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Transition Metal Eight-Coordination. 8. Stereochemical Integrity, Geometrical Isomers, and Isomerization of Mixed Ligand Tungsten(IV) Chelates Containing Picolinic Acid and 8-Quinolinol Derivatives

Craig J. Donahue and Ronald D. Archer*

Contribution from the Department of Chemistry, Graduate Research Center Tower A, University of Massachusetts, Amherst, Massachusetts 01003.

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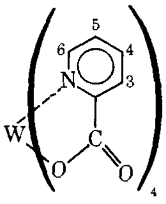
Abstract: The entire series of eight-coordinate tetrakis $W(mpic)_n(dcq)_{4-n}$ complexes has been prepared, isolated, and characterized. The proton magnetic resonance (^1H NMR) spectrum of $W(mpic)_3(dcq)$ has two methyl signals of 2:1 intensity even at 50 °C and provides the first example of "stereochemical integrity" or pseudorigidity on a ^1H NMR time frame for an eight-coordinate tetrakis (chelate) complex above room temperature. Another first, the separation of two geometrical isomers (designated α and β) for an eight-coordinate transition-metal complex from solution, has been obtained for $W(mpic)_2(dcq)_2$ through liquid and thin layer chromatography, which have been used to separate the entire series. Spectroscopic rate studies indicate the kinetics parameters $E_a = 114$ kJ mol^{-1}, $\Delta H^{\ddagger} = 111$ kJ mol^{-1}, and $\Delta S^{\ddagger} = 35$ J mol^{-1} deg^{-1} for the isomerization of the β isomer toward the ($\beta \rightleftarrows \alpha$) equilibrium, where $K_{eq} \sim 5$ in the temperature range studied. Chemical analysis, magnetic moments, and electronic and ^1H NMR spectra together allow consistent stereochemical conclusions. The inertness and the π-acceptor and π-donor site preferences for d^2 dodecahedral complexes allow for the "stereochemical integrity" observations, even with polytopal transformations, which normally produce nonrigidity.

In order to evaluate the stereochemical dynamics of inert d^2 eight-coordinate complexes, we decided to synthesize mixed ligand complexes based on the inert $W(pic)_4$[2] and $W(q)_4$[3] complexes, **1** and **2**, respectively, where the ligands are derivatives of picolinic acid (Hpic) and 8-quinolinol (Hq). Prior to this study, previous reports of eight-coordinate transition-metal tetrakis chelates all indicated fast exchange limit proton magnetic resonance (^1H NMR) signals well below room temperature.[4] In fact, Fay and his co-workers[4a] have designated the tetrakis(N,N-dimethyldithiocarbamato)tantalum(V) as stereochemically rigid based on its nonequivalent



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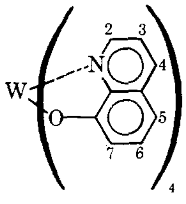

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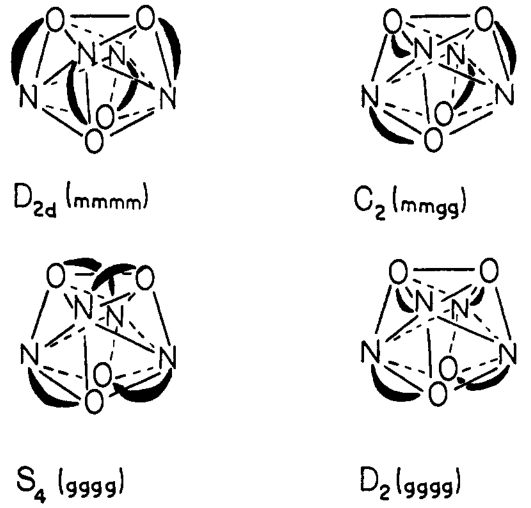

Figure 1. The four dodecahedral $W(ON)_4$ isomers which are consistent with Orgel's rule[9] that π acceptors should occupy the B positions in d^2 eight-coordinate species.

