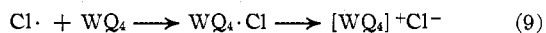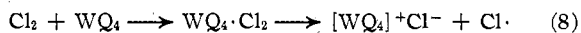
Discussion

For the purposes of discussion, the tungsten(V) tetrakis(8-quinolinolato) derivatives are formulated as monomeric, completely chelated eight-coordinate cations. Low solubilities precluded meaningful molecular (or average ionic) weight measurements, but electrophoresis experiments have confirmed the salt-like nature of the products. The disproportionation reaction suggests a coordination similarity with the tung-

(12) R. G. Charles, H. Freiser, R. Friedel, L. E. Hilliard, and W. D. Johnston, *Spectrochim. Acta*, **8**, 1 (1956).

sten(IV) complexes,[4] one of which is known to be eight-coordinate and completely chelated.[1a]

Synthesis and Reactivity.—A plausible mechanism for the oxidation of the WQ_4 species[4] to $[WQ_4]^+$ involves direct electron transfer. The chlorine oxidation is very rapid and indicative of such a process. A possible reaction path might be

$$Cl_2 + WQ_4 \longrightarrow WQ_4 \cdot Cl_2 \longrightarrow [WQ_4]^+Cl^- + Cl \cdot \quad (8)$$

$$Cl \cdot + WQ_4 \longrightarrow WQ_4 \cdot Cl \longrightarrow [WQ_4]^+Cl^- \quad (9)$$

Reaction mechanisms for the other reactions are less certain. The fact that the $[WQ_4]^+$ species are formed with melts of the more acidic dihalo derivatives, whereas no evidence of such an oxidation has been found in the parent 8-quinolinol melts, suggests that the proton (or the Q^- ion) is involved in the melt redox processes, possibly

$$H^+ + WQ_4 \rightleftarrows WQ_4 \cdot H^+ \rightleftarrows [WQ_4]^+ + H \cdot \quad (10)$$
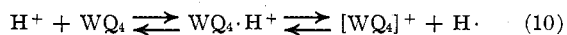
In the melt reactions the hydrogen radical probably is scavenged by the excess ligand which easily can be reduced to the 1,2,3,4-tetrahydro-8-quinolinol derivative.[13]

Although the tungsten(V) complex of 5,7-dichloro-8-quinolinol is formed from the tungsten(IV) complex with a variety of oxidizing agents, pure complexes with a variety of ligands are somewhat difficult to obtain because of the subsequent disproportionation reaction (eq 7). Evidence for comparable tungsten(V) complexes with other 8-quinolinol derivatives has been obtained from absorption and electron spin resonance spectra.

The disproportionation reaction has been used to aid in purifying the corresponding tungsten(IV) complexes.[4b] The tungsten(VI) species was characterized by infrared spectroscopy, and its identity as tungstate is quite logically based on known tungsten(VI) chemistry[14] and the disproportionation reaction spectral observations.

Electron Spin Resonance Spectra.—The electron spin resonance spectra are most consistent with the $[WQ_4]X$ species as pseudo-dodecahedral isomers of $D_2\text{-}gggg$ or $C_2\text{-}mmgg$[15] with $g_3 = g_z$ and with g_1 and g_2 equal to g_x and g_y, but not necessarily in that order. The separation of g_1 and g_2 is only slightly over half the separation of g_2 and g_3 (average < 0.58), and g_z or $g_{||}$ is expected to be further from 2.0023 than are g_x and g_y or $g_\perp$ in

dodecahedral or pseudo-dodecahedral stereochemistries in which the unpaired electron is in the d orbital of b_1 symmetry (in the D_{2d} point group).[9,16] The hyperfine splitting associated with g_z or $g_{||}$ (C in Table I) should be of greater magnitude than the hyperfine splittings associated with g_x and g_y (A and B in Table I) as is observed. Finally, the nonequivalence of g_x and g_y is indicative of isomerization from the "pure" D_{2d} stereochemistry (the *mmmm* isomer) observed for $W(QBr)_4 \cdot C_6H_6$.[1a] The x and y coordinates are equivalent in D_{2d} symmetry. Isomerization also had been considered a strong possibility for the tungsten(IV) dihalo derivatives based on the electronic absorption spectra of $W(QCl_2)_4$ and $W(QBr_2)_4$ relative to the monohalo and unsubstituted tungsten(IV) complexes.

