the mercury(II)–cyclohexanediaminetetraacetate (Hg–CyDTA) complex brought about by complexing anions. These workers concluded that the anions, coordinated to Hg ions in ternary Hg–anion–CyDTA complexes, facilitate the formation of a nitrogen-protonated intermediate and thus accelerate the overall acid dissociation of the complex. Hydrogen ion and anion dependencies of the line broadening in the HgEGTA spectrum suggest that the anions play a similar role in the dissociation of the HgEGTA complex. However, more quantitative information on the ternary complexes in the EGTA system would be necessary before the detailed mechanism and the rate constants for the dissociation reaction can be established.

Acknowledgments.—The authors thank Drs. J. S. Leigh, Jr., and Jacques Reuben for their comments on the manuscript.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, GOESSMANN LABORATORY,
UNIVERSITY OF MASSACHUSETTS, AMHERST, MASSACHUSETTS 01002

Transition Metal Eight-Coordination. II. Synthesis and Characterization of Several Tetrakis(8-quinolinolato)tungsten(IV) Chelates[1a]

BY WESLEY D. BONDS, JR., AND RONALD D. ARCHER*

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A series of tungsten(IV) 8-quinolinol complexes of the type WL_4 (where L = 8-quinolinol or a derivative thereof) has been synthesized and spectrally and magnetically characterized. For L = 5-chloro-, 5-bromo-, 5,7-dichloro-, and 5,7-dibromo-8-quinolinolato, synthesis is feasible from sealed-tube melt reactions between either $K_3W_2Cl_9$ or $W(CO)_6$ and the appropriate quinolinol derivative. For the parent complex, salts of $W_2Cl_9^{3-}$ are required. Synthesis in high-boiling basic organic solvents is also feasible as shown by the synthesis of the L = 5-acetyl-8-quinolinolato derivatives from $W(CO)_6$ and the ligand in pyridine. Chemical investigation indicates inertness to alcoholic KOH. Electronic spectra (5–36 kK) of these complexes display low-energy charge-transfer bands (14–15 kK, $\epsilon > 10^4$) plus the ligand transitions usually observed in 8-quinolinol complexes with other metal ions. The dihalo derivatives also show two low-intensity bands in the near-infrared region (9.9–11.2 kK) which are absent in the other derivatives. Magnetic measurements indicate that the complexes are spin paired. Together the observations constitute evidence for the first unequivocal series of inert, completely chelated eight-coordinate complexes of d^2 spin-paired electronic configuration.

Introduction

Although hundreds of octahedral complexes are known which are inert to substitution reactions, the octacyano ions were the only substitution-inert eight-coordinate complexes known prior to this study.[2] Whereas most eight-coordinate complexes of transition elements are d^0 or easily oxidized d^1 complexes,[3] we have synthesized a series of completely chelated, spin-paired d^2 eight-coordinate complexes which are inert to alcoholic KOH.

A stereochemical rule regarding the geometry in transition metal eight-coordinate species was formulated by Orgel in 1960.[4] He suggested that eight-coordinate systems of the type MA_4B_4 (M = d^2 metal ion; A = ligand without π-acceptor properties; B = π-acceptor ligand) should adopt a dodecahedral stereochemistry with the π-acceptor B ligands forming a flattened tetrahedral array to give maximum overlap with the filled metal $d_{x^2-y^2}$ orbital, while nonacceptor A ligands should occupy the elongated tetrahedral positions of the dodecahedron. Hoard and Silverton[5] later designated these positions as B and A dodecahedral sites, respectively. The proposal by Orgel was based on the reported stoichiometries of $Mo(CN)_4(OH)_4^{4-}$,[6] $W(CN)_4(OH)_4^{4-}$,[6] $Mo(CN)_4(OH)_3H_2O^{3-}$,[6,7] and $ReCl_4(diars)_2^+$.[8] Recent crystallographic and infrared evidence[9] has disproved the formulation of the molybdate and tungstate species, and the $ReCl_4(diars)_2^+$ structure is unknown. The steric bulk of the diars and chloride ligands may preclude electronic structure control; therefore, other MA_4B_4 complexes appeared necessary if Orgel's postulate were to be checked.

The preparation of MA_4B_4 complexes of d^2 electronic configuration with four π-acceptor ligating atoms and four other donors should allow an evaluation of Orgel's postulate. The ligand 8-quinolinol appeared ideal because the unsaturated nitrogen atoms are σ donors

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[1] Taken in part from the Ph.D. dissertation of W. D. B., University of Massachusetts, 1970. Abbreviations: HQ, 8-quinolinol; HQCl, 5-chloro-8-quinolinol; $HQCl_2$, 5,7-dichloro-8-quinolinol; etc. 1 kK = 1000 cm^{-1}. Part I: R. D. Archer and W. D. Bonds, Jr., *J. Amer. Chem. Soc.*, **89**, 2236 (1967).

[2] (a) A. W. Adamson, J. P. Welker, and M. Volpe, *ibid.*, **72**, 4030 (1950); (b) E. L. Goodenow and C. S. Garner, *ibid.*, **77**, 5268 (1955); (c) H. Baadsgaard and W. D. Treadwell, *Helv. Chim. Acta*, **38**, 1669 (1955).

[3] (a) E. L. Muetterties and C. M. Wright, *Quart. Rev., Chem. Soc.*, **21**, 109 (1967); (b) S. J. Lippard, *Progr. Inorg. Chem.*, **8**, 109 (1967); (c) R. V. Parish, *Coord. Chem. Rev.*, **1**, 439 (1966). However (d) D. G. Hendricker and R. L. Bodner, *Inorg. Nucl. Chem. Lett.*, **6**, 187 (1970), and (e) 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; (f) A. Clearfield, P. Singh, and I. Bernal, *Chem. Commun.*, 389 (1970).

