CONTRIBUTION FROM GOESSMANN CHEMICAL LABORATORY, UNIVERSITY OF MASSACHUSETTS, AMHERST, MASSACHUSETTS 01002,
AND THE DEPARTMENT OF CHEMISTRY, BROOKHAVEN NATIONAL LABORATORY, UPTON, NEW YORK 11973

Transition Metal Eight-Coordination. III. Tetrakis(5-bromo-8-quinolinolato)tungsten(IV)–Benzene. An Eight-Coordinate Dodecahedral $M(AB)_4$ System[1a,e]

BY WESLEY D. BONDS, JR.,[1b] RONALD D. ARCHER,*[1c] AND WALTER C. HAMILTON[1d]

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Tetrakis(5-bromo-8-quinolinolato)tungsten(IV)–benzene, $W(C_9H_5NOBr)_4 \cdot C_6H_6$, crystallizes in space group $P\bar{1}$ of the triclinic system with two formula weights per cell [a = 19.076 (8), b = 8.199 (3), c = 15.293 (5) Å, α = 63.90 (3), β = 85.32 (4), and γ = 102.32 (3)°]. A total of 2954 unique, observed reflections were collected to $2\theta = 40°$ with Mo Kα radiation and the structure was refined to a conventional residual of 6.4% by full-matrix least-squares methods. This tetrakis complex allows the first crystallographic evaluation of Orgel's postulate regarding eight-coordinate d^2 MA_4B_4 stereochemistry. The complex contains dodecahedrally coordinated tungsten and closely approximates D_{2d} symmetry. The four quinolinol ligands span the Hoard–Silverton designated m edges with the π-donor oxygen atoms (W–O$_{av}$ = 2.065 Å) occupying A positions while the π-acceptor nitrogen atoms (W–N$_{av}$ = 2.198 Å) are located at the B sites diagonal to the filled metal $d_{x^2-y^2}$ orbital. A nonbonded intramolecular oxygen–oxygen contact of 2.33 Å along the dodecahedral a edges emphasizes the importance of ligand–ligand interactions in this eight-coordinate species. The role of metal–ligand π bonding and ligand constraints in determining eight-coordinate complex stereochemistry is extensively discussed.

Introduction

Despite extensive investigations into the stereochemistry of eight-coordinate complexes, as witnessed by the recent proliferation of structure reports and review articles,[2-6] prediction of the geometry expected for a specific eight-coordinate species is difficult. At least seven discrete eight-coordinate polyhedra have been identified through X-ray structural investigations.[7] As with the more common coordination numbers, only two geometries are prevalent in transition metal eight-coordination, the D_{2d} dodecahedron and the D_{4d} square antiprism (Figure 1).[8] However, unlike the bimorphism exhibited with other coordination numbers, eight-coordination remains unique in that these two complex polyhedra have been observed in a growing number of instances without completely satisfactory explanations. Definite stereochemical patterns have not been established with regard to either ligand types or particular counterions. Furthermore, calculations by several investigators[3a,4,9] on simple MX_8^{n-} (M = transition metal ion, X = first period donor) systems have suggested that ligand–ligand repulsion forces and crystal field stabilization energies are similar for the dodecahedral and square-antiprismatic cases.

The only stereochemical rule regarding geometry in transition metal eight-coordinate complexes was formulated by Orgel in 1960.[10] He suggested that eight-coordinate systems of the type MA_4B_4 (M = d^1 or d^2 metal ion, A = π-nonbonding or π donor, and B = π acceptor) should adopt a dodecahedral stereochemistry with the π-acceptor B ligands forming a flattened tetrahedral array near the d_{xy} orbital and diagonal to the occupied metal $d_{x^2-y^2}$ orbital, while the A ligands should occupy positions beyond the d_{xz}–d_{yz} maxima toward the z axis. This proposal was based on the reported stoichiometries of several complexes: $Mo(CN)_4(OH)_4^{4-}$,[11] $W(CN)_4(OH)_4^{4-}$,[12] $Mo(CN)_4(OH)_3(H_2O)^{3-}$,[11,13] and $ReCl_4(diars)_2^+$.[14] Recent crystallographic evidence disproved the formulation of the molybdate and tungstate species[15,16] while the structure of $ReCl_4(diars)_2^+$ remains unknown. Archer and Bonds[17] reported the synthesis of tetrakis(8-quinolinolato)tungsten(IV), a possible $M(AB)_4$ system,[18] 3 years ago and predicted its stereochemistry with Orgel's rule. Despite an excellent chemical analysis, low solubility prevented physico-

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(1) (a) Presented in part at the 1970 Winter Meeting, American Crystallographic Association, New Orleans, La., March 1970; see Abstracts, No. C11. (b) From the Ph.D. thesis of W. D. Bonds, Jr., University of Massachusetts, 1970. (c) Department of Chemistry, University of Massachusetts, Amherst, Mass. 01002. (d) Department of Chemistry, Brookhaven National Laboratory, Upton, N. Y. 11973. (e) Abbreviations used: HQ, 8-quinolinol; HQBr, 5-bromo-8-quinolinol; HMQ, 2-methyl-8-quinolinol; Cp, cyclopentadienyl; NTA^{3-}, nitrilotriacetate; NES^-, *N*-ethylsalicylaldimine anion; ox^{2-}, oxalate; diars, *o*-phenylenebis(dimethylarsine).

(2) R. V. Parish, *Coord. Chem. Rev.*, **1**, 439 (1966).

(3) (a) D. L. Kepert, *J. Chem. Soc.*, 4736 (1965); (b) R. J. H. Clark, D. L. Kepert, R. S. Nyholm, and J. Lewis, *Nature (London)*, **199**, 559 (1963).

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

(5) E. L. Muetterties and C. M. Wright, *Quart. Rev., Chem. Soc.*, **21**, 109 (1967).

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

(7) These polyhedra include the D_{2d} trigonal faced dodecahedron (a 2:2:2:2 polyhedron relative to the principal axis); the D_{4d} square antiprism (4:4); the O_h cube (4:4); the D_{6h} hexagonal bipyramid (1:6:1); the D_{6d} puckered hexagonal bipyramid (1:3:3:1(; the C_{2v} hendecahedron or bicapped trigonal prism (4:2:2); and the C_{2v} trigonal faced dodecahedron (2:5:1).

(8) Discrete cubic coordination is known only in Na_3MF_8 (M = U, Pa, or Np) complexes [D. Brown, J. F. Easey, and C. E. F. Rickard, *J. Chem. Soc. A*, 1161 (1969)]. The hexagonal bipyramid and puckered hexagonal bipyramid are associated almost exclusively with uranyl complexes, whose structures are obviously influenced by the linear UO_2^{2+} fragment. A distorted hendecahedron has been reported for $[Eu(acac)_3(H_2O)_2] \cdot H_2O$ [A. L. Il'inskii, L. A. Aslanov, V. I. Ivanov, A. D. Khalilov, and O. M. Petrukhin, *Zh. Strukt. Khim.*, **10**, 285 (1969)] and the 2:5:1 dodecahedron is known in $Np(S_2CN(C_2H_5)_2)_4$ [D. Brown, D. G. Holah, and C. E. F. Rickard, *Chem. Commun.*, 280 (1969)].

(9) R. V. Parish and P. G. Perkins, *J. Chem. Soc. A*, 345 (1967).

(10) L. E. Orgel, *J. Inorg. Nucl. Chem.*, **14**, 136 (1960).

(11) W. R. Bucknell and W. Wardlaw, *J. Chem. Soc.*, 2981 (1927).

(12) K. N. Mikhalevich and V. N. Litvinchuk, *Russ. J. Inorg. Chem.*, **4**, 800 (1959).

(13) A. W. Adamson and J. R. Perumareddi, *Inorg. Chem.*, **4**, 247 (1965).

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

(15) S. J. Lippard, H. Nozaki, and B. J. Russ, *Chem. Commun.*, 118 (1967).

(16) V. W. Day and J. L. Hoard, *J. Amer. Chem. Soc.*, **90**, 3374 (1968).

(17) R. D. Archer and W. D. Bonds, Jr., *ibid.*, **89**, 2236 (1967).

(18) We have expanded the Hoard–Silverton notation[4] regarding dodecahedral eight-coordinate complexes containing multidentate ligands: $(AA)^{n-}$, $(BB)^{n-}$, or $(AB)^{n-}$ denotes a bidentate ligand spanning the coordination sites enclosed in parentheses. An $(AB)^{n-}$ ligand may, however, chelate along an m or a g edge. Notation such as $M(AA)_2B_4$ refers to two bidentate ligands spanning a edges and four monodentate B ligands, as in $TiCl_4(diars)_2$. It is important to remember that this nomenclature is correct only with reference to the positions in the coordination dodecahedron, because an unsymmetrical bidentate chelating agent may "flip" coordination positions on going to an electronically different metal ion and an AA donor might become a BB donor, etc.