^1H NMR methyl resonances below −62 °C. The very inert nature of the d^2 $W(q)_4$ type complexes in the presence of base[5] and the lack of ligand exchange in $W(pic)_4$[2a] indicate that ligand dissociation should not be a complication for NMR studies. The nonequivalent donors were also expected to be an asset to slower exchange in much the same way that fast exchange limit ^1H NMR signals occur approximately 200 °C higher in the mixed tungsten phosphine hydride complexes than in the corresponding $W(CN)_8^{4-}$ ion, where all donors are equivalent.[6] Previous structural studies[8] have shown that the nitrogen and oxygen atoms in 8-quinolinolates differ sufficiently in their abilities to anticipate compliance to Orgel's rule[9] for these complexes. That is, for d^2 ions, anticipated ground states of complexes with four π acceptors (such as unsaturated nitrogen atoms) and four π donors (such as oxygen anionic donors) will occupy dodecahedral B and A positions, respectively. The B and A positions are the designations of Hoard and Silverton.[10] Compliance to this rule reduces 93 possible dodecahedral isomers[11] to only four ground-state isomers (Figure 1), or even fewer when steric considerations are included.[12] As is discussed below, not only have slow exchange limit ^1H NMR spectra been observed, but geometrical isomers have been obtained as well.[14,16]

Experimental Section

Ligands. Picolinic acid (Eastman) and 5,7-dichloro-8-quinolinol (Aldrich) were used without further purification.

5-Methyl-8-quinolinol. This ligand was prepared with a modification of the Skraup reaction procedure of Hollingshead.[18] 2-Amino-4-methylphenol (10.04 g, 81.7 mmol, prepared by the method of Proskouriakoff and Titherington[19]) was mixed with 6.20 g (40.6 mmol) of 4-methyl-2-nitrophenol (Aldrich's 2-nitro-*p*-cresol). Then 24 g (260 mmol) of glycerol, which had been dried by heating at 185 °C for 1 h followed by cooling in a desiccator over P_4O_{10}, was added to the mixture in a 2-L three-neck flask. Then 20.1 g (20.5 mmol) of concentrated sulfuric acid was added to the doughlike mixture in small portions. The resulting yellow-brown solution was heated under reflux conditions for 4 h and then cooled. The resulting brown residue was pulverized and dissolved in 400 mL of water, and made slightly basic with sodium hydroxide, then acidic (pH 3-4) with glacial acetic acid. Steam distillation produced a yellow distillate. Addition of ammonium hydroxide to make the distillate slightly basic caused the precipitation of 5-methyl-8-quinolinol. The crude product was washed with water, dried in vacuo over potassium hydroxide, and recrystallized from ethanol, yield 56%.

Anal. Calcd for $C_{10}H_9NO$: C, 75.45; H, 5.70; N, 8.80. Found: C, 75.11; H, 5.88; N, 8.14.

7-Bromo-5-methyl-8-quinolinol was prepared using a modified procedure of Beauford and Beauford.[20] 5-Methyl-8-quinolinol (2.69 g, 17.0 mmol) was dissolved in 50 mL of glacial acetic acid to which a 5% bromine solution in glacial acetic acid was added dropwise over a period of 30 min with stirring. After allowing the solution to stand for 2 h, it was neutralized with concentrated ammonium hydroxide. The product was subsequently cooled, filtered, and washed with large quantities of water and dried over potassium hydroxide. The product was recrystallized from boiling ethanol and redried in vacuo over potassium hydroxide, yield 95%.

Anal. Calcd for $C_{10}H_8NOBr$: C, 50.45; H, 3.39; N, 5.88. Found: C, 50.84; H, 3.64; N, 5.91.

5-Methylpicolinic acid was prepared by the method of Jerchel, Bauer, and Hippchen.[21] The ligand was purified by vacuum sublimation slightly below its melting point, mp 166-167 °C, lit.[21] 163-164 °C. The H^1 NMR spectrum is consistent with the desired product.

Other Reagents. Tungsten hexacarbonyl (Pressure Chemical) was purified by vacuum sublimation at 100 °C onto a cold finger at dry ice temperature. Fisher spectrograde acetone and chloroform and other reagent grade chemicals were used without further purification.

Tungsten(IV) Mixed-Ligand Complexes. $W(mpic)_n(dcq)_{4-n}$ Complexes. After degassing 50 mL of mesitylene, 0.41 g (3 mmol) of 5-methylpicolinic acid, 0.64 g (3 mmol) of 5,7-dichloro-8-quinolinol, and 0.42 g (1.2 mmol) of tungsten hexacarbonyl were added to the mesitylene contained in a two-neck 100-mL round-bottom flask. Attached to the flask was a fitted stopcock and a water-cooled reflux condenser fitted with a three-way stopcock. After the system was purged with prepurified nitrogen for several minutes the solution was heated under reflux conditions for 4 h under a back pressure of nitrogen. The solvent was removed from the resulting dark blue solution by flash evaporation, and the resulting product was subjected to vacuum sublimation at 150 °C, which removed the unreacted tungsten hexacarbonyl and ligands, and the reduced ligands.