[4] L. E. Orgel, *J. Inorg. Nucl. Chem.*, **14**, 136 (1960). For π bonding Orgel only considered π-acceptor ligands. He classed π donors as non-π-bonding ligands.

[5] J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, **2**, 235 (1963).

[6] (a) O. Collenberg, *Z. Anorg. Allg. Chem.*, **136**, 246 (1924); (b) W. R. Bucknall and W. Wardlaw, *J. Chem. Soc.*, 2981 (1927); and subsequent references, *e.g.*, K. N. Mikhalevich and V. N. Litvinehuk, *Russ. J. Inorg. Chem.*, **4**, 800 (1959).

[7] The corresponding tungsten species was also postulated.

[8] J. E. Fergusson and R. S. Nyholm, *Chem. Ind.* (*London*), 1555 (1958).

[9] (a) V. W. Day and J. L. Hoard, *J. Amer. Chem. Soc.*, **90**, 3374 (1968); (b) S. J. Lippard, H. Nozaki, and B. J. Russ, *Chem. Commun.*, 118 (1967); (c) S. J. Lippard and B. J. Russ, *Inorg. Chem.*, **7**, 1686 (1968). Interestingly, the anhydrous form of $K_2[Mo(CN)_4(OH)_2]$ was reported in 1932: (d) W. F. Jakob and C. Michalewicz, *Rocz. Chem.*, **12**, 576 (1932).

and potential π acceptors[10] whereas the phenolic oxygen atoms are easily ionized to give strong σ and π donation. In this paper we report the preparation and properties of a series of inert tetrakis tungsten(IV) complexes with 8-quinolinol and several derivatives which should allow a comparison with the labile MQ_4 complexes already reported (where M is a metal ion in oxidation state IV and Q is the anion of 8-quinolinol or a derivative thereof). Known species include tin(IV),[11] thorium(IV),[12] uranium(IV),[13] titanium(IV),[14] zirconium(IV),[15] hafnium(IV),[15] and niobium(IV)[16] complexes, which provide different types of metal–ligand bonding and a number of metal ion sizes for comparison with the WQ_4 species. A comparison of the d^0, d^1, and d^2 transition metal MQ_4 complexes should detect the isomerization predicted for MA_4B_4 systems with a change in electronic configuration. That is, the extension of Orgel's postulate to d^0 complexes predicts that π donors (rather than π acceptors) should occupy the B positions.[17]

The low solubility of the parent WQ_4 complex necessitated the preparation of other derivatives which in turn has led to the interesting results reported herein, a derivative which provided crystals suitable for a single-crystal X-ray study,[18] and the detection of some tetrakis d^1 complexes of tungsten(V).[19] A communication on the parent WQ_4 complex has appeared previously.[20] More synthetic details for WQ_4 are given herein.

Results

Synthesis.—We have uncovered a number of methods for preparing the WQ_4 derivatives, although the preferred method for a specific complex appears to depend on the properties of the ligand. Whereas the halogenated derivatives of 8-quinolinol (5-chloro, 5-bromo, 5,7-dichloro, and 5,7-dibromo) form the desired WQ_4 complexes by the reaction of the appropriate ligand and either salts of $W_2Cl_9^{3-}$ or $W(CO)_6$ in an anhydrous, anaerobic melt reaction, the reaction of 8-quinolinol with $W(CO)_6$ under similar conditions results in none of the desired products. The reaction of $W_2Cl_9^{3-}$ salts with 8-quinolinol does give the tetrakis complex.

The addition of sodium 8-quinolinolate to the melt reaction of 8-quinolinol and $(NH_4)_3[W_2Cl_9]$ accelerates the reaction very markedly. The blue-green color of the WQ_4 species was clearly visible after 1 min at 85°, whereas a similar reaction without the addition of the sodium salt required between 15 and 20 min at 160° to develop a tint of approximately the same intensity. Ionizable hydrogen is necessary for the $W(CO)_6$ reaction. When the reaction was attempted solely with the anionic form of the ligand, no reaction occurred.

Dissolution of the ligands and $W(CO)_6$ in pyridine (or derivatives) have allowed the preparation and isolation of other complexes. The 5-acetyl derivatives have been prepared pure by this method, and evidence for other derivatives has been obtained by spectral methods.

The discovery that the complexes are inert to alcoholic KOH has led to the use of methanol–water (1:2 v/v) solutions of KOH for purification of the complexes. Excess ligand and tungsten salts are soluble in the base solutions and any tungsten(V) species are partially recovered as the tungsten(IV) chelate as the result of a disproportionation reaction.[19]

Attempts to extend the above reactions to molybdenum with K_3MoCl_6 and $Mo(CO)_6$ have been unsuccessful. Instead, tarry residues suggestive of ligand decomposition have resulted.

Infrared Spectra.—The infrared spectra obtained for the complexes in the KBr region are typical of other complexed 8-quinolinol infrared spectra[21] as noted previously.[20] The absence of an OH stretch in double-beam measurements[20] allowed the conclusion that we were preparing tungsten(IV) complexes. A copy of a typical spectrum is available upon request from the authors.