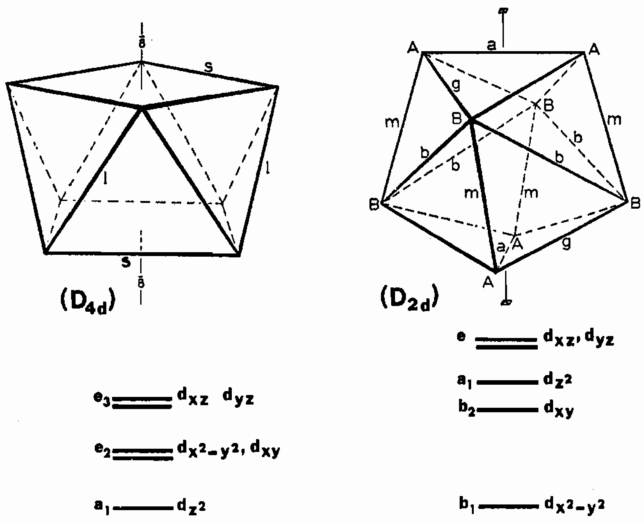

Figure 1.—The D_{4d} square antiprism and the D_{2d} dodecahedron from ref 4 and idealized crystal-splitting diagrams based on assignments in ref 21 and 22. The ordering for the upper d levels in D_{2d} symmetry is very angle dependent.

chemical measurements which could have unequivocably established this species as a completely chelated, mononuclear tungsten(IV) complex. In the absence of suitable chemical precedents, the $M(AB)_4$ structure assignment was inconclusive when based solely on the observed spectral and magnetic properties.

Meanwhile, a systematic study on a series of tetrakis tungsten(IV)[19] and tungsten(V)[20] complexes progressed in these laboratories. Intense ($\epsilon > 10^4$) charge-transfer bands in the visible region (14 kK and up) have prevented easy spectral correlations with the d–d transitions predicted for D_{4d}[21] and D_{2d}[22] octacoordinate species. To correlate our accumulating synthetic and spectral data with a known structure and to find the first crystallographic test of Orgel's postulate, we have undertaken an X-ray structure determination on tetrakis(5-bromo-8-quinolinolato)tungsten(IV). The benzene solvate, $W(C_9H_5NOBr)_4 \cdot C_6H_6$, was the first of these complexes to yield crystals suitable for such an analysis.

Experimental Section

Tetrakis(5-bromo-8-quinolinolato)tungsten(IV) was prepared in a melt reaction of $W(CO)_6$ and 5-bromo-8-quinolinol by methods described elsewhere.[19] Sufficiently large single crystals were obtained by allowing a hot, saturated benzene solution of the complex to cool slowly. The crystals were recovered by filtering in air and were dried for 10 hr *in vacuo* at 180°.

Anal. 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. Those specimens selected for further study were handled without the benefit of an inert atmosphere or sealed capillaries with no apparent decomposition. Although the deeply colored crystals had well-developed faces which appeared black-purple when viewed with reflected light, the characteristic blue-green color common to the tungsten(IV)–8-quinolinol species became immediately apparent on crushing or redissolving the crystals in a nonpolar organic solvent. A number of twins (>75%) which had formed in this batch were readily distinguishable on inspection of the $(0kl)$ net with precession photography.

Equiinclination Weissenberg and precession photographs failed to reveal the presence of symmetry elements, and the crystal was assigned to the triclinic system. Unit cell parameters (a = 19.076 (8), b = 8.199 (3), c = 15.293 (5) Å; α = 63.90 (3), β = 85.82 (4), γ = 102.32 (3)°) and setting angles were determined from a least-squares refinement[23] of 44 reflections centered[24] on a General Electric diffractometer (Nb-filtered Mo Kα (λ 0.71069 Å) radiation). The experimentally determined density, 1.88 g/ml, as measured by flotation in aqueous zinc chloride compares well with that of 1.86 g/ml calculated for two formula units per cell. A Delaunay reduction[23] provided a triclinic primitive cell with parameters: a = 13.812, b = 19.076, c = 8.199 Å; α = 102.32, β = 96.11, γ = 78.03°. The transformation matrix to this cell is defined by

$$\begin{bmatrix} a \\ b \\ c \end{bmatrix}_{\text{Delaunay}} = \begin{bmatrix} 0 & -1 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} a \\ b \\ c \end{bmatrix}$$

A piezoelectric test was not performed and the space group was assumed to be $P\bar{1}$ with the origin at the inversion center. Successful refinement of the structure confirms this choice.

The crystal finally selected for intensity data collection was a rod-shaped parallelepiped with faces indexed as belonging to the {100}, {010}, and the {101} forms. Its volume of 0.00231 mm³ was calculated from the perpendicular distances between the various faces: $(100)-(\bar{1}00)$ = 0.065 mm, $(010)-(0\bar{1}0)$ = 0.288 mm, and $(101)-(\bar{1}0\bar{1})$ = 0.093 mm. The specimen was mounted with the b^* axis coincident with the ϕ axis of the goniostat. Tetrakis(5-bromo-8-quinolinolato)tungsten(IV)–benzene has a linear absorption coefficient[25] of 72.00 cm⁻¹ for Mo Kα radiation.

A card-controlled General Electric quarter-circle diffractometer equipped with niobium-filtered Mo Kα radiation was employed in intensity data collection. A takeoff angle of 2° was utilized with a circular receiving aperture 2 mm in diameter placed 31 mm from the crystal. Counter response remained essentially linear throughout the range of observed counting rates. The moving-crystal, moving-counter scan technique was employed in conjunction with a θ–2θ scan.[24] The La Placa variable-scan algorithm[26] was used in the setting program both to allow the initial 20-sec low-angle background to be made precisely within the region where the niobium filter cutoff and the Mo Kα peak have a minimal effect on the background count as well as to account for variation in peak width throughout the range of 2θ values scanned. A scan was then made at 1°/min through the peak and a second 20-sec background was recorded. Three standard reflections monitored every 35 reflections (~3 hr) deviated less than ±3% during data collection. The data were adjusted for this irregular variation assuming the initial 35 reflection data block to have a unit scale factor. Although 3855 independent reflections lie within the annular ring $2° \leq 2\theta \leq 40°$ within which meaningful data could be collected with this crystal, mechanical failure to the diffractometer control unit prevented 706 mostly

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(19) W. D. Bonds, Jr., and R. D. Archer, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, No. INOR 167; *Inorg. Chem.*, in press.

(20) W. D. Bonds, Jr., and R. D. Archer, Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, No. INOR 215; to be submitted for publication.

(21) E. König, *Theor. Chem. Acta*, **1**, 23 (1962).

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

(23) TRACER II, which was expanded from the original TRACER by S. L. Lawton, Mobile Oil Corp., Paulsboro, N. J., was used to determine the reduced cell and test for hidden symmetry. MUDDY1, the local setting angles program, was used to refine cell parameters and orientation angles. Program DATAPH was employed in the calculation of Lorentz and polarization corrections and performed the absorption correction by the method described by (a) P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Crystallogr.*, **18**, 1035 (1965). LINUS is Brookhaven's version of Busing and Levy's ORFLS full-matrix least-squares program. This program can correct observed data for extinction effects as discussed by (b) W. H. Zachariasen, *ibid.*, **23**, 558 (1967), and by (c) P. Coppens and W. C. Hamilton, *ibid.*, *Sect. A*, **26**, 71 (1970). ORFFE is our version of the Busing, Martin, and Levy function and error program by the same name. In addition, JIMDAP, a modification of Zalkin's FORDAP program (A. Zalkin, "A FORTRAN Crystallographic Program for Fourier Analysis," University of California, Livermore, Calif., unpublished results), and Johnson's ORTEP ellipsoid plot program were used during the course of this investigation.

(24) T. C. Furnas, "Single Crystal Orienter Instruction Manual," The General Electric Co., Milwaukee, Wis., 1957.

(25) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham, England, 1968, p 166.

(26) S. J. La Placa, unpublished results. This calculation, performed in subroutine RANGER of MUDDY1,[23] determines the position for the initial, low-angle background count and varies the scan length with the Bragg angle according to the following conditions: the scan for some reflection, hkl, began at $2\theta_{\text{low}} = 2 \sin^{-1} \theta_{\text{MoK}\alpha} - C$ if $\Delta_{hkl} > C$ or at $2\theta_{\text{low}} = 2 \sin^{-1} \theta_{\text{MoK}\alpha} - k\Delta_{hkl}$ if $\Delta_{hkl} \leq C$ where Δ_{hkl} is given by $2(\sin^{-1} \theta_{\text{MoK}\alpha} - \sin^{-1} \theta_{\text{Nb-abs}})$. where Nb-abs is the absorption edge of the Nb filter, and C and k are empirically determined constants. For this crystal, C was 1.20° and k was 0.65. The scan was completed when $2\theta_{\text{high}} = 2 \sin^{-1} \theta_{\text{MoK}\alpha} + C$. The average width of a peak at half-height was 0.30°.