$W(mpic)_n(pic)_{4-n}$, $W(mpic)_n(mq)_{4-n}$, and $W(mpic)_n(bmq)_{4-n}$ complexes were prepared in an analogous fashion to the $W(mpic)_n(dcq)_{4-n}$ series. In each case an equal molar ratio of the two ligands was allowed to react in a 5:1 molar ratio of total ligand to tungsten hexacarbonyl.

Chromatographic Separation of the $W(mpic)_n(dcq)_{4-n}$ Complexes. After initial thin layer chromatographic (TLC) studies to select a suitable solvent system, an E. Merck prepacked size B preparative "silica gel 60" column was used to separate the $W(mpic)_n(dcq)_{4-n}$ series. The column was connected to the solvent reservoir and alternatively to a detachable glass syringe by means of a three-way stopcock. Approximately 5-8 mL of a saturated chloroform solution of the crude product mixture was drawn up into the syringe, a filter was attached to the head of the syringe, and the solution was injected into the column. The ligand impurity band (band 1) and the first three metal-complex bands [$W(dcq)_4$, $W(mpic)(dcq)_3$, and α-$W(mpic)_2(dcq)_2$] were collected using chloroform as the eluent. After this third complex band was removed (band 4), the eluent was made more polar by the addition of acetone to give an approximate eluent composition of 85% chloroform, 15% acetone. After the removal of the next two bands [β-$W(mpic)_2(dcq)_2$ and $W(mpic)_3(dcq)$], the eluent composition of 70% chloroform, 30% acetone was used to effect a more rapid recovery of the final band, $W(mpic)_4$. After six complete runs the respective bands from each of the runs were combined. Each band was then subjected to another separation to ensure that its separation from the other components was complete. The same column was used for the entire procedure without any appreciable loss in the quality of the separations. In order to observe the individual bands on the column it was necessary to point a strong intensity lamp directly at the column, which otherwise appeared black due to the strong charge-transfer transitions of the complexes. After the second separation of the complexes the solutions were taken to dryness by flash evaporation and dried in vacuo at 100 °C over potassium hydroxide and paraffin for 48 h.

Anal. Calcd for $W(mpic)_4$: C, 46.17; H, 3.32; N, 7.69. Found: C, 45.90; H, 3.88; N, 7.32.

Anal. Calcd for $W(mpic)_3(dcq)\cdot{}^1\!/_5CHCl_3$: C, 43.75; H, 2.70; N, 6.76; Cl, 11.12. Found: C, 43.51; H, 3.06; N, 6.36; Cl, 11.17.

Anal. Calcd for β-$W(mpic)_2(dcq)_2\cdot{}^1\!/_8CHCl_3$: C, 43.01; H, 2.26; N, 6.24; Cl, 17.29. Found C, 42.80; H, 2.77; N, 5.58; Cl, 17.28.

Anal. Calcd for α-$W(mpic)_2(dcq)_2\cdot{}^1\!/_6CHCl_3$: C, 42.83; H, 2.25; N, 6.21; Cl, 17.69. Found: C, 42.83; H, 2.52; N, 6.07; Cl, 17.70.

Table I. Ligand Abbreviations

bmq$^-$ = 7-bromo-5-methyl-8-quinolinolato
bq$^-$ = 5-bromoquinolinolato
dcq$^-$ = 5,7-dichloro-8-quinolinolato
mpic- = 5-methylpicolinato
–
mq$^-$ = 5-methyl-8-quinolinolato
pic$^-$ = picolinato = pyridine-2-carboxylato
q$^-$ = 8-quinolinolato

Anal. Calcd for W(mpic)(dcq)$_3$: C, 42.58; H, 1.89; N, 5.84; Cl, 22.18. Found: C, 42.10; H, 2.23; N, 5.67; Cl, 21.76.

Physical Studies. Electronic spectra of the complexes were recorded from 10 000 to 40 000 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 cell contained the same solvent as the sample solution.

Magnetic Susceptibility Measurements. The Faraday method was used for determining the magnetic susceptibility of the mixed-ligand complexes. CoHg(SCN)$_4$ was used to calibrate the balance. Sample size was ca. 5 mg. The diamagnetism of the ligands was corrected by summing the Pascal constants.[22]

Proton Nuclear Magnetic Resonance Spectra. The ^{1}H NMR spectra of these complexes were either measured on a 60-MHz Perkin-Elmer R12A or a 90-MHz Perkin-Elmer R32 nuclear magnetic resonance spectrometer. All variable temperature studies were performed on the latter instrument. All spectra were referenced against tetramethylsilane. CDCl$_3$ or CD$_2$Cl$_2$ was used as the solvent. Reported temperatures of spectra are accurate to ±2 °C.