Magnetic Susceptibility Measurements.—The room-temperature magnetic measurements on the halogenated complexes are indicated in Table I. The chelates are diamagnetic or may possess a small paramagnetism ($\leq$0.5 BM) common in lower valence "dia-

TABLE I

MAGNETIC PROPERTIES OF HALOGENATED 8-QUINOLINOL COMPLEXES OF TUNGSTEN(IV)

Complex	$10^6\chi_M$(exptl),[a] cgsu	$10^{16}\chi_M$(cor),[b] cgsu	μ, BM
W(5-chloro-8-quinolinolato)$_4$	-400 ± 100	70 ± 150	0.4[d]
W(5,7-dichloro-8-quinolinolato)$_4$	-550 ± 100	0 ± 150	0
W(5-bromo-8-quinolinolato)$_4$[c]	-500 ± 100	50 ± 150	0.4[d]
W(5,7-dibromo-8-quinolinolato)$_4$	-700 ± 100	100 ± 150	0.5[d]

[a] Measured by the Faraday method. [b] Diamagnetic corrections were made from ligand measurements and Pascal constants. [c] The benzene solvate was used for this salt. [d] Zero within experimental error.

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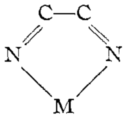
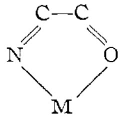
[10] Although nonchelated heterocyclic nitrogen donors are not always good π acceptors, complexes containing the



ring have long been considered as π acceptors. *E.g.*, (a) P. Krumholz, *J. Amer. Chem. Soc.*, **75**, 2163 (1953), showed that glyoxal and biacetyl complexes of iron(II) have properties similar to those of 2,2,-bipyridyl and *o*-phenanthroline complexes. All show a strong visible transition assigned as primarily $\pi^* \leftarrow d$ (*cf.* L. Morpurgo and R. J. P. Williams, *J. Chem. Soc. A*, 73 (1966), and R. J. P. Williams, *ibid.*, 137 (1955)). (b) K. Sone, *Bull. Chem. Soc. Jap.*, **25**, 1 (1952), has shown that the 8-quinolinol complex of iron(II) is of a similar type with an intense absorption at *ca.* 560 nm. The π-acceptor property coupled with the ease of oxidation of iron(II) and reduction of 8-quinolinol gives the iron(III) complex upon standing. Formally, the quinone resonance form gives a



ring. Our spectral observations also suggest reasonable π-acceptor properties by 8-quinolinol.

[11] K. Ramaiah and D. F. Martin, *Chem. Commun.*, 130 (1965).

[12] G. R. Horton and W. W. Wendlandt, *J. Inorg. Nucl. Chem.*, **25**, 247 (1963), and references cited therein.

[13] W. W. Wendlandt and G. R. Horton, *ibid.*, **19**, 272 (1961).

[14] D. Cunningham, I. Douck, M. J. Frazer, W. E. Newton, and B. Rimmer, *J. Chem. Soc. A*, 2133 (1969).

[15] M. J. Frazer and B. Rimmer, *ibid.*, *A*, 2273 (1968).

[16] R. L. Deutscher and D. L. Kepert, *Chem. Commun.*, 121 (1969).

[17] R. J. H. Clark, J. Lewis, R. S. Nyholm, P. Pauling, and G. B. Robertson, *Nature (London)*, **192**, 222 (1961).

[18] W. D. Bonds, Jr., R. D. Archer, and W. C. Hamilton, *Inorg. Chem.*, **10**, 1764 (1971).

[19] W. D. Bonds, Jr., and R. D. Archer, to be submitted for publication.

[20] R. D. Archer and W. D. Bonds, Jr., *J. Amer. Chem. Soc.*, **89**, 2236 (1967).

[21] (a) J. E. Tackett and D. T. Sawyer, *Inorg. Chem.*, **3**, 692 (1964); (b) R. G. Charles, H. Freiser, R. Friedel, L. E. Hilliard, and W. D. Johnston, *Spectrochim. Acta*, **8**, 1 (1956).

TABLE II

ELECTRONIC ABSORPTION SPECTRA OF 8-QUINOLINOL COMPLEXES OF TUNGSTEN(IV)[a]

WQ_4	$W(QCl)_4$	$[W(QBr)_4]\cdot C_6H_6$	$W(QCl_2)_4$	$W(QBr_2)_4$	Tentative assignment
...	...	...	9.9 (500)	9.9 (500)	d ← d
...	...	...	11.2 (450)	11.2 (450)	d ← d
14.3 (29,000)[b]	14.2 (34,000)	14.1 (33,400)	14.3 (32,700)	14.2 (33,500)	π^* ← d
15.3 (23,000)[b]	15.3 (21,300)	15.2 (23,000)	15.6 (22,200)	15.6 (21,100)	π^* ← d
25.6 (6000)[b]	24.4 (11,000)	24.3 (9200)	24.3 (9000)	24.6 (10,500)	Ligand
	30.6 (6500)	28.6 (7000)	30.0 (7200)	30.4 (7000)	Ligand
	32.3 (6500)	32.3 (6200)	32.1 (5500)	31.8 (6400)	Ligand

[a] Recorded at room temperature in dry, air-free benzene; absorption maxima are reported in kK; the number in parentheses denotes the extinction coefficient determined from measurements at three different concentrations. [b] Reported previously.[20]

magnetic" tungsten species and generally ascribed to temperature-independent paramagnetism.[22]

Electronic Absorption Spectra.—The electronic absorption spectra of these complexes (Table II) are characterized by two intense absorption maxima at the red end of the visible region (14.1–15.6 kK; ϵ (21–34) × 10^3), and in the case of the dihalo derivatives two bands in the near-infrared region also occur at 9.9 and 11.2 kK with $\epsilon \sim 500$. Higher energy bands typical of 8-quinolinol complexes appear at higher energies. Typical spectra are shown in Figure 1.