TABLE I

FINAL POSITIONAL AND THERMAL PARAMETERS[a] FOR $W(C_9H_5NOBr)_4 \cdot C_6H_6$

Atom	x	y	z	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
W	0.22202(4)	0.03216(9)	0.21779(5)	2.09(3)	9.9(3)	3.59(4)	0.99(5)	-0.28(2)	-2.82(6)
Br1	-0.4614(1)	-0.1478(4)	0.4324(2)	3.84(9)	62.5(10)	12.3(2)	9.6(3)	-4.38(12)	-20.1(4)
Br2	-0.3953(1)	-0.3503(4)	0.2852(2)	5.17(10)	42.1(7)	6.6(2)	-1.3(2)	1.79(10)	-11.1(3)
Br3	-0.1377(1)	-0.1294(4)	0.1003(2)	3.03(8)	53.4(8)	8.7(2)	5.5(2)	-2.45(9)	-9.7(3)
Br4	-0.0345(1)	-0.0163(3)	0.3518(1)	4.55(9)	34.8(6)	5.7(1)	0.2(2)	1.35(9)	-8.5(2)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
		Ring 1					Ring 3		
1C2	0.3614(9)	0.286(2)	0.241(1)	4.1(4)	3C2	0.1236(11)	0.301(3)	0.111(1)	5.6(5)
1C3	0.4295(10)	0.315(3)	0.276(1)	4.9(4)	3C3	0.0594(11)	0.340(3)	0.075(1)	5.5(5)
1C4	0.4600(10)	0.174(3)	0.325(1)	4.5(4)	3C4	0.0024(12)	0.200(3)	0.081(2)	6.3(5)
1C5	0.4484(10)	-0.170(3)	0.386(1)	5.0(4)	3C5	-0.0462(10)	-0.153(3)	0.140(1)	4.7(4)
1C6	0.4109(11)	-0.340(3)	0.398(1)	5.6(4)	3C6	-0.0341(11)	-0.325(3)	0.182(1)	4.7(4)
1C7	0.3423(9)	-0.366(2)	0.364(1)	4.2(4)	3C7	0.0314(9)	-0.354(2)	0.213(1)	3.7(4)
1C8	0.3203(9)	-0.201(2)	0.318(1)	3.6(3)	3C8	0.0821(9)	-0.199(2)	0.204(1)	3.0(3)
1C9	0.3588(8)	-0.026(2)	0.303(1)	2.9(3)	3C9	0.0713(8)	-0.016(2)	0.158(1)	2.4(3)
1C10	0.4249(9)	-0.006(2)	0.339(1)	3.6(3)	3C10	0.0075(10)	0.009(2)	0.126(1)	3.7(4)
1N	0.3271(6)	0.114(1)	0.2571(8)	2.5(2)	3N	0.1271(7)	0.117(2)	0.1540(9)	3.2(3)
1O	0.2588(6)	-0.207(1)	0.2805(1)	3.5(2)	3O	0.1450(5)	-0.205(1)	0.2354(7)	3.0(2)
		Ring 2					Ring 4		
2C2	0.2516(9)	-0.173(2)	0.091(1)	3.9(4)	4C2	0.1507(10)	-0.289(3)	0.439(1)	4.4(4)
2C3	0.2766(10)	-0.183(2)	0.003(1)	4.8(4)	4C3	0.1121(11)	-0.363(3)	0.535(1)	5.1(4)
2C4	0.3106(10)	-0.022(2)	-0.081(1)	4.6(4)	4C4	0.0886(10)	-0.253(3)	0.569(1)	4.8(4)
2C5	0.3572(10)	0.338(3)	-0.165(1)	4.6(4)	4C5	0.0875(10)	0.084(3)	0.523(1)	4.6(4)
2C6	0.3678(9)	0.495(2)	-0.154(1)	4.5(4)	4C6	0.1045(10)	0.273(2)	0.449(1)	4.7(4)
2C7	0.3414(9)	0.496(2)	-0.065(1)	4.2(4)	4C7	0.1514(10)	0.336(3)	0.360(1)	4.8(4)
2C8	0.3028(8)	0.316(2)	0.016(1)	2.8(3)	4C8	0.1704(8)	0.204(2)	0.335(1)	3.0(3)
2C9	0.2973(8)	0.156(2)	0.005(1)	3.3(3)	4C9	0.1486(8)	0.015(2)	0.409(1)	2.8(3)
2C10	0.3222(9)	0.154(2)	-0.083(1)	3.2(3)	4C10	0.1072(9)	-0.047(2)	0.500(1)	3.8(4)
2N	0.2614(7)	-0.004(2)	0.0902(9)	2.9(3)	4N	0.1683(7)	-0.100(2)	0.3738(10)	3.8(3)
2O	0.2724(5)	0.297(1)	0.1006(7)	3.1(2)	4O	0.2108(5)	0.241(1)	0.2530(7)	2.7(2)
				Benzene Solvate					
BzC1	-0.227(2)	0.228(5)	0.263(2)	10.0(8)	BzC4	-0.285(2)	-0.006(5)	0.458(2)	9.9(8)
BzC2	0.227(2)	-0.048(5)	-0.299(2)	10.2(8)	BzC5	-0.286(2)	0.176(5)	0.420(3)	11.4(9)
BzC3	0.259(2)	0.076(5)	-0.404(3)	10.7(9)	BzC6	-0.258(2)	0.310(5)	0.321(3)	11.3(9)

[a] The standard deviations of the least significant figure(s) are given in parentheses. [b] Anisotropic thermal parameters ($\times 10^3$). The form of the ellipsoid is that given in the text.

higher order reflections from being collected. Integrated intensities were obtained in the usual way: $I = C_t - {}^1/_2(t_c/t_b)(B_1 + B_2)$, where I is the integrated intensity, C_t is the total integrated count in time t_c, and B_1 and B_2 are the background counts obtained in time t_b. The standard deviation of the integrated intensity was estimated from Poisson counting statistics: $\sigma^2(I) = C_t + [{}^1/_2(t_c/t_b)]^2(B_1 + B_2)$. The 3149 collected reflections were corrected for Lorentz, polarization, and absorption effects[23] and the 106 reflections for which $I_{cor} \leq 0$ were treated as unobserved. A Wilson plot yielded an approximate absolute scale factor and an overall thermal parameter of 3.32 Å^2.

Structure Solution and Refinement

Although a three-dimensional, sharpened, origin-removed Patterson function clearly showed the tungsten–tungsten vector, assignment of the other heavy-atom vectors was ambiguous. The four bromine atoms were located after comparison of the Patterson with a Fourier difference synthesis phased on the tungsten atom. A second difference Fourier, phased with the five heavy atoms, revealed a dodecahedrally coordinated array of nitrogen and oxygen donors about the tungsten, while the quinolinol carbons appeared as four sheets of electron density arranged about the metal in the unmistakable *mmmm* "paddlewheel" configuration, as distinguished from the "pinwheel" *llll* isomer of antiprismatic coordination.[4] In the paddlewheel configuration the chelate rings are perpendicular to the principal axis of rotation, whereas the pinwheel *llll* isomer has diagonal planes as do the *gggg* isomers of the dodecahedral symmetry. The structural parameters were refined with our full-matrix least-squares program LINUS,[23] on the Brookhaven CDC 6600 computers, whose available core allowed simultaneous refinement of positional and thermal parameters for all 55 nonhydrogen atoms. Atomic scattering factors for W, Br, C, N, and O were taken from the calculations of Cromer.[27] Both the real and imaginary parts of the anomalous scattering correction[27] were included for tungsten and bromine. The aromatic moieties were refined as rigid groups with internal positional parameters obtained from the bis(8-quinolinolato)copper(II) structure of Palenik.[28] Anisotropic thermal parameters in the form $\exp(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$ were included for the heavy atoms, and a subsequent difference Fourier revealed the benzene solvate carbon atoms.

The refinement, initially carried out on F^2 with trial weights based on $\sigma = [\sigma^2(I) + (0.01F^2)^2]^{1/2}$, converged to $R_1 = 10.3\%$ and $R_2 = 17.6\%$ when rigid-group constraints were released and all positional and isotopic parameters were varied. The refinement was then shifted to an F basis with $\Sigma w(|F_o| - |F_c|)^2$ being minimized and the conventional unweighted and weighted residuals were defined as $R_1 = \Sigma(||F_o| - |F_c||)/|F_o|$ and $R_2 = \Sigma(||F_o| - |F_c||)^2/\Sigma(w|F_o|)^2$. The unweighted data were examined for systematic errors. Plots of $|F_o - F_c|/\sigma$ *vs.* $|F_o|$ were typical for those of a small crystal[29] and provided the basis for the final weighting scheme: $\sigma = 8.39 - 0.138F$ for $F < 40.0$; $\sigma = 2.88$ for $40.0 \leqq F \leqq 100.0$; $\sigma = 0.0322F - 0.50$ for $F > 100.0$. Analysis of $|F_o - F_c|/\sigma$ *vs.* $(\sin\theta)/\lambda$ indicated that the 69 lowest angle reflections had observed amplitudes that deviated generally more than 6σ from the calculated values regardless of the magnitude of F_o or the sign of the error. A refinement of the isotropic

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(27) "International Tables for X-Ray Crystallography," in Vol. IV, preparation.

(28) G. J. Palenik, *Acta Crystallogr.*, **17**, 687 (1964).

(29) G. H. Stout and L. H. Jensen, "X-Ray Structure Determination," Macmillan, New York, N. Y., 1968.

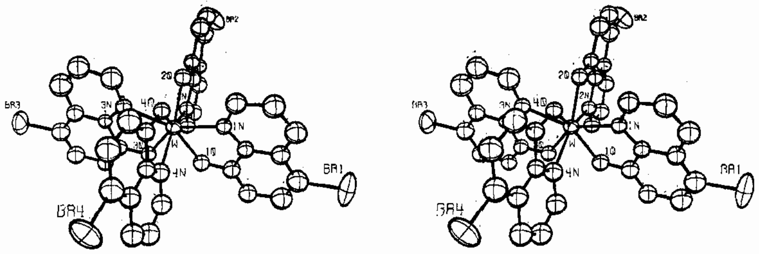

Figure 2.—The $W(QBr)_4$ complex unit with atoms represented by 50% probability ellipsoids or spheres. The two views constitute a stereoscopic pair that can be viewed with a small hand stereoscope.