Kinetic Studies. The β-W(mpic)$_2$(dcq)$_2$ complex used in the kinetic studies of the conversion of the β isomer to the α isomer was obtained by chromatographic separation of a mixture of α-W(mpic)$_2$(dcq)$_2$ and β-W(mpic)$_2$(dcq)$_2$ on a small (1.5 by 0.25 in.) silica gel column using a 4:1 v/v chloroform to acetone solvent mixture. The slow conversion of the β isomer back to an equilibrium mixture was recorded at appropriate time intervals by recording the electronic spectra of the solution from 600 to 700 nm on a Hitachi Model EPS-3T spectrophotometer. Matched Beckman 5.00 cm, jacketed cells were used. The sample cell was maintained at a constant temperature to within ±0.2 °C by means of a Haake constant temperature bath. The reference cell contained the same solvent (4:1 v/v chloroform/acetone) as the sample solution. In all cases less than 6 min transpired between the time the complex was obtained off the column and the recording of the first spectra. During this time interval the solution was maintained at approximately the same temperature as the jacketed sample cell. A nitrogen atmosphere was maintained in the spectrophotometer sample chamber during these studies.

Plots of $\ln (\Delta A_\infty - \Delta A_t)/(\Delta A_\infty - \Delta A_0)$ vs. time (t) provided slopes equal to $-(k_1 + k_{-1})$ or $-k_1(1 + 1/K)$, where k_1 is the $\beta \rightarrow \alpha$ specific rate constant, k_{-1} is the $\alpha \rightarrow \beta$ specific rate constant, K is the $\beta \rightleftarrows \alpha$ equilibrium constant, and ΔA is a two-wavelength absorbance difference, which was used to compensate for baseline drift. Activation and transition state parameters were obtained using normal procedures.

Results

Synthesis of W(mpic)$_n$(dcq)$_{4-n}$ Complexes. As was the case with the previously prepared tetrakis(8-quinolinolato)tungsten(IV) complexes,[3,5] no stable intermediates were observed during the course of the reaction. Tungsten(V) eight-coordinate complexes[23] were not observed during these syntheses. The only color change observed during the course of the reaction was the dramatic change from the initial colorless solution to an opaque inklike blue solution, which indicated the formation of the tetrakis complexes.

Although equal moles of the two ligands were used in the synthesis, chromatographic separation of the W(mpic)$_n$(dcq)$_{4-n}$ series indicated a predominance of the W(mpic)$_4$, W(mpic)$_3$(dcq), and W(mpic)$_2$(dcq)$_2$ complexes over the W(mpic)(dcq)$_3$ and W(dcq)$_4$ complexes. Maximum solubility of the W(mpic)$_4$ complex in methylene chloride was estimated to be approximately 0.2 M. Solubility of the complexes decreases, in all solvents tried, as the picolinato ligands are replaced by quinolinolato ligands. The W(dcq)$_4$ complex, which is the least soluble of the series, is soluble in methylene chloride to a concentration less than 10^{-4} M.

Table II. Silica Gel TLC R_f Values for the W(mpic)$_n$(dcq)$_{4-n}$ Series

Band	Complex	Chloroform	10:1 v/v[a]	4:1 v/v[a]
1		b	b	b
2	W(dcq)$_4$	>0.9	>0.9	>0.9
3	W(mpic)(dcq)$_3$	0.29	0.9	0.9
4	α-W(mpic)$_2$-(dcq)$_2$	0.11	0.74	0.83
5	β-W(mpic)$_2$(dcq)$_2$	0.02	0.18	0.39
6	W(mpic)$_3$(dcq)	0.01	0.13	0.32
7	W(mpic)$_4$	<0.01	0.06	0.16

[a] Chloroform/acetone solutions. [b] At the solvent front.

Chromatographic Separation of W(mpic)$_n$(dcq)$_{4-n}$ Complexes. Seven bands were recovered by column chromatography from the crude product after the reaction mixture had been sublimed. The first band was yellow-brown in color at the solvent front. The ^{1}H NMR spectrum of the mixture in CCl$_4$ consists of strong multiplets at 1.30 and 0.90 ppm, a weaker multiplet at 7.55 ppm, and a doublet at 4.13 ppm. The single band was separated by TLC using 3:1 v/v chloroform/hexane into two brown spots and one yellow spot. These results suggest that the first band consists of residual and reduced ligands.

The remainder of the bands (see Table II) ranged from light blue-green in color, through several shades of blue, and finally to purple. To test the purity of each collected band, a sample was subjected to a TLC separation.