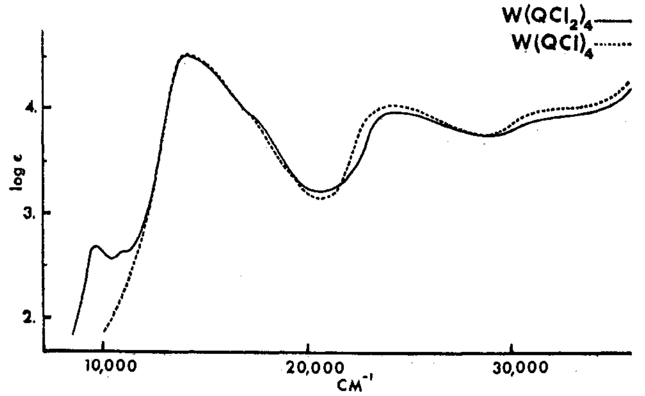


Figure 1.—The absorption spectra of $W(QCl_2)_4$ (———) and $W(QCl)_4$ (- - -).

Other Studies.—Attempts to determine the oxidation state of tungsten by oxidation with permanganate were precluded by the low precision of the method.[23] On the other hand, oxidation with 1 equiv of halogen does produce analogous WQ_4^+ species, which in turn disproportionate in base to give 50% WQ_4 and 50% tungsten(VI).[19]

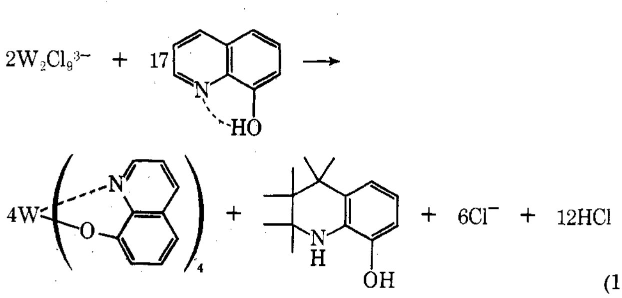
Low solubilities have thwarted attempts to determine the molecular weight of the WQ_4 species in solution. A single-crystal X-ray study of the benzene solvate of tetrakis(5-bromo-8-quinolinolato)tungsten(IV)[18] does show that these species can exist as discrete, monomeric, completely chelated, eight-coordinate tungsten complexes.

Chemically, the complexes are inert to base hydrolysis but can be decomposed by acids. Solutions of the complexes slowly decompose in solvents which have not been properly dried.

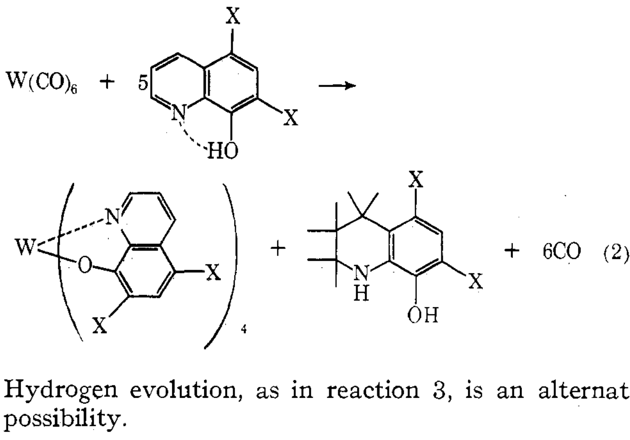
Discussion

Synthesis.—The synthesis of the tetrakis complexes of tungsten(IV) from both tungsten(III) and tungsten(0) starting materials is indicative of the stability of these eight-coordinate d^2 species. No details regarding the actual mechanism of the reaction have yet been undertaken. However, the high yields obtained for the reactions starting with tungsten hexacarbonyl appear to rule out a disproportionation reaction in terms of tungsten redox. By analogy we feel that a similar statement can be made for the tungsten(III) starting material.

The reduction of 8-quinolinol to the 1,2,3,4-tetrahydro derivative during the oxidation of $W_2Cl_9^{3-}$, as in eq 1, is feasible and is analogous to the chromium(II) study of King and Garner.[24] Since these authors offered no proof, we made an attempt to observe the tetrahydro or the 1,2-dihydro compound by fractional sublimation and fractional crystallization techniques without success. The reduced species are also complexing agents and may form mixed complexes which decompose during subsequent treatment. The preparation of the tetrakis dihalo species from tungsten hexacarbonyl and the appropriate ligand is indicated in eq 2.



(1)



(2)

Hydrogen evolution, as in reaction 3, is an alternate possibility.

$$W_2Cl_9^{3-} + 8HQ \longrightarrow 2WQ_4 + 3Cl + 6HCl + H_2 \qquad (3)$$

The greater reactivity of the melt reactions in the presence of the anionic form of the ligand is not sur-

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[22] B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience, New York, N. Y., 1960, Chapter 6.

[23] J. P. Phillips and F. J. O'Hara, *Anal. Chem.*, **23**, 535 (1951).

[24] W. R. King, Jr., and C. S. Garner, *J. Chem. Phys.*, **18**, 689 (1950).

prising. The ionizable hydrogen forms a chelate ring in the parent ligand; therefore, both the nitrogen and oxygen donors should be more reactive in the anionic form. This result also explains the easier synthetic reactions using the halogenated derivatives, which are more acidic than the unsubstituted ligand.[25] This observation also suggested the use of the high-boiling basic solvent pyridine and the corresponding sterically hindered 2,4,6-trimethylpyridine as reaction media. The solvents appear to be suitable for ligands which do not melt at reasonable temperatures or decompose on melting, even though the concentrations of ligand available to the tunsten are considerably less than in the melt reactions. The necessity of some ionizable hydrogen for the $W(CO)_6$ reaction has been demonstrated from the pure quinolinolate salt attempt, which produced no reaction.