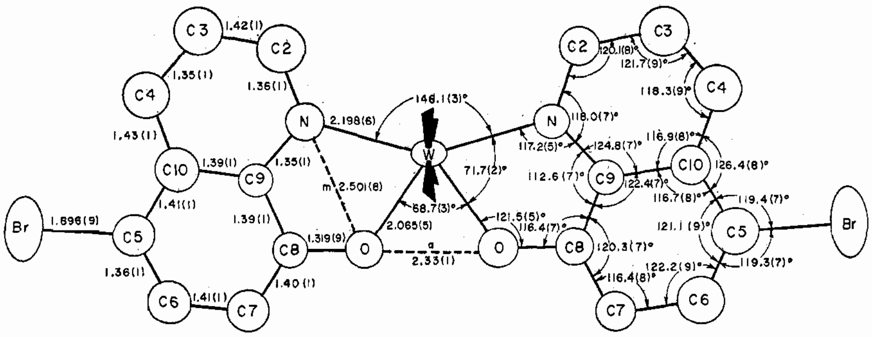

Figure 3.—Ligand 3 (left) and ligand 1 (right) with atoms depicted by 50% probability spheres or ellipsoids. Bond lengths and angles are averages of all chemically equivalent values in the $W(QBr)_4$ complex unit.

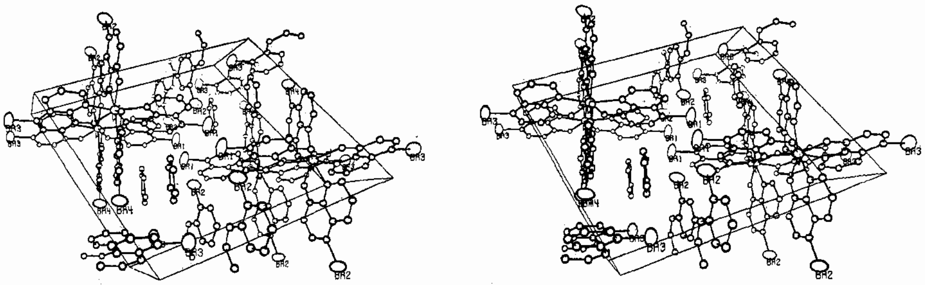

Figure 4.—Stereoscopic packing diagram for $[W(QBr)_4]\cdot C_6H_6$ as viewed along the *b* axis.

extinction correction[23b,c] resulted in no significant improvement and a value of the extinction coefficient *g* (as defined by Zachariasen[23b]) not significantly different from zero. For a related study of this correction see ref 23c. Whether the error in the low-angle data originates in errors in the atomic scattering factor or in the anomalous dispersion corrections for the heavy atoms, or neglect of the 26 hydrogens per formula unit, or from some other yet undefined systematic error remains unknown. The unweighted residual fell from 7.2 to 6.4% with a slight improvement in the consistency in the bond lengths and angles among the four crystallographically independent quinolinol ring systems when the low-angle data were excluded from the refinement.

The final parameters from the last least-squares cycle (R_1 = 6.4%, R_2 = 6.1%), together with their estimated standard deviations, are listed in Table I.[30] The strongest peaks in the final difference Fourier synthesis ranged from 0.7 to 1.8 $e^-/Å^3$ and are located near the inversion centers of the cell. Several ripples (0.6–0.8 $e^-/Å^3$) were found in the vicinity of the heavy atoms while a number of the smaller peaks (0.4–0.6 $e^-/Å^3$) near the ring carbons are probably due to uncorrected anisotropic thermal motion. Observed peak heights for the various atoms are as follows: W, 111; Br, 28–35; N, 5–8; O, 6–8; C, 2.5–6.5 $e^-/Å^3$.

Results and Discussion

Crystal and Molecular Structure.—A stereoscopic view of the $W(QBr)_4$ complex molecule is given in Figure 2, while two of the chelated quinolinols, together with averaged bond lengths and angles, can be found in Figure 3. The structure consists of interlocking complex units which occupy general positions in the cell; the benzene solvate molecule is located in a rather large hole parallel to one of the quinolino rings (Figure 4).

Tetrakis(5-bromo-8-quinolinolato)tungsten(IV) is definitely a dodecahedral $M(AB)_4$ complex which obeys Orgel's rule. Although the complex molecule shares no symmetry with the crystal lattice, it retains almost perfect D_{2d} symmetry characteristic of the *mmmm* dodecahedral stereoisomer (Figure 5). Applying the test of Lippard and Russ[31] to the WN_4O_4 coordination polyhedron, we calculate a dihedral angle of 88.1° between the weighted least-squares planes (Table II) containing the two interpenetrating ABBA trapezoids, one of which is shown in Figure 3. These planes are perpendicular in the D_{2d} dodecahedron, whereas the angle between corresponding planes in the idealized D_{4d} square antiprism is 77.4°.

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(30) A listing of structure factor amplitudes will appear immediately following this article in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth Street, N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.

(31) S. J. Lippard and B. J. Russ, *Inorg. Chem.*, **7**, 1686 (1968).

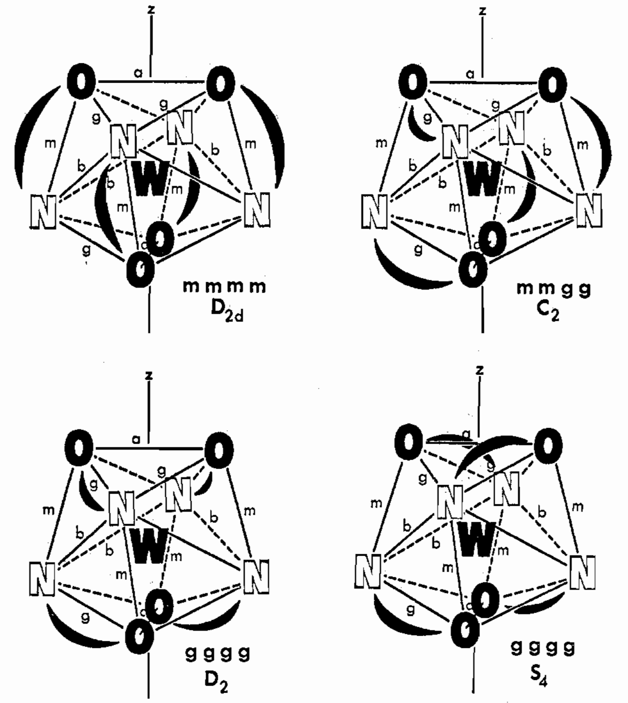

Figure 5.—The four possible stereoisomers for dodecahedral $W(QBr)_4$ with the π-acceptor nitrogens and π-donor oxygens positioned at B and A sites according to Orgel's postulate. Isomers are named according to the polyhedral edges spanned as suggested in ref 4.

TABLE II

TABLE OF WEIGHTED LEAST-SQUARES PLANES

$Ax + By + Cz - D = 0^a$

Atoms		A	B	C	D	Mean dev, Å	Mean σ, Å
			Planes through the Ligands				
Ligand 1:	C_9NO	7.85	−2.68	−13.12	1.10	0.011	0.016
Ligand 2:	C_9NO	18.12	−1.06	5.69	−5.23	0.031	0.016
Ligand 3:	C_9NO	6.20	−3.10	−13.91	1.72	0.017	0.016
Ligand 4:	C_9NO	16.62	1.11	8.24	−5.83	0.035	0.017
			Planes through the Benzene Ring				
Benzene:							
BzC1–BzC6		14.17	3.46	9.22	−0.25	0.12	0.03
			Planes through the Trapezoids				
N1, O1, W, N3, O3		6.53	−2.84	−13.71	1.63	0.046	0.009
N2, O2, W, N4, O4		17.95	−0.41	6.21	−5.32	0.053	0.009

[a] x, y, and z are fractional coordinates in the triclinic system.

TABLE III

$W(QBr)_4$ COORDINATION POLYHEDRON

r_a,[a] Å		r_b, Å		O_n–W–O_{n+2}, deg	
W–O1	2.071 (11)	W–N1	2.187 (12)	O1–W–O3	68.4 (4)
W–O2	2.070 (9)	W–N2	2.201 (12)	O2–W–O4	69.0 (4)
W–O3	2.066 (9)	W–N3	2.214 (14)	O–W–O_{av}	68.7 (3)
W–O4	2.052 (10)	W–N4	2.193 (13)		
W–O_{av}[b]	2.065 (5)	W–N_{av}	2.198 (6)	N_n–W–N_{n+2}, deg	
				N1–W–N3	148.1 (5)
a, Å		b, Å		N2–W–N4	148.1 (5)
O1–O3	2.326 (15)	N1–N2	3.336 (16)	N–W–N_{av}	148.1 (3)
O2–O4	2.334 (14)	N2–N3	3.170 (18)		
O–O_{av}	2.330 (10)	N3–N4	3.285 (19)	N_n–W–O_n, deg	
		N4–N1	3.103 (17)	N1–W–O1	72.8 (4)
		N–N_{av}	3.224 (9)	N2–W–O2	71.8 (4)
g, Å				N3–W–O3	70.8 (4)
N1–O2	2.634 (16)			N4–W–O4	71.4 (4)
N1–O4	2.637 (16)	m, Å		N–W–O_{av}	71.7 (2)
N2–O1	2.632 (16)	N1–O1	2.528 (15)		
N2–O3	2.660 (15)	N2–O2	2.507 (16)		
N3–O2	2.719 (16)	N3–O3	2.483 (16)	N_n–W–N_{n+1}, deg	
N3–O4	2.626 (16)	N4–O4	2.480 (16)	N1–W–N2	99.0 (4)
N4–O1	2.679 (17)	N–O_{av}	2.501 (8)	N2–W–N3	91.8 (5)
N4–O3	2.643 (16)			N3–W–N4	96.4 (5)
N–O_{av}	2.653 (6)			N4–W–N1	90.2 (4)
				N–W–N_{av}	94.4 (3)

[a] Polyhedral parameters are listed according to the Hoard–Silverton nomenclature. [b] Weighted means.