The consistency of $\langle g \rangle$ from room temperature to liquid nitrogen temperatures gives no indication of stereochemical nonrigidity. However, the absence of a significant shift does not prove that the species are rigid. The possibility of one isomer predominating at all temperatures is quite possible.

Electronic Spectra.—The spectral assignments cannot be made with absolute certainty. However, position, intensity, and substituent effects are helpful in deducing tentative assignments.

The two low-intensity near-infrared transitions are logically assigned as d–d transitions from the $d_{z^2-y^2}$ orbital (b_1 orbital in D_{2d} symmetry and sometimes designated as d_{xy} when the C_2 symmetry axes are not used as a basis for assigning the Cartesian coordinates). The observation of only one transition for the complexes without 7-halo substitution is consistent with the larger d-orbital splitting expected when less repulsion exists between the oxygen donors. More details on the 7-halo substitution problem have been discussed previously.[4a] The first transition appears at a similar energy for the 5-bromo derivative and the 7-halo-substituted species, but the second transition is masked by the visible charge-transfer band even though the charge-transfer band is at a higher energy than in the 7-halo-substituted species. Even the first d–d transition is at higher energy for the 5-acetyl derivative and again the second is obscured. The 12–14-kK energy range is logical for 8-quinolinol ligands. The first d–d transition in the $[W(CN)_8]^{3-}$ ion is apparently near 25 kK, although the exact position is uncertain. The band appears to be obscured by or mixed with charge-transfer transitions.[17] The asymmetry of the first observed transition[17,18] in $[W(CN)_8]^{3-}$ is quite apparent, such that the original interpretation as a simple d–d transition at 28.0 kK[18] is questionable. Allowing for oxygen donors rather than cyanide the transitions observed from 12 to 14 kK are consistent with the lower ligand field strength. The energies of d–d transitions for cyanide complexes are 1.5 to 3.0 times that of oxygen donors, such as water.[19]

Interpretation of the more intense transitions in the visible spectra as transitions to the metal d level from

(13) S. Szmaragd and E. Briner, *Helv. Chim. Acta*, **32**, 1278 (1949). Evidence for the reduced species in our tungsten reactions comes from the proton magnetic resonance spectra in CD_3OD of sublimates of residues from the reaction of $W(CO)_6$ and HQCl. In addition to a residual OH at -4.20 ppm, broad peaks at -2.79 and -1.61 ppm are consistent with the ortho (b) and the meta and para (a) protons of the

a
a
b
N
H
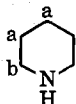
moiety; *cf.*, R. M. Silverstein and G. C. Bassler, "Spectroscopic Identification of Organic Compounds," Wiley, New York, N. Y., 1967, p 137. No N–H signal was observed, which is consistent with the usual quadrupolar broadening; *cf.* R. M. Silverstein and G. C. Bassler, *ibid.*, p 123.

(14) R. V. Parish, *Advan. Inorg. Chem. Radiochem.*, **9**, 315 (1966).

(15) The isomer designations are based on the Hoard-Silverton notation (ref 5a). The four dodecahedral isomers which have phenolic oxygens in the A positions are shown in ref 1a. The possibility of a partial N ↔ O isomerization cannot be ruled out conclusively but is considered unlikely electronically; *cf.* ref 1a.

(16) B. R. McGarvey, *J. Chem. Phys.*, **37**, 2001 (1962).

(17) A. Golebiewski and H. Kowalski, *Theor. Chim. Acta*, **12**, 293 (1968).