Our inability to extend the reaction to molybdenum is consistent with the trend in higher oxidation states for tungsten than for molybdenum as a result of differing redox potentials. The reaction between $MoCl_3(C_5H_5N)_3$ and 8-quinolinol in benzene under reflux conditions gives $MoCl(C_5H_5N)Q_2$.[26] A report of the synthesis of MoQ_3 from HQ and $K_2[MoCl_5(H_2O)]$ in methanol has also appeared.[27] A disturbing aspect of the MoQ_3 report is the presence of infrared absorptions at 910 and 930 cm^{-1},[27] such as are found in terminal or bridging oxygen vibrations in molybdenum complexes, *e.g.*, $Mo_2O_3Q_4$.[26,28]

The inertness of the WQ_4 complexes to basic media has simplified purification procedures somewhat, but pure complexes with a number of derivatives, such as the 2-methyl-8-quinolinol ligand, have eluded us to date. Spectral measurements are consistent with the desired product, but the stability is apparently enough lower to make the pure tetrakis complex difficult to isolate. Steric factors may be important with the 2-methyl derivative; in fact, the isomer obtained with the 5-bromo derivative[18] (*mmmm* using the Hoard and Silverton[5] nomenclature) should be less stable with the 2-methyl derivative.

Magnetic Moments and Chemical Inertness.—These complexes are apparently spin-paired d^2 species, which is logical for eight-coordinate, completely chelated complexes of tungsten(IV). Energy level diagrams for eight-coordinate dodecahedral species, such as are shown in Figure 2, indicate one low-lying d-like energy level orthogonal to the σ-bonding matrix and capable of π bonding. This situation is analogous to spin-paired d^6 octahedral complexes, which have three filled t_{2g} levels (π bonding, orthogonal to σ matrix) for the six electrons and are fairly inert to nucleophilic attack.[29] Furthermore, the spin-paired octacyano d^2 species are also inert.[2] Even so, the inertness of these chelates in basic media is somewhat amazing when compared to other lower valence tungsten complexes. On the other hand, like other 8-quinolinol chelates, these complexes are decomposed by either strong or weak acids.

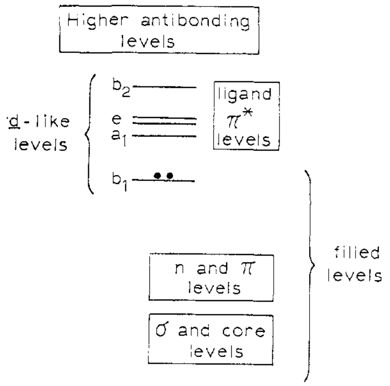

Figure 2.—Simplified energy level diagram for WQ_4-type dodecahedral complexes. The order of the higher d-like levels is uncertain.

Whereas we had assumed eight-coordination based on the infrared data and the magnetic susceptibilities, the structural determination of $K_3Na[Mo(CN)_4O_2]\cdot 6H_2O$[9a] showed that strongly distorted octahedral d^2 complexes can be diamagnetic. Partial chelation of the tetrakis complexes would not be expected to form an octahedral complex distorted sufficiently to allow for spin pairing, but, as noted above, for better proof an X-ray study of one derivative was solved.[18]

Recent reports of sulfur donor *N,N*-dialkyldithiocarbamate complexes in which molybdenum(IV) and tungsten(IV) are potentially eight-coordinate[30] need to be critically evaluated. The higher magnetic moments reported for the S-donor complexes (1–1.2 BM) suggest less inert behavior might be found than in the case of the quinolinol complexes since spin-free forms should be labile. If the S-donor complexes are truly eight-coordinate d^2 species, they may be suitable intermediates for forming other d^2 complexes like MoQ_4, etc.

Electronic Spectra.—The intense ($\epsilon > 10^4$) low-energy (13–16 kK) bands observed for the tungsten(IV) complexes are logically assigned as charge-transfer bands by virtue of their intensities.[31] The choice of metal to ligand ($\pi^* \leftarrow d$) is preferred because (1) the bands are shifted from the higher energies (18–20 kK) observed for the tungsten(V) species,[19] whereas a ligand to metal ($d \leftarrow n$ or π) type transition should occur at higher energies in the tungsten(IV) species—contrary to the experimental evidence and (2) the optical electronegativities[31,32] of the metal and the ligand are probably not close enough to give such a low-energy transition for ligand to metal charge transfer. The b_1 level is filled in the d^2 complex so one ligand level would have to be almost degenerate with the b_1 level in order to obscure the $d \leftarrow d$ transitions. Another possibility, ^1L_a and ^1L_b ligand transitions, seems less likely because transitions are still observed at the normal positions ($\sim$24 and 29 kK)[33] for these transitions. However, the ^1L_a ligand absorption is a transition from the electron-rich oxygen "long pairs" of π type symmetry to a π^* ring orbital. Lone-pair repulsions in the crowded WO_4N_4 coordination dodecahedron[18] could red-shift one or more such transitions in the manner observed as a

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[25] L. G. Sillén and A. E. Martell, *Chem. Soc., Spec. Publ.*, **No. 17**, 597, 607, 608 (1964).

[26] W. Andruchow, Ph.D. Dissertation, Tulane University, 1966.

[27] Q. W. Choi, J. S. Oh, K. W. Lee, and W. Lee, *Daehan Hwahak Hwoejee*, **12**, 146 (1968).