The four quinolinol nitrogen atoms occupy the Hoard–Silverton[4] designated dodecahedral B positions (Figure 1) and lie 2.187–2.214 Å (Table III) from the metal. These donors describe a flattened tetrahedron (tetrahedron angle ~94.4°) and the W–N bonds make an average angle $\theta_B = 74.1°$, where θ_B is the angle which the B positioned nitrogen atoms make with the idealized S_4 axis of the complex. The quinolinol ligands span the poyhedral m edges with an average bite of 2.501 (8) Å and are chelated to the tungsten through phenolic oxygens located at the A sites. Short, intramolecular oxygen–oxygen contacts of 2.33 (1) Å occur along the a edges. The 68.7 (3)° O–W–O angles result in the 1C8–1O···O3–3C8 and 2C8–O2···O4–4C8 bonds lying within 4.0° of collinearity. Other polyhedral parameters (Table III) indicate a remarkable degree of regularity in the WN_4O_4 structure although crystal packing forces slightly compress the complex molecule along one of the dodecahedral pseudo-C_2 axes. The b and g edges and the N_n–W–N_{n+1} angles are sensitive to this distortion, but averaging the observed values yields a set of polyhedral parameters comparable to those obtained for $K_4[Mo(CN)_8]\cdot 2H_2O$[32] and $((C_4H_9)_4N)_3[Mo(CN)_8]$,[33] the only other structurally characterized octacoordinate tungstates or molybdates of dodecahedral symmetry.

Differences between chemically identical bond lengths and angles in the four crystallographically independent quinolinol ligands are statistically insignificant. Isotropic thermal parameters for ligands 1 and 3 are graphically depicted in Figure 3. Mean-square amplitudes of vibration for the light atoms are quite consistent from ligand to ligand (Table I) and seem reasonable when the chemical environments of the various positions are considered. The 1.896 (9) Å C5–Br bonds are almost perpendicular to the longest (0.35–0.40 Å) bromine thermal ellipsoidal axes in all four ligands. Best least-squares planes through the C_9NO portions of the quinolinols are defined by the equations given in Table II along with average deviations from planarity of the ring atoms. Larger deviations (~2σ) for the light atoms in ligands 2 and 4 may result from crystal-packing effects introduced by the benzene solvate molecule.

Uncertainties in the benzene C–C bond lengths (average 1.39 (2) Å) and ring angles (average 120 (10)°) as well as deviations from planarity arise from the high degree of thermal motion ($B_{av} = 10.6$ Å). The C_6H_6 molecule parallels ligand 4 with 3.41–3.99 Å contacts occurring between all six benzene carbons and the atoms of the quinolinol moiety. The benzene Bz–C4 carbon is apparently bent out of the least-squares plane by Br1 (Br1···Bz–C4 = 3.43 Å) toward 4C9 (Bz–C4···4C9 = 3.41 Å) of a symmetry-related complex unit. Contacts with 1C9 and 1C10 (3.61–3.99 Å) as well as with 2C4, 2C5, and 2C6 (3.48–3.89 Å) complete the solvate cage. An intermolecular Br1···Br2 contact of 3.63 Å, which is 0.3 Å less than the sum of two bro-

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(32) (a) J. L. Hoard and H. H. Nordsieck, *J. Amer. Chem. Soc.*, **61**, 2853 (1939); (b) J. L. Hoard, T. A. Hamor, and M. D. Glick, *ibid.*, **90**, 3177 (1968).

(33) B. J. Corden, J. A. Cunningham, and R. Eisenberg, *Inorg. Chem.*, **9**, 356 (1970).

TABLE IV

CRYSTALLOGRAPHIC DATA FOR 8-QUINOLINOL COMPLEXES

Compound	M–N, Å	M–O, Å	Δ_{N-O},[a] Å	N···O,[b] Å	Ref
PdQ_2	2.02	2.02	0.0	2.71	45
$ZnQ_2 \cdot 2H_2O$	2.099	2.066	0.033	2.72	46
β-CuQ_2	1.973	1.930	0.043	2.65	28
α-CuQ_2	1.984	1.939	0.045	2.66	47
$W(QBr)_4 \cdot C_6H_6$	2.20	2.07	0.13	2.50	This study
$SnQ_2(CH_3)_2$	2.35	2.11	0.24	2.68	48
$(QH_2)(SeOCl_3)$	...	...	...	2.64	49
$UO_2Q_2(QH)$	2.56	2.32	0.24	2.61	50
$(Al(MQ)_2)_2O$	2.085	1.813	0.272	2.59	51
$TiCl(Cp)Q_2$	2.26	1.97	0.29	2.59	52
$TiCl_2Q_2$	2.20	1.89	0.31	2.56	53
MoO_2Q_2	2.32	1.98	0.34	...	39
$ThQ_4(OS(CH_3)_2)_2$	2.62	2.32	0.30	2.60	54
	2.70		0.38	2.64	

[a] (M–N) – (M–O). [b] Calculated where unavailable.

mine van der Waals radii,[34] occurs through the center of the cell. The Br–Br repulsion apparently orients the bromine thermal ellipsoids away from one another (Figure 4). Br3 and Br4 lie directly above the 2C9–2C10 (3.53 Å) and 3C9–3C10 (3.43 Å) bond axes, respectively. Whether this positioning is indicative of specific nonbonded interactions in the lattice is uncertain.

The $W(QBr)_4$ Coordination Polyhedron.—The 2.198-Å W–N bonds are 0.16 Å longer than the amido nitrogen bonds in $W[N(CH_3)_2]_6$,[35] the only nitrogen-coordinated tungsten complex available for comparison. This difference is logical considering the reduction in oxidation state from VI to IV, the diminution of nitrogen change, and the increase in coordination number in our compound. Searching molybdenum structural reports (because molybdenum and tungsten have virtually identical crystal radii)[36] we find insufficient evidence to decide on a good metal–nitrogen bond distance. *E.g.*, the $Na_2[Mo_2O_4(cysteine)_2] \cdot 5H_2O$ amine nitrogens are 2.22 Å from the seven-coordinate Mo(V) ion,[37] while the Mo(IV) $[Mo(Cp)_2(NH_2CH_2CH_2S)]I$ complex contains a 2.21-Å Mo–N bond.[38] However, opposing effects arising from changes in coordination number, metal charge, and trans effect operating in the $Mo_2O_4(cysteine)_2^{2-}$ ion cloud a meaningful comparison with $W(QBr)_4$. MoO_2Q_2,[39] MoO_3(dien),[40] and $Mo(CO)_3$dien[41] all contain longer 2.32-Å Mo–N bonds, which have been discussed in terms of O–Mo–N and OC–Mo–N trans effects. $Mo(NCS)_6^{3-}$ (Mo–N = 2.09 Å)[42] and $Mo(Cp)(CO)_2NHNC(CO_2C_2H_5)COH$ (Mo–N = 2.11 Å)[43] both display shorter Mo–N bonds which are probably the result of increased nitrogen to metal π donation and contracted coordination spheres similar to the $W[N(CH_3)_2]_6$ complex.

The observed 2.067-Å tungsten–oxygen bond is nearly that expected for a W–O bond order of 1.0.[44] A W–N bond of similar strength should only be about 0.03–0.04 Å longer.[44b] Thus we are forced to conclude that unlike the MA_4B_4 complex idealized by Orgel's assumption, M–A bonds are stronger than M–B bonds in $W(QBr)_4$. A comparison of the $W(QBr)_4$ parameters with other reported quinolinolato structures is enlightening. The quinolinolato structures listed in Table IV can be divided into two categories according to the differences in metal–nitrogen and metal–oxygen bond distances (Δ_{N-O}): $\Delta_{N-O} < 0.05$ Å in d^8 and d^{10} systems; $\Delta_{N-O} \geq 0.24$ Å in d^0 (including f^m) systems of varying geometry.[45–54] Schlemper[48] has rationalized these differences with Pearson's hard and soft acids and bases concept,[55] and this argument provides a qualitative explanation for the intermediate 0.13-Å Δ_{N-O} value found in $W(QBr)_4$. However, this type of generalization avoids features in the structure and bonding necessary for a more complete understanding of 8-quinolinol coordination chemistry.

The Sn(IV), Ti(IV), and Mo(VI) complexes in Table IV are all cis octahedral with the quinolinol nitrogens trans to the monodentate ligands. The possibility of a trans effect loosening M–N bonds in these compounds has been discussed both by Studd and Swallow[53] and by Atovmyan and Sokolova[39] and may contribute to these larger Δ_{N-O} values.

The actinide complexes listed in Table IV also show equally large Δ_{N-O} values. Therefore, for cases involving metal ions with empty d levels the M–N distance appears to be at least 0.2 Å longer than the M–O distance. Inasmuch as the charge on the metal allows for considerable π donation by the negative phenolic oxygens without appreciable π back-donation to the nitrogen atoms,[56] such a difference is logical. For the

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(34) L. Pauling, "Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260.

(35) D. C. Bradley, M. H. Chrisholm, C. E. Heath, and M. B. Hursthouse, *Chem. Commun.*, 1261 (1969).

(36) R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, **25**, 925 (1969).

(37) J. R. Knox and C. K. Prout, *Chem. Commun.*, 1227 (1968).

(38) J. R. Knox and C. K. Prout, *Acta Crystallogr., Sect. B*, **25**, 2482 (1969).