(18) J. R. Perumareddi, A. D. Liehr, and A. W. Adamson, *J. Amer. Chem. Soc.*, **85**, 249 (1963).

(19) C. K. Jørgenson, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962, p 113. Exact assignments of the d-d transitions (*i.e.*, $a_1 \leftarrow b_1$, etc.) cannot be made unambiguously because of the severe angle and parameter dependence of the d-like energy levels; *cf.* D. W. Smith, *J. Chem. Soc. A*, 1024 (1971), and references cited therein.

the oxygen lone pairs of π symmetry is based on the observed shifts to higher energy for the series 5,7-dihalo, 7-bromo-5-methyl < 7-chloro-5-nitro < 5-bromo < 5-acetyl. The polarization of the oxygen lone pairs by a halogen in the 7 position should lower the energy of any ligand to metal transition relative to 5-bromo species, and the π-attracting nitro and acetyl groups should make the transfer of electron from the π symmetry oxygen more difficult than in other complexes which have an electron-donating halogen in the same (5) position.

The inverse charge-transfer transition observed for the tungsten(IV) complexes[4a] should be shifted toward higher energies because only one electron is in the b_1 level in the tungsten(V) species, eliminating the electron–electron repulsion which undoubtedly lowers the energy in the tungsten(IV) species. Whether this transition is combined with one of the other transitions in the tungsten(V) complexes or lies at higher energy further out in the ultraviolet has not been ascertained. None of the observed absorption bands shows the shifts expected for a transition primarily from ligand to metal.

The near-ultraviolet absorptions have been assigned as intraligand transitions analogous to previous assignments by others.[20] The second peak (27.2–29.0 kK) could be a second ^1L_a band if the isomer is *mmgg* or if configurational interactions split the ^1L_a transitions appreciably. The ^1L_a and ^1L_b bands are usually further separated in 8-quinolinol complexes and, further, unreported transitions are observed in the ultraviolet region at even higher energies.

A recent report of tetrakis(8-quinolinolato)niobium(IV) by Deutscher and Kepert[21] assigns a transition at 12.3–12.5 kK (diffuse reflectance to solution) as d to π and 17.7 to 19.15 (diffuse reflectance to solution) as π to d without justification, although Deutscher may have clearly assigned these elsewhere.[22] We find a 0.6-kK shift from mull to solution for our main ligand to metal transition in $[W(QCl_2)_4]Cl$ which appears logical for our ionic complex; *i.e.*, the chloride ions in intimate contact with the cation polarize the nonbonding electrons of the oxygen causing a ground-state destabilization. We observed no detectable shift for our d to π transition for the corresponding tungsten(IV) complex. The large shift observed by Deutscher and Kepert for their neutral niobium(IV) complex (17.7–19.15 kK) is somewhat surprising.

Magnetic Moment.—The magnetic moment of 1.7 BM for the $[W(QCl_2)_4]^+$ species at room temperature is only approximate and may be as low as 1.6 BM, again between the spin-only value and the even lower values reported for the octahedral alkoxy species (*e.g.*, 1.36 BM for $[W(OC_2H_5)Cl_5]^-$ and 1.53 BM for $[W(OC_2H_5)_2-Cl]^-$).[10c] Niobium(IV) oxine is reported to possess a room-temperature magnetic moment of 1.60 BM.[21]

Summary

Tungsten(V) eight-coordinate complexes with bidentate ligands appear to exist at least when four π donors and four π acceptors are used in ligating atoms. The generality of this type for eight-coordinate d[1] complexes is still uncertain. However, the tungsten(V) complexes appear to be more stable than the corresponding niobium(IV) species, recently synthesized by Kepert and Deutscher.[21] Both series of d[1] complexes are plagued with redox problems. The niobium(IV) complexes are easily oxidized, whereas the acid-stable tungsten(V) complexes disproportionate in base to the very stable d[2] tungsten(IV) chelate and the well-known d[0] tungstate ion. Electron spin resonance results imply a distorted dodecahedral structure for the tungsten(V) complexes.