[28] J. Selbin, *Angew. Chem., Int. Ed. Engl.*, **5**, 712 (1966).

[29] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, N. Y., 1967, p 141 ff.

[30] (a) R. N. Jowitt and P. C. H. Mitchell, *Inorg. Nucl. Chem. Lett.*, **4**, 39 (1968); (b) D. C. Bradley and M. H. Gitlitz, *J. Chem. Soc. A*, 1152 (1969); (c) J. N. Smith and T. M. Brown, *Inorg. Nucl. Chem. Lett.*, **6**, 441 (1970).

[31] A. B. P. Lever, "Inorganic Electronic Spectroscopy," Elsevier, New York, N. Y., 1968, Chapter 8.

[32] C. K. Jørgensen, *Solid State Phys.*, **13**, 376 (1962); *Mol. Phys.*, **6**, 43 (1963); and subsequent references.

[33] L. Morpurgo and R. J. P. Williams, *J. Chem. Soc. A*, 73 (1966).

result of coulombic repulsions in the ground state, but the intensities are higher than expected. The intensities also appear to be too large to be predominantly $d \leftarrow d$ transitions, which in the dodecahedral octacyanomolybdate(IV) and -tungstate(IV) are of the order of 10^2. Hence, the $\pi^* \leftarrow d$ assignment is preferred and analogous to that made for the iron(II)–diimine complexes,[31,34] which also possess low-energy ($\sim$20 kK) high-intensity bands ($\epsilon \sim 10^4$). Further details must await polarized spectral data.

Another feature of the electronic spectra are the low-energy, low-intensity bands found in the near-infrared spectra of the dihalo species. These absorptions could be $d \leftarrow d$ transitions arising from stereochemical changes with the addition of extra electron density from the electron-rich halogen atoms. Whereas the addition of a halogen in the 7 position on the ring does not directly pose a steric problem for the *mmmm* isomer, as is shown in Figure 3, the added electron density of the potentially overlapping electron clouds may cause a loosening of the dodecahedral coordination or a rearrangement of the WO_4N_4 polyhedron. An alternative is a $\pi^* \leftarrow n$ or other ligand transition with a large shift due to the added repulsions. Solvent effect studies might help elucidate definitive assignments for these near-infrared bands, but low solubilities may preclude a wide enough range of solvents in which to observe the shifts.

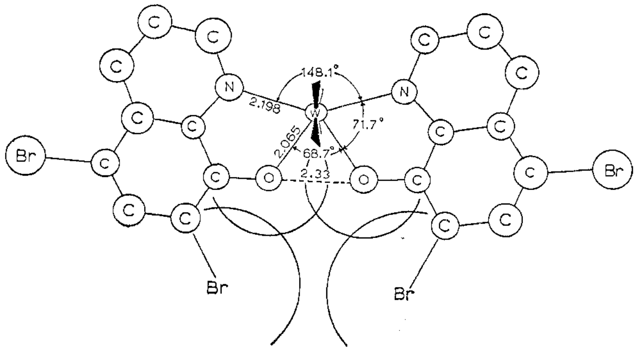

Figure 3.—van der Waals radii of bromine (7 position) and oxygen in the BAAB trapezoidal plane using the geometrical data obtained for $(WQBr)_4$.[18]

The unique absorption spectra observed for the tungsten(IV) quinolinolates have also allowed us to ascertain suitable reaction conditions for the preparation of other derivatives. For example, the 5-nitro-8-quinolinolato derivative apparently can be formed by photochemical activation of solutions of the ligand and $W(CO)_6$ in inert organic solvents at room temperature. After 3 hr at 25° in CCl_4 a green color developed. Spectral measurements indicated a strong absorption at 13.5 kK apparently due to the formation of some of the tetrakis complex. The shift to lower energy is consistent with either a metal to ligand or intraligand transition. A deep blue complex was obtained when 2-methyl-8-quinolinol was allowed to react in 2,4,6-trimethylpyridine with $W(CO)_6$ under reflux conditions for several hours. In this case the absorption maximum occurs at *ca.* 14.3 kK.

Conclusion.—The tetrakis(8-quinolinol)tungsten(IV) complexes noted herein constitute the first unequivocal series of inert, completely chelated eight-coordinate complexes of d^2 electronic configuration.

Experimental Section

Preparation of Materials.—K_3MoCl_6 (Shattuck Chemical Co.) was recrystallized before use[35] and stored in a vacuum desiccator over KOH pellets. $K_3W_2Cl_9$ and $(NH_4)_3W_2Cl_9$ were prepared by electrolytic reduction of tungstic acid in concentrated hydrochloric acid following the method of Jonassen.[36] This complex was twice recrystallized immediately before use and stored *in vacuo* over KOH pellets. Tungsten and molybdenum hexacarbonyls (Climax Molybdenum Corp. and Pressure Chemical Co.) were sublimed at 100° *in vacuo* and stored in a desiccator over KOH pellets prior to use.

The various 8-quinolinols (Aldrich Chemical Co.) were sublimed *in vacuo* at oil bath temperatures ranging 10–20° above their melting points: 8-quinolinol, mp 75.5–76°; 5-chloro-8-quinolinol, mp 123–124°; 5-bromo-8-quinolinol, mp 124–125°; 5,7-dichloro-8-quinolinol, mp 181–182°; 5,7-dibromo-8-quinolinol, mp 197–198°.

Reagent grade solvents were dried and distilled under prepurified nitrogen according to the procedures listed.

(1) **Benzene** was refluxed with 5 g of benzophenone and 5 g of sodium metal per liter until the blue-purple sodium ketyl complex had formed. The solvent was then distilled into an oven-dried vessel.