(39) L. O. Atovmyan and Yu. A. Sokolova, *Chem. Commun.*, 649 (1969).

(40) F. A. Cotton and R. C. Elder, *Inorg. Chem.*, **3**, 397 (1964).

(41) F. A. Cotton and R. M. Wing, *ibid.*, **4**, 314 (1965).

(42) J. R. Knox and K. Eriks, *ibid.*, **7**, 84 (1968).

(43) J. R. Knox and C. K. Prout, *Acta Crystallogr., Sect. B*, **25**, 1952 (1969).

(44) (a) F. A. Cotton and R. M. Wing, *Inorg. Chem.*, **4**, 867 (1965); (b) J. L. Hoard, private communication.

(45) C. K. Prout and A. G. Wheeler, *J. Chem. Soc.*, 1286 (1966).

(46) G. J. Palenik, *Acta Crystallogr.*, **17**, 696 (1964).

(47) R. C. Hoy and R. H. Morris, *ibid.*, **22**, 476 (1967).

(48) E. O. Schlemper, *Inorg. Chem.*, **6**, 2012 (1967).

(49) A. W. Cordes, *ibid.*, **6**, 1204 (1967).

(50) D. Hall, A. D. Rae, and T. N. Waters, *Proc. Chem. Soc., London*, 21 (1964).

(51) Y. Kuschi and Q. Fernando, *J. Amer. Chem. Soc.*, **92**, 91 (1970).

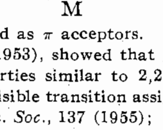
(52) J. D. Matthews and A. G. Swallow, *Chem. Commun.*, 882 (1969).

(53) B. F. Studd and A. G. Swallow, *J. Chem. Soc. A*, 1961 (1968).

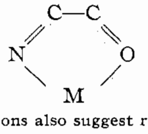
(54) N. Singer, B. F. Studd, and A. G. Swallow, *Chem. Commun.*, 342 (1970).

(55) R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 3533 (1963).

(56) 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 2,2′-bipyridyl and *o*-phenanthroline. All show a strong visible transition assigned as primarily π* ← d: (b) R. J. P. Williams, *J. Chem. Soc.*, 137 (1955); (c) L. Morpurgo and R. J. P. Williams, *ibid., A*, 73 (1966); (d) A. B. P. Lever, "Inorganic Electronic Spectroscopy," American Elsevier, New York, N. Y., 1968, Chapter 8. (e) 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.

TABLE V

POLYHEDRAL PARAMETERS FOR DODECAHEDRAL COMPLEXES OF THE HEAVIER TRANSITION METALS

Complex	Isomer	r_a, Å	r_b, Å	r_a/r_b	Ref
		Reported Structures			
d^0: $Zr(ox)_4^{4-}$	*mmmm*	2.30	2.17	1.03	57
$Zr(NTA)_2^{2-}$	$M(AA'B_2)_2$	2.25 (O) 2.44 (N)	2.12	1.06 1.15	58
$Zr(NES)_4$	S_4-*gggg*	2.54	2.06	1.24	59
$TiCl_4(diars)_2$	$M(AA)_2B_4$	2.71	2.44	1.11	60
d^1: $(R_4N)_3[Mo(CN)_8]^c$		2.12	2.12	1.00	33
d^2: $K_4[Mo(CN)_8]^d$		2.16	2.16	1.00	32
$W(QBr)_4$	*mmmm*	2.07	2.20	0.93	This study
	Hypothetical $M(AB)_4(d^0) \leftrightarrow M(AB)_4(d^2)$ Congeners^a				
d^0: $Zr(QBr)_4$	*gggg*	2.38	2.04	1.17	
d^2: $W(NTA)_2^{2-\,b}$	$M(A_2BB')_2$	2.17	2.25 (N) 2.07 (O)	0.96 1.05	
$W(NES)_4^b$	*gggg*	2.09	2.34	0.89	

[a] M–A = 1.05(M′–B) + 0.07 Å; M–B = 0.95(M′–A) + 0.07 Å; M = d^2 metal ion; M′ = d^0 metal ion; $A_M = B_{M'}$ = π donor; $A_{M'} = B_M$ = π acceptor. [b] Ligand constraints make these hypothetical complexes highly questionable. [c] R = *n*-butyl; the sodium salt (tetrahydrate) of tungsten is reported to be antiprismatic: L. D. C. Bok, J. G. Leipoldt, and S. S. Basson, *Acta Crystallogr., Sect. B*, **26**, 684 (1970). [d] The red salt which precipitates after irradiation of the $Mo(CN)_8^{4-}$ in the presence of hydrazine and cadmium(II) is reported to contain an antiprismatic octacyanomolybdate grouping [J. Chojnacki, J. Grochowski, L. Lebioda, B. Oleksyn, and K. Stadnicka, *Rocz. Chem.*, **43**, 273 (1969)], and $H_4[W(CN)_8]\cdot 6H_2O$ is reported to contain an antiprismatic octacyanotungstate grouping [S. S. Basson, L. D. C. Bok, and J. G. Leipoldt, *Acta Crystallogr., Sect. B*, **26**, 1209 (1970)].

d^8 and d^{10} complexes, the π donation of the oxygen atoms is limited by repulsions between the filled π-symmetry d orbitals of the metal and the π electrons on the oxygen, but back-donation is quite favorable for the nitrogen π acceptors and Δ_{N-O} drops to less than 0.05 Å. The tungsten(IV) complex of this study is an intermediate example with π donation by oxygen in the A positions being quite feasible, but with only two d electrons to overlap with the four nitrogen π acceptors. Thus the observed 0.13-Å Δ_{N-O} value is logical.

The disparity in the W–N and W–O bond distances is also significantly less than the Zr–N and Zr–O differences in the d^0 $Zr(NTA)_2^{2-}$ and $Zr(NES)_4$ complexes (Table V),[32,33,57–60] where the non-π-bonding nitrogen atoms occupy dodecahedral A positions as expected from electronic considerations. However, these bond lengths can be corrected to give a more reasonable comparison with the tungsten(IV) d^2 congeners of $Zr(NES)_4$ and $Zr(NTA)_2^{2-}$ (Table V). The A↔B ligand interchange neglects ligand constraints and simply assumes that M–A and M–B bond distances in the tungsten and zirconium $M(AB)_4$ congeners are a function of (1) the change in metal crystal radii (Zr(IV)–W(IV) = 0.07 Å)[36] and (2) ligand–ligand repulsions and/or stronger π bonding by the B ligands (using an idealized (M–A)/(M–B) ratio of 1.05).[4] Thus $W(QBr)_4$ (d^2: O at A; N at B) is converted to its $Zr(QBr)_4$ congener (d^0: N at A; O at B) to give calculated bond lengths: $Zr-O_A$ = 0.07 Å + 0.95(2.07 Å) = 2.04 Å; $Zr-N_B$ = 0.07 Å + 1.05(2.20 Å) = 2.38 Å. The 2.04-Å Zr–O bond is only slightly shorter than the 2.06-A Zr–O bond in $Zr(NES)_4$. Although the calculated 2.38-Å Zr–N bond for $Zr(QBr)_4$ is considerably shorter than $Zr(NES)_4$ (Zr–N = 2.54 Å) and $Zr(NTA)_2^{2-}$ (Zr–N = 2.44 Å) metal–nitrogen bonds, the contracted quinolinol bite and increased W–N multiple bonding could account for this difference. Reverse arguments explain the $W(NES)_4$ bond lengths, but the $W(NTA)_2^{2-}$ distances appear less reasonable. In addition, NTA^{3-} and NES^{2-} ligand constraints make these particular isomers sterically unlikely.

The $W(QBr)_4$ phenolic oxygens are only 2.33 (1) Å apart and, therefore, interpenetrate each other's van der Waals radius by about 0.54 Å.[34] Excepting cases which involve ligand-constrained bidentate O–O donors (O_2^{2-}, NO_3^-, CO_3^{2-}, etc.), this contact is one of the closest observed in a transition metal coordination sphere. The O–O approach seems reasonable when the availability of energetically favorable tungsten d-type orbitals and electron delocalization through the extensive quinolinol ring systems are considered. While the possibility of some O–O bonding cannot be entirely ignored, the 2.33-Å separation is 0.85 Å longer than that expected for an O–O single bond.

Ligands composing each ABBA trapezoid seem to be forced sideways along their respective m edges toward the pseudo-S_4 axis of the complex. This action opens θ_B to 74.1° and compresses θ_A to 34.4°. As the NNNN tetrahedron is flattened, tungsten–nitrogen $d\pi \rightarrow p\pi$ overlap increases and would eventually maximize at $\theta_B = 90°$. The WN_4O_4 polyhedral geometry therefore seems to be the result of donor–donor interactions coupled with ligand constraints and metal–ligand π-bonding effects. On the other hand, the $W(QBr)_4$ angular parameters are almost identical with those calculated by Racah[61] for the dodecahedral d^4sp^3 hybrid with maximum bond strengths: $\theta_A = 34.6°$; $\theta_B = 72.8°$. Thus the final structure allows for maximum covalency in the metal–ligand bonds.

The Quinolinol Rings.—Alternation in carbon–carbon bond lengths in the 5-bromo-8-quinolinolato ring systems follows values found for other 8-quinolinolato structures (Table V) and those calculated for quinoline.[62] This finding is in accord with the ring carbon bond lengths in $(Al(MQ)_2)_2O$,[51] the only other sub-

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(57) G. L. Glen, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, **2**, 250 (1963).