When a sample from either the fourth or fifth band was subjected to the purity test, two spots were observed. Reelution of either of the two spots always led to the reappearance of two components having the same R_f values as the two spots in the previous run. A two-dimensional thin layer chromatographic separation (i.e., developing the plate in one direction and then rotating the plate 90° and developing again) of either a sample from the fourth or fifth band produced four spots from one (a set of two spots in the first direction, and two sets of two spots in the second direction). This behavior was only observed for the fourth and fifth bands collected by column chromatography. Development of a sample from any of the other tungsten complex bands (i.e., 2nd, 3rd, 6th, or 7th) by the thin layer chromatographic technique always yielded a single spot.

The visible spectra of the complexes constituting the fourth and fifth bands were different if the spectra were obtained directly as the bands came off the column. On aging or heating, however, the same two solutions gave identical spectra. (See isomerization results below.)

Elemental analysis together with this time-dependent equilibration property allowed us to assign these isomers as indicated in Table II. The two W(mpic)$_2$(dcq)$_2$ isomers were arbitrarily designated α and β based solely on their chromatographic behavior.

Synthesis of Other Mixed Ligand Tungsten(IV) Chelates. The reaction of picolinic acid and 5-methylpicolinic acid with tungsten hexacarbonyl yields the series W(mpic)$_n$(pic)$_{4-n}$. This series proved difficult to separate chromatographically into its *pure* components. The mixed ligand complexes of this series have virtually identical visible spectra and similar molecular weights. Of the various series of complexes obtained by the reaction of 5-methylpicolinic acid and 5,7-dichloro-8-quinolinol, 5-methyl-8-quinolinol, and 7-bromo-5-methyl-8-quinolinol, only the 5,7-dichloro-8-quinolinol/5-methylpicolinic acid combination produced a series that could be completely separated by the chromatographic procedures described. The W(mpic)$_n$(mq)$_{4-n}$ series was only partially recovered. The

Table III. Magnetic Properties of $W(mpic)_n(dcq)_{4-n}$ Complexes[a]

Complex	$\chi_g \times 10^6$	$\chi_m \times 10^6$ (exptl)	$\chi_m \times 10^6$ (cor)[b]	μ_{eff}, μ_B
$W(dcq)_4$	−0.35	−350 ± 100	120 ± 150	0.5[c]
$W(mpic)(dcq)_3$	−0.29	−275 ± 100	125 ± 150	0.5[c]
α-$W(mpic)_2(dcq)_2$	−0.31	−300 ± 100	50 ± 150	0.3[c]
β-$W(mpic)_2(dcq)_2$	−0.47	−400 ± 100	−50 ± 150	0
$W(mpic)_3(dcq)$	−0.59	−475 ± 100	−125 ± 150	0
$W(mpic)_4$	−0.36	−250 ± 100	0 ± 150	0

[a] Measured by the Faraday method. [b] Diamagnetic corrections were made using Pascal constants.[22] [c] Zero within experimental error.

Table IV. Electronic Absorption Spectra[a] of $W(mpic)_n(dcq)_{4-n}$ Complexes

$W(mpic)_4$[b]	$W(mpic)_3(dcq)$[b]	α-$W(mpic)_2(dcq)_2$[c]	β-$W(mpic)_2(dcq)_2$[c]	$W(mpic)(dcq)_3$[b]	$W(dcq)_4$[b]
16 000 (20 400)	16 000 (22 000)	15 400 (27 000)	15 100 (28 500)	14 800 (38 100)	14 200 (44 500)
17 800 (20 000)	17 400 (sh, 19 100)	16 900 (sh, (sh, 0 2 20 600)	16 100 (sh, 24 100)	15 700 (sh, 24 300)	
22 400 (sh, 6100)	22 100 (sh, 3200)				
26 600 (sh, 2700)	24 900 (sh, 3600)	25 600 (5700)	27 000 (4800)	25 300 (7400)	24 400 (9600)
	26 700 (3800)				
34 800 (sh, 17 450)	33 100 (sh, 2700)			30 700 (sh, 4900)	30 600 (6700)
	35 500 (sh, 9200)			32 300 (sh, 5500)	31 900 (7300)
37 100 (28 000)	38 200 (46 500)			38 700 (93 000)	38 900 (106 600)

[a] The values given are in cm^{-1}; the numbers in parentheses are ϵ values; sh = shoulder. [b] Spectra recorded in chloroform. [c] Spectra recorded in 4:1 v/v chloroform/acetone.

Table V. The 90-MHz ^1H NMR Spectra of $W(mpic)_n(dcq)_{4-n}$ Complexes at 35 °C in CD_2Cl_2