(2) **Tetrahydrofuran** was refluxed with benzophenone and sodium as above and then distilled.

(3) **Methanol** was refluxed overnight with about 5 g of calcium hydride per liter and then distilled.

(4) **Carbon tetrachloride** was dried by azeotropic distillation and the middle two-thirds fraction was collected.

(5) **Methylene chloride** was refluxed for 2–3 days with about 5 g of calcium hydride per liter and distilled.

(6) **Chloroform** was refluxed and cooled under nitrogen before use to remove dissolved oxygen.

Sealed-Tube Melt Synthesis of Tetrakis (8-quinolinolato) Complexes.—Salts of the metal complex chloride or the metal carbonyl were stirred with an excess of the appropriate 8-quinolinol at temperatures exceeding the melting point of the ligand. Heating and stirring were accomplished in a 50-ml round-bottom, oven-dried flask equipped with a Teflon-covered magnetic stirrer bar and heated in a silicone oil bath. The flask was vacuum-sealed when used with the tungsten and molybdenum complex chlorides but supplied with a vent into a nitrogen stream to prevent significant CO overpressures when the carbonyls were used. The complexes were handled in double-wall glove bags under prepurified nitrogen unless otherwise indicated.

Reaction of 8-Quinolinol with $W_2Cl_9^{3-}$.—$(NH_4)_3W_2Cl_9$ (5.0 g, 6.7×10^{-3} mol) or $K_3W_2Cl_9$ (5.0 g, 6.2×10^{-3} mol) was ground with 20.0 g (0.14 mol) of freshly sublimed 8-quinolinol in an oven-dried mortar and pestle. The melt flask was immersed in a 140° bath and its contents were stirred for 4 hr. The color of the molten ligand turned deep blue-green after about 20 min and gradually changed to violet (by reflected light) as crystals of the complex were deposited on the sides of the reaction vessel.

Excess ligand and 8-quinolinium chloride were removed by sublimation at 140° and 0.9 mm. The remaining material was removed to the air and leeched alternately with 50-ml quantities of methanol and water until the washings were colorless. The blood red methanol washings yielded 0.8 g of an intensely red material on evaporation, while about 10% (0.5–0.6 g) of the unreacted chloro complex was recovered from the aqueous washings. The remaining complex was rinsed with 100 ml of anhydrous diethyl ether and dried at room temperature *in vacuo* over P_4O_{10} for 1 day. Yield of the tetrakis complex was 5.81 or 65% of the tungsten actually reacted. A slow (40 days) recrystallization was accomplished by Soxhlet extraction with sodium-dried benzene in an inert atmosphere.

Anal.[37] Calcd for the recrystallized $W(C_9H_6NO)_4$: C, 56.84; H, 3.16; N, 7.37; W, 24.21. Found: C, 56.92; H, 3.15; N, 7.30; W, 23.84.

The complex has a solubility of approximately 10^{-6} mol/l. in dry benzene or dry dichloromethane. It slowly decomposes in wet nonpolar solvents to give lavender solutions.

Microscopic examination of the recrystallized product revealed well-shaped, square, aqua platelets by transmitted light which appeared violet in reflected light. While heating the

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(35) K. H. Lohmann and R. C. Young, *Inorg. Syn.*, **4**, 97 (1953).

(36) H. B. Jonassen, A. R. Tarsey, S. Cantor, and G. F. Helfrich, *ibid.*, **5**, 139 (1957).

(37) Analyses by Huffman Laboratories, Wheatridge, Colo.

complex on a hot-stage microscope gave no observable change after 8 hr at 170°, it was found that the crystals slowly turned lavender on standing in the atmosphere.

Reaction of 8-Quinolinol and Sodium 8-Quinolinolate with $(NH_4)_3W_2Cl_9$.—Sodium 8-quinolinolate (5.0 g, 0.03 mol), $(NH_4)_3W_2Cl_9$ (2.0 g, 2.7×10^{-3} mol), and 8-quinolinol (15.0 g, 0.1 mol) were sealed in the melt flask previously described. After 1 min in an 85° oil bath, deep blue-green spots began to spread across the melt flask walls. The melt turned deep blue-green after 30 min but the increased concentration of salts evidently prevented efficient stirring and the melt appeared unmixed. After 3 hr at this temperature the flask was cooled and opened, and the excess ligand was sublimed at 80° and 0.2 mm. Comparison of the 13,000–20,000-cm^{-1} absorption spectrum of the sublimation residue with that of a conventionally prepared sample of WQ_4 indicated the formation of WQ_4 in this reaction.

Reaction of 5-Bromo-, 5-Chloro-, 5,7-Dibromo-, and 5,7-Dichloro-8-quinolinol with $K_3W_2Cl_9$ and $W(CO)_6$.—$W(CO)_6$ (3.52 g, 0.01 mol) or $K_3W_2Cl_9$ (5.0 g, 6.2×10^{-3} mol) and an excess of the halo-substituted 8-quinolinol were allowed to react at temperatures 15–30° above the melting point of the ligand as prescribed above. The reaction mixture turned blue-green on melting and became deep purple after 1–2 hr. When $W(CO)_6$ was used, CO was rapidly evolved initially, but the rate gradually lessened and ceased entirely after 4–5 hr. The reactions were terminated after 6–8 hr and the blue-green complexes were separated by one of the following procedures.

(A) Excess ligand and the 8-quinolinolium chloride were sublimed from the product at 160° and 0.2 mm. The tetrakis species were extracted from the product mixtures with dry benzene by the Soxhlet extraction technique.