(58) J. L. Hoard, E. Willstadter, and J. V. Silverton, *J. Amer. Chem. Soc.*, **87**, 1610 (1965).

(59) D. C. Bradley, M. B. Hursthouse, and I. F. Rendall, *Chem. Commun.*, 368 (1970).

(60) (a) R. J. H. Clark, J. Lewis, R. S. Nyholm, P. Pauling, and G. B. Robertson, *Nature (London)*, **192**, 222 (1961); (b) R. J. H. Clark, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 2460 (1962).

(61) G. Racah, *J. Chem. Phys.*, **11**, 214 (1943).

(62) K. Nishimoto and L. S. Forster, *Theor. Chem. Acta*, **4**, 155 (1966).

stituted 8-quinolinolato structure available for comparison. The 1.319 (9) Å C8–O bond length is quite similar to those in the complexes listed in Table V with the exception of $TiCl_2Q_2$ (C8–O = 1.37 Å)[53] and $(QH_2)(SeOCl_3)$ (C8–O = 1.37 Å).[49] If this discrepancy reflects the degree of C8–O multiple bonding, then the longer 1.37-Å distances in the 8-quinolinolium ion and the Ti(IV) complex may be due to the removal of oxygen electron density by the quinolinolium proton or by delocalization into the Ti(IV) d orbitals, respectively. This electron withdrawal could lower the C8–O bond order and lengthen the bond.

π Bonding in MA_4B_4 Systems.—The π-bonding matrix of an $MX_8{}^{n-}$ or $MA_4B_4{}^{n-}$ complex of D_{2d} symmetry is complicated by the lack of orthogonality with the σ-bonding matrix with the exception of the b_1 irreducible representation (Table VI). Therefore, treatments which only include the b_1 levels can determine the energy level in which the d-like electron(s) resides in the ground state but cannot provide definite conclusions regarding stereochemistries, bond lengths, and total π-bonding effects. Unfortunately, *exact* calculations are not presently feasible for such a system, but the middle ground of the angular overlap model (AOM)[63] with the retention of all d-orbital possibilities gives more information on the complete π-bonding picture.

TABLE VI

ANGULAR OVERLAP PARAMETERS FOR d-ORBITAL BONDING IN MA_4B_4 SPECIES[a]

	D_{2d} [b]			
	a_1	b_1	b_2	e[d]
σ_A	1.13	0.00	0.29	2.58
σ_B	0.60	0.00	2.56	0.84
$\pi_A{}^{\parallel}$	1.50	0.00	0.56	0.91
$\pi_B{}^{\parallel}$	0.48	0.00	0.78	1.26
$\pi_A{}^{\perp}$	0.00	0.26	0.00	1.28
$\pi_B{}^{\perp}$	0.00	1.28	0.00	0.20

	D_{4d} [c]		
	a_1	e_2[d]	e_3[d]
σ	0.05	3.10	4.85
$\pi^{\parallel}$	1.26	2.16	2.24
$\pi^{\perp}$	0.00	2.32	0.89

[a] See footnote 61; the σ values are ±0.01 but the π values are probably only ±0.10 considering the approximation made. [b] $\theta_A = 34°$; $\theta_B = 74°$. [c] $\theta = 58°$. [d] Total overlap is given. For simplified energy level diagrams the perturbation of the levels from a nonbonding position is related to half the total overlap of the doubly degenerate levels.

Comparison of the entire d-orbital π-bonding scheme in the MA_4B_4 dodecahedron by the AOM method shows that both the A and B ligands are substantially involved in π bonding. Whereas the b_1 levels usually discussed[4] have about five times as much interaction (as determined by the square of the overlap integral, Table VI) with the B ligands, the a_1 and e levels have significantly greater interactions with the A ligands than with the B ligands. The b_2 interactions are appreciably lower and are similar in magnitude for both A and B ligands.

For eight-coordinate d^0 complexes of D_{2d} symmetry which have four π-donor ligating atoms and four π acceptors, the choice between the A and B positions is clear-cut if steric factors do not override π-electronic considerations: the π donors will occupy B positions. The a_1, b_2, and e orbitals of the metal d level are partially occupied as a result of σ bonding, so the π donors will gain more stability by interaction with the empty b_1 level than with the partially filled levels. Electrostatic considerations also predict this orientation. This conclusion is in agreement with the corollary of Orgel's rule, as first suggested by Clark, *et al.*,[60] and used to explain the $TiCl_4(diars)_2$ structure. The π-donor halides are expected and observed at the B sites. A recent report of the $Zr(NES)_4$ structure[59] also has the π-donor oxygens at the B positions. Generally the π-acceptor or weaker π-donor ligands should be relegated to the dodecahedral A sites in the d^0 complexes.

Spin-paired d^2 complexes of the MA_4B_4 dodecahedral configuration should have the π donors and π acceptors reversed from the d^0 complexes, consistent with Orgel's hypothesis, but possibly for reasons other than that stressed by Orgel. For these d^2 complexes, the b_1 level on the metal is filled, but the other d orbitals are only partially occupied, again as the result of σ bonding. Therefore, the π donors are again more stable if occupying a position of low electron density; this time the A positions. Similarly the π-acceptor B ligands can gain more stability by overlap with filled orbitals, so that they logically occupy the B locations in these d^2 species.

The $W(QBr)_4$ structure, which could possibly adopt configurations other than the one observed, fits this d^2 pattern. The $\pi^{\perp}$-acceptor nitrogens are in the B positions and the π-donor oxygens are at the A sites. The short O···O separation is consistent with significant π donation by the oxygens to the tungsten largely *via* the a_1 and e bonding matrices. In fact, the overlap for $\pi^{\perp}$ is significantly greater than $\pi^{\parallel}$ in the A positions, and the oxygen atoms are probably somewhat distorted from the usual cylindrically symmetrical electron density profile.

For d^1 complexes arguments similar to the d^2 species are weaker because the occupancy level of the σ-bonded d orbitals is closer to that of the b_1 level. The latter is only half-filled. However differences in the electronegativities of carbon and tungsten (even in the 5+ oxidation state) are sufficient to expect some ionic character in the σ bonds. However, d^1 $NbCl_4(diars)_2$[64] and $VCl_4(diars)_2$[60] are isostructural with $TiCl_4(diars)_2$, contrary to Orgel's postulate, while the structure of $ReCl_4(diars)_2{}^+$ is still an open question.

Consequently, for eight-coordinate complexes in which other steric forces are reasonably balanced, we suggest that the MA_4B_4 complexes will follow Orgel's hypothesis for the d^2 cases and probably for the d^1 cases as well, primarily from π-donor considerations. The corollary should hold for the d^0 structures, with the π

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(63) (a) K. B. Yatsimirskii, *Teor. Eksp. Khim.*, **2**, 451 (1966); *Theor. Exp. Chem. (USSR)*, **2**, 342 ff (1966), and references cited therein. (b) The bonding is considered to be proportional to the squared overlap parameter based on the angular part of the wave function. Following Yatsimirskii, the σ values were adjusted proportionately to give a total of 8.00 for the eight σ interactions. The π values were adjusted proportionately to give relative values corresponding to calculations of σ and π bonding (C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory," W. A. Benjamin, New York, N.Y., 1965, pp 128–132) rather than using an unrelated number. A scale factor for the π bonding was developed by a comparison of the $CrF_6{}^{3-}$ overlaps calculated by Ballhausen and Gray (*op. cit.*) with angular values at ±22.5° from the σ bonds (1/4 of 90°). Similar values for the MA_4B_4 complex at 17 and 18° (1/4 the angle from one ligand to the next) were scaled accordingly to obtain the π values. Therefore, the π values are more approximate than the σ values but are closer to reality than the prevalent crystal field calculations which allow no π inclusion.

(64) R. J. H. Clark, D. L. Kepert, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 2865 (1965).

donors occupying the B positions. For chemically useful purposes, however, it is important to realize that for the early transition series metal ions oxygen π donors will generally be incorporated into most MA_4B_4 systems. The extraordinary affinity of oxygen for these metals has been frequently demonstrated, especially for higher valence molybdenum and tungsten, and special effects arising from strong M–O bonds should not be unexpected in this or any other stereochemistry.

The equivalent metal–carbon bond lengths noted for the A and B sites in the $Mo(CN)_8^{4-}$ and $Mo(CN)_8^{3-}$ ions[32,33] are logical with this more complete π-bonding picture. Based on observations with octahedral complexes, Δ_π is only about 10% of Δ_σ for the cyano species.[65] Greater π overlap in the eight-coordinate D_{2d} complexes and the higher oxidation states might raise this to at most 20%. The relative electronegativities of the atoms suggest a transfer of about one-third of the electron density to the σ-bonded metal levels, and overlap and population considerations using the σ density indicate a spread of not more than 15% π bonding in the A positions to 25% π bonding in the B position. This small difference combined with the expected lengthening of $Mo-(CN)_b$ bonds due to ligand $d_{x^2-y^2}$ coulombic repulsions[32b] can account for the indistinguishable bond lengths. Similar considerations for the mixed donor–acceptor MA_4B_4 complexes indicate that the π-donor ligands rather than the π-acceptor ligands determine the occupation of the A and the B sites.