Experimental Section

Solvents.—Reagent grade solvents were dried and distilled under prepurified nitrogen according to the procedures given previously.[4b]

Ligands.—The ligands, except for the methyl derivatives, were obtained from Aldrich Chemical Co. and resublimed prior to use.

5-Methyl-8-quinolinol.—This compound was prepared using a Skraup reaction, modifying the method used by Hollingshead.[23] 2-Amino-4-methylphenol (10.04 g, 81.7 mmol), prepared from 4-methyl-2-nitrophenol using the method of Proskouriakoff and Titherington,[24] was intimately mixed with 6.20 g (40.6 mmol) of 4-methyl-2-nitrophenol. Glycerine, which had been dried by heating to $180 \pm 5°$ for 45 min and allowed to cool in a desiccator over P_4O_{10}, was added to the solid mixture in a 2-l. flask. To the resulting dough-like mixture under a hood was added 20.1 g of H_2SO_4 in small portions, causing an exothermic reaction. The yellow-brown liquid was then heated under reflux conditions for 4 hr and then set aside to cool. The resulting brown solid was broken up, dissolved in 400 ml of H_2O, and made slightly acid (pH 3–4) with glacial acetic acid. This solution was steam distilled, yielding a lime-green distillate. Addition of 5 M NH_4OH until slightly basic caused precipitation of 5-methyl-8-quinolinol. The crude product (yield, 93%) was washed well with water, dried overnight *in vacuo* over KOH, and recrystallized as small needles from boiling ethanol.

Anal. Calcd for $C_{10}H_9NO$: C, 75.45; H, 5.70; N, 8.80. Found:[25] C, 75.22; H, 5.73; N, 8.82.

7-Bromo-5-methyl-8-quinolinol.—This compound was prepared by a modification of a method used by Beauford and Beauford.[26] 5-Methyl-8-quinolinol (6.55 g, 41.2 mmol) was dissolved in 80 ml of glacial acetic acid, and 41 ml of a 5.4% (v/v) Br_2 solution in glacial acetic acid was added dropwise over a period of 30 min. The reaction mixture was allowed to stand for 2 hr and then made neutral with *ca.* 71 ml of concentrated NH_4OH. After cooling, the off-white precipitate was collected and washed with copious amounts of H_2O, followed by a wash with a few milliliters of a 50% (v/v) aqueous ethanol solution. The product was dried overnight *in vacuo* over KOH pellets, yield 99%. The product was recrystallized with boiling 95% ethanol and redried *in vacuo* over KOH.

Anal. Calcd for $C_{10}H_8NOBr$: C, 50.45; H, 3.39; N, 5.88. Found:[25] C, 50.82; H, 3.39; N, 5.80.

Reaction of Tetrakis(5,7-dichloro-8-quinolinolato)tungsten(IV) with Chlorine.—Tetrakis(5,7-dichloro-8-quinolinolato)tungsten(IV) (0.1 g, 1 × 10^{-4} mol), prepared as previously described,[4b] was dissolved in 100 ml of azeotropically distilled carbon tetrachloride. When 25 ml of a saturated Cl_2–CCl_4 solution was added to this solution with constant stirring, a fine purple precipitate quickly formed. The complex was collected by filtration and washed with an additional 100 ml of carbon tetrachloride. Drying overnight *in vacuo* at room temperature produced 0.1 g of the complex, a stoichiometric quantity.

Anal. Calcd for $W(C_6H_4NOCl_2)_4Cl$: C, 40.36; H, 1.51; N, 5.23; Cl, 29.78. Found: C, 40.40; H, 1.60; N, 5.10; Cl, 29.10.

The product is soluble in dichloromethane, chloroform, and methanol and very slightly soluble in hot benzene and carbon tetrachloride. Attempts to exchange the cationic complex on

(20) (a) L. Morpurgo and R. J. P. Williams, *J. Chem. Soc. A*, 73 (1966); (b) H. H. Perkampus and K. Kortum, *Z. Anal. Chem.*, **190**, 111 (1962).