(B) In this method, the melts were finely ground and removed to the air where they were stirred 1–2 hr in 250 ml of a 1:2 methanol–water solution containing 10 g of KOH pellets. The purple color immediately disappeared on treatment with the alkali and dirty, blue-green solids were separated from the yellow-green solutions by filtration. These precipitates were washed with 100 ml of the solvent and dried overnight in a vacuum desiccator over KOH pellets at room temperature. The complexes were recrystallized by benzene extraction as previously described. The yield was 40–65% for all four species.

Anal.[38] Calcd for $W(C_9H_5NOCl)_4$: C, 48.11; H, 2.23; N, 6.24; Cl, 15.81. Found: C, 48.10; H, 2.25; N, 5.89; Cl, 15.89. Calcd for $W(C_9H_5NOBr)_4 \cdot C_6H_6$: C, 43.67; H, 2.25; N, 4.85; Br, 27.73. Found: C, 43.59; H, 2.24; N, 4.91; Br, 27.68. Calcd for $W(C_9H_4NOCl_2)_4$: C, 41.70; H, 1.54; N, 5.41; Cl, 27.41; O, 6.18. Found: C, 41.74; H, 1.58; N, 5.29; Cl, 27.39; O, 6.18. Calcd for $W(C_9H_4NOBr_2)_4$: Cr, 31.03; H, 1.15; N, 4.02. Found: C, 31.14; H, 1.10; N, 3.86.

Recrystallized tetrakis(5-chloro-8-quinolinolato)tungsten(IV) precipitated from benzene as square, aqua platelets similar to those of the parent complex, while the tetrakis-5-bromobenzene solvate formed large, triclinic parallelepipeds. Although the tetrakis-dihalo species precipitated in microcrystalline aggregates from benzene, rod-shaped orthorhombic crystals formed when 1,4-dichlorobenzene solutions were slowly cooled.

The solubility of these complexes in benzene and dichloromethane ranges from 10^{-3} to 10^{-5} *M*. The 5-bromo and dihalo tetrakis species show no apparent decomposition after several weeks' exposure to the atmosphere but the 5-chloro tetrakis complex decomposes after 1 week in a humid environment. Dilute nitric acid decomposes these complexes to purple solutions, initially, which are converted to yellow solutions on standing for several minutes. All four species maintain their blue-green color in ethanolic KOH solutions after 1 week or more.

Reaction of 8-Quinolinol with $W(CO)_6$.—$W(CO)_6$ (3.5 g, 0.01 mol) and 8-quinolinol (20.0 g, 0.14 mol) were allowed to react for 3 days at 130° in the manner previously described. The reaction mixture turned yellow-brown after 1 hr and evolved CO slowly for 1–1.5 days. A small amount (~1–2 mg) of brown material sublimed during the separation phase but decomposed before all of the excess ligand had sublimed. The remaining material was recrystallized by Soxhlet extraction with dry benzene or tetrahydrofuran under a prepurified N_2 atmosphere. The yield was 3–5.0 g. Microscopic examination of the recrystallized product showed ill-defined brown and yellow-brown crystal masses but no trace of the blue-green tetrakis species. The complex(es) seemed to be unaffected by a 2-week exposure to the atmosphere. This material is soluble in benzene, methylene chloride, and chloroform but dissolves most easily in methanol or ethanol. No further investigations were attempted.

Tetrakis(5-acetyl-8-quinolinato)tungsten(IV).—A deep blue-green solution resulted when 3.5 g (0.01 mol) of $W(CO)_6$ and 9.5 g (0.05 mol) of 5-acetyl-8-quinolinol were stirred in 50 ml pyridine under reflux conditions for 8.5 hr. The solution was dumped into a solution of 10 g of KOH (0.18 mol) in 500 ml of H_2O, stirred for 30 min, filtered, and dried *in vacuo* overnight. The crude product was extracted with benzene to give a recrystallized product; yield 37%.

Anal. Calcd for $W(C_{11}H_8NO_2)_4$: C, 56.91; H, 3.47; N, 6.03. Found: C, 56.81; H, 3.40; N, 6.07.

Spectrally Characterized Products.—The procedures noted above appear to be limited by temperature considerations. Two additional methods for preparing the tetrakis complexes include (A) photochemical activation and (B) the use of 2,4,6-trimethylpyridine as a solvent. The following two cases are given as illustrations.

(A) When *ca.* 1 g of $W(CO)_6$ and 3 g of the 5-nitro-8-quinolinol ligand were partially dissolved in CCl_4 under nitrogen and irradiated (sunlamp) for 3 hr, a green coloration was noted; λ_{max} 745 nm (13.4 kK).

(B) When 3.5 g (0.01 mol) of $W(CO)_6$ and 8.5 g (0.05 mol) of 2-methyl-8-quinolinol were stirred in 50 ml of 2,4,6-trimethylpyridine heated under reflux conditions for 12 hr, the air-sensitive deep blue product exhibited a strong peak at 700 nm (14.3 kK). Purification of the complex, expected to be sterically hindered, has proven difficult. No carbonyl peaks appear in the vibration spectrum of the species, so substitution on $W(CO)_6$ appears to be complete.

Electronic Spectra.—Electronic spectra of these complexes were recorded from 5000 to 36,000 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. All samples were run against a similarly prepared KBr reference pellet.

Magnetic Susceptibility Measurements.—The Faraday method was used for determining the magnetic susceptibility of the substituted quinolinol complexes. $CoHg(SCN)_4$ was used to calibrate the balance. Sample size was *ca.* 1 mg. Diamagnetic corrections were made using the value given by Selwood[39] 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.[39]

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