Similar conclusions can be drawn by coulombic considerations as well as by the molecular orbital stability arguments cited, but electrostatic calculations[66] have normally led to the conclusion that the D_{4d} antiprism is preferred. Our simplified AOM molecular orbital estimates suggest equal σ bonding and no significant differences in the total π bonding between the D_{4d} and D_{2d} configurations for MX_8^{n-} type systems. This finding is consistent with the square-antiprismatic geometries reported for d^0 NbF_8^{3-} and d^1 ReF_8^{2-} and $Na_3[W(CN)_8]$; crystal-packing effects and ligand–ligand repulsions may be quite important in determining the chosen stereochemistry. Like Parish,[2] we find more stability for the low-energy d orbital in the D_{2d} case. Therefore, other things being equal, complexes containing either four or eight π acceptors and d^2 (and some d^1) configurations should prefer the D_{2d} dodecahedral geometry. Mixed donor–acceptor MA_4B_4 species should also prefer the D_{2d} configuration since the energy situation appears similar for both stereochemistries except for the donor site preferences noted above, which could tip the stability toward the D_{2d} stereochemistry.

Ligand Constraints in $M(AB)_4$ Systems.—Bidentate and polydentate ligand wrapping patterns in eight-coordinate complexes are complicated by the variability of dodecahedral and square-antiprismatic edge lengths and the differences in metal–ligand bond distances. While the short N···O ligand bite along the dodecahedral m edges (2.501 Å, Table III) in $W(QBr)_4$ may be dismissed as an artifact of the crowded W^{4+} coordination sphere, it is interesting that the longer g edges (2.653 Å) were not spanned. In fact, molecular models convinced us that the S_4- or D_2-*gggg* dodecahedral stereoisomers (Figure 5) would also minimize interligand contacts in the $W(QBr)_4$ molecule and provide additional stability from internal hydrogen bonding. However the observed geometry is consistent with the observation that every reported ML_4 complex (M = transition metal ion, L = bidentate ligand) is *mmmm* where L forms a three-, four-, or five-membered chelate ring with the metal ion. The only transition metal octacoordinate complexes containing six-membered chelate rings, $Zr(acac)_4$[67] and $Zr(NES)_4$,[59] are *ssss* square antiprismatic (s_{av} 2.67 Å) and S_4-*gggg* dodecahedral (g_{av} 2.78 Å), respectively.

Another $M(AB)_4$ possibility, the *mmgg* stereoisomer, is sterically feasible, but we agree with Parish[2] that this structure seems intuitively less reasonable if a "most favorable" polyhedron[4] is required. Similarities in the solid-state and solution spectra of $W(QBr)_4$ as well as the nature of its synthetic origin lead us to believe that the thermodynamically most stable isomer prevails. These facts are difficult to rationalize with a small, tightly packed *mmgg* polyhedron where ligand bites would conceivably differ by 0.15 Å or more. The same type of argument may partially explain the nonexistence of *ssll* square-antiprismatic stereoisomers.

The stereochemistry of transition metal dodecahedral complexes containing multidentate ligands can be explained if it is assumed that (1) the nature of the metal–ligand bond determines the donor coordination site while (2) the adjusted bite and gross steric requirements of the ligand determine which polyhedral edge is to be spanned (and there are no asymmetric π-bonding ligands). Unsymmetrical bidentate chelating agents $(AB)^{n-}$ (A is a π donor, B is a π acceptor, etc.) are expected to span only dodecahedral m or g edges. Thus the rigid, five-membered chelate rings in $W(QBr)_4$ form across smaller m edges with the O and N donors attached at the electronically appropriate A and B positions. The WQ_4^+ and NbQ_4 complexes should also be D_{2d}-*mmmm* if the single d electron can exert sufficient stereochemical influence on the coordination sphere geometry. However, the d^0 ZrQ_4 and TiQ_4 complexes should be either S_4- or D_2-*gggg* (N at A, O at B) since the steric properties of the quinolinol ring systems do not allow the "flipped" ligand to remain chelated along the m edges. This steric difficulty can be seen by mentally rotating the two ligands in one $[W(QBr)_4]$ABBA trapezoid (Figure 3) 180° about the bisectors of the chelate bite angles. The quinolinol bite may cause abnormally long metal–nitrogen bonds, larger θ_A and θ_B angles, or distortions to other polyhedral forms in these MQ_4 complexes. The attachment of bulky groups to C2 or C7 (Figure 3) of the quinolinolato moiety in the d^1 and d^2 chelates may sufficiently alter the ligand's steric and/or electronic properties to necessitate the formation of a *gggg* or square-antiprismatic stereoisomer.

The geometry of $Zr(NES)_4$ is S_4-*gggg* with the imino nitrogens located at A sites and the phenolic oxygens situated at the B positions.[59] This arrangement clearly fits our assumption when donor site preferences and the larger, more flexible salicylaldiminato chelate ring (N···O = 2.78 Å) are considered. However, nonbonded interactions across the dodecahedral a

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(65) R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 1524 (1965).

(66) D. G. Blight and D. L. Kepert, *Theor. Chim. Acta*, **11**, 51 (1968), and references cited therein.

(67) J. V. Silverton and J. L. Hoard, *Inorg. Chem.*, **2**, 243 (1963).

edges are probably minimized in this configuration, especially with respect to the *mmmm* stereoisomer with the same N and O arrangement. In the dodecahedral bis(nitrilotriacetato)zirconate(IV) anion[56] and M(AA'-B_2)$_2$ system the two nitrogen atoms are positioned at the A sites as predicted from electronic considerations, while the π-donor acetato oxygens are linked to the metal at the B and remaining A sites across m (2.62 Å), g (2.78 Å), and a (2.68 Å) edges. This variation in edge length emphasizes the strong influence which coordination sphere geometry exerts on ligand bite. Hoard's point that the NTA^{3-} ligand makes "maximal use of short ring spans" is well taken.[58]

The various parameters affecting eight-coordination stereochemistry seem to be of nearly equal value. The more stable systems, therefore, should be the result of a number of concurring effects. For instance, the stereochemistries discussed above could have been rationalized in terms of just ligand constraint effects; *i.e.*, the tungsten complex is *mmmm* (N at B, O at A) because (1) steric restrictions imposed by the ligand will not permit *mmmm* (N at A, O at B) and (2) the dodecahedral g edges and the antiprismatic s and l edges are longer and less favored than the m edges in the configuration actually found. Similar arguments could be made for the other complexes. Therefore, further investigations are in progress in these laboratories to test some of the predictions cited herein. Hopefully, we can shortly place the π-bonding effect as well as other steric considerations on a more quantitative basis.

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CONTRIBUTION FROM THE INSTITUT FÜR ANORGANISCHE CHEMIE,
UNIVERSITÄT BERN, CH-3000 BERN 9, SWITZERLAND

The Crystal Structure of Manganese(II) Hexacyanoruthenate (II) Octahydrate, $Mn_2[Ru(CN)_6] \cdot 8H_2O$

BY MAX RÜEGG, ANDREAS LUDI,* AND KONRAD RIEDER

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The crystal structure of manganese(II) hexacyanoruthenate(II) octahydrate, $Mn_2[Ru(CN)_6] \cdot 8H_2O$, has been determined from three-dimensional X-ray data using integrated Weissenberg photographs. The polynuclear cyanide crystallizes in the monoclinic space group C_{2h}^5-$P2_1/n$. The unit cell dimensions are $a = 9.488$ (2), $b = 12.494$ (2), $c = 7.606$ (3) Å, $\beta = 98.8$ (1)°. The measured density is 1.90 g/cm^3; the calculated value is 1.90 g/cm^3 with two formula units per cell. Least-squares refinement gave a final R factor of 5.4% for 1476 reflections. Ruthenium is coordinated by six cyanide ions in a slightly distorted octahedron. The average Ru–C and C–N distances are 2.028 (6) and 1.160 (8) Å. All cyano groups are bonded through nitrogen to manganese. Each Mn is coordinated by three nitrogen atoms and three water molecules. Two such distorted octahedra of the facial form are linked together to form a binuclear unit $Mn_2N_6(H_2O)_4$ by sharing one edge, two water molecules acting as bridging ligands. The distance between the two Mn is 3.705 (1) Å. Average Mn–N and Mn–O bond lengths are 2.150 (6) and 2.304 (6) Å. Eight waters of crystallization are connected by hydrogen bonds to the coordinated water molecules. The distances between the different oxygen atoms are between 2.73 and 3.23 Å.

Introduction

The most common structure of the polynuclear transition metal cyanides is the cubic face-centered unit cell of the Prussian blue analogs.[1] In a recent paper we have reported a single-crystal study of manganese(II) hexacyanocobaltate(III) hydrate, a typical member of the cubic cyanides.[2] It was shown that this structure is characterized by fractional occupancies of certain crystallographic positions and that the water molecules are present as coordinated as well as zeolitic water. Compounds with the same simple cubic X-ray pattern are obtained by the reaction of a hexacyanometalate(III) with a variety of divalent metal ions.[1,2] Equally sparsely soluble precipitates result when the tervalent metal ion in the cyano complex is replaced by a divalent one, *e.g.*, Fe(II), Ru(II), and Os(II). The hexacyanometalate(II) salts of nickel and copper still belong to the cubic system.[3] The X-ray pattern of the corresponding manganese and also cobalt salts, however, cannot be assigned anymore to the cubic system. Since we could obtain single crystals in the case of manganese(II) hexacyanoruthenate(II) we concentrated our studies of noncubic Prussian blue analogs on this compound.

The ambident coordination of the cyanide ion in manganese(II) hexacyanoruthenate(II) is demonstrated by the position of the CN stretching frequency. This vibration mode is observed at 2077 cm^{-1} in the polynuclear compound[4] and at 2048 cm^{-1} in the mononuclear $Ru(CN)_6{}^{4-}$ complex ion.[5] This frequency shift is characteristic for carbon- and nitrogen-bonded

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