(21) R. L. Deutscher and D. L. Kepert, *Inorg. Chim. Acta*, **4**, 645 (1970).

(22) R. L. Deutscher, Ph.D. Thesis, University of Western Australia, 1969, quoted in ref 21.

(23) R. G. W. Hollingshead, *Anal. Chim. Acta*, **12**, 201 (1955).

(24) A. Proskouriakoff and R. J. Titherington, *J. Amer. Chem. Soc.*, **52**, 3978 (1930).

(25) Analyses by C. Meade, University of Massachusetts Microanalytical Laboratory.

(26) A. Beauford and G. Beauford, French Patent M2346 (March 22, 1964); *cf. Chem. Abstr.*, **61**, 646d (1964).

a Dowex 50W-8(20-50 mesh) strongly acidic cation exchange resin (Na$^+$ form) in anhydrous methanol failed. However, the purple species migrated toward the cathode compartment of a Gelman cellulose polyacetate electrophoretic apparatus operated at 300 V and 1.0 mA with a KCl-saturated methanol electrolyte.

This complex is reasonably stable to treatment with dilute hydrochloric or nitric acids but undergoes a 1:1 stoichiometric disproportionation when allowed to react with excess 0.1 N methanolic KOH solution (Figure 1) or allowed to stand in "wet" reagent grade CH_2Cl_2 or C_6H_6. Stirring dichloromethane solutions of the complex with mossy tin or copper turnings converts $[W(QCl_2)_4]Cl$ to $W(QCl_2)_4$ as shown by comparison of the visible spectra. Although treatment of carbon tetrachloride solutions of $W(QCl_2)_4$ with Br_2–CCl_4 appears to yield results similar to those outlined above, $W(QCl_2)_4$ solutions treated with I_2–CCl_4 appear unchanged.

Reaction of Tetrakis(5,7-dichloro-8-quinolinolato)tungsten(IV) with 72% Perchloric Acid.—Tetrakis(5,7-dichloro-8-quinolinolato)tungsten(IV) (0.59 g, 5.7 × 10^{-4} mol) was stirred in the air with 300 ml of dichloromethane to which 100 ml of ethanol was slowly added. Addition of 70–72% perchloric acid (30 ml, 0.35 mol) to the ethanol–dichloromethane mixture resulted in the immediate formation of a deep purple solution. After stirring for 5 min the solution was filtered to remove about 10 mg of the unreacted tungsten(IV) complex. This filtrate was washed four times with equal volumes of water in a separatory funnel and dried by shaking with 20.0 g of calcium chloride. The solution was again filtered and rotary evaporated at room temperature under a water-aspirator supplied vacuum. This material was dried overnight at room temperature over P_4O_{10} *in vacuo*, yield 0.15 g, 23%.

Anal. Calcd for $W(C_9H_4NOCl_2)_4ClO_4$: C, 38.05; H, 1.41; N, 4.93; Cl, 28.13. Found:[26] C, 38.20; H, 1.87; N, 5.27; Cl, 25.98. The low chlorine value may be related to the decomposition method employed.

Reaction of Tetrakis(5,7-dichloro-8-quinolinolato)tungsten(IV) with 5,7-Dichloro-8-quinolinol.—Tetrakis(5,7-dichloro-8-quinolinolato)tungsten(IV) (0.1 g, 9.7 × 10^{-5} mol) and 5,7-dichloro-8-quinolinol (15.0 g, 0.07 mol) were sealed in a melt flask (in the usual manner[4b]). After 8 hr of reaction at 190°, the melt had become deep purple in color. Excess ligand was removed by sublimation at 160° (0.1 mm). The residue was washed with carbon tetrachloride until no blue-green WQ_4 remained and then dissolved in 200 ml of dichloromethane. Visible absorption spectra (14,000–25,000 cm^{-1}) of the carbon tetrachloride washings were similar to those of the WQ_4 starting material while the dichloromethane spectrum was comparable to that of $[WQ_4]Cl$ prepared by chlorine oxidation.

Tetrakis(5,7-dibromo-8-quinolinolato)tungsten(V) Chloride.—The crude blue tungsten(IV) chelate, $W(QBr_2)_4$,[4a] was extracted with dry, air-free benzene under a nitrogen atmosphere for several hours. The extraction solution was filtered and treated with a solution of Cl_2 in CCl_4. The purple tungsten(V) complex was dried *in vacuo* at room temperature over P_4O_{10}.

Anal. Calcd for $W(C_9H_6NOBr_2)_4Cl$: C, 30.30; H, 1.13; N, 3.93. Found:[26] C, 30.20; H, 1.41; N, 3.97.

Tetrakis(7-bromo-5-methyl-8-quinolinolato)tungsten(V) 7-Bromo-5-methyl-8-quinolinolate.—In an attempt to prepare the tungsten(IV) chelate with the 7-bromo-5-methyl-8-quinolinol ligand, 0.47 g (1.34 mmol) of $W(CO)_6$ and an excess of the ligand (1.70 g, 7.14 mmol) were dissolved in 75 ml of dry, oxygen-free

pyridine. The mixture was heated in a nitrogen atmosphere under reflux conditions for 8 hr yielding a blue-green solution. The crude tungsten(IV) product was obtained by flash evaporating the solvent. During the subsequent 15-hr vacuum sublimation at 125° to remove excess ligand and any volatile impurities, the complex oxidized to the violet tungsten(V) complex as indicated by electronic and electron spin resonance spectra.

Anal. Calcd for $W(C_{10}H_7NOBr)_4(C_{10}H_7NOBr)$: C, 43.86; H, 2.58; N, 5.11. Found: C, 45.05; H, 3.07; N, 4.63. The purity was less than ideal, but sufficient for spectral comparisons.

Other Complexes.—The other tungsten(V) chelates studied were prepared analogously to the method indicated above for the dibromo derivative and have been used for spectral comparisons. Complete oxidation was checked *via* absence of strong (ϵ <10^4) 700-nm peak of the tungsten(IV) chelate.

Electronic Spectra.—Electronic spectra of the complexes were recorded from 5000 to 30,000 cm^{-1} on a Hitachi Model EPS-3T spectrophotometer at room temperature. Matched Supracil cells of 1.000-cm path length were employed in the double-beam measurements. The reference contained the same solvent as the solution.

Infrared Spectra.—Infrared spectra of the substituted quinolinol complexes were recorded on a Beckman Model IR-10 spectrophotometer. The potassium bromide disk technique was used in which 1–3 mg of sample was ground with 0.2 g of KBr (Harshaw Chemical Co., Infrared Quality reagent) for about 15 min pressed into a disk (0.5 in. diameter × 2 mm) with a ram and die under 20,000 psi for 15–20 min. Samples were run against a similarly prepared KBr reference pellet.

Electron Spin Resonance Spectra.—The esr spectra were recorded at room and liquid nitrogen temperatures in dichloromethane (10^{-4} to 5 × 10^{-3} M) on a Varian E-9 spectrometer. The field was measured by reference to an internally sealed sample of N,N-diphenylpicrylhydrazyl. Interpretation of the low-temperature solid solution spectra followed the procedures suggested by Sands[27] and Kneubühl.[10]

Magnetic Susceptibility Measurements.—The Faraday method was used for determining the magnetic susceptibility. $CoHg(SCN)_4$ was used to calibrate the balance. Sample size was *ca.* 1 mg. Diamagnetic corrections were made using the value given by Selwood[28] for the tungsten(IV) core and by direct measurement of the ligand paramagnetism. The ligand paramagnetism was within experimental error of that obtained from Pascal's constant summation.[28]

(27) R. H. Sands, *Phys. Rev.*, **99**, 1222 (1955).

(28) P. W. Selwood, "Magnetochemistry," Interscience, New York, N. Y., 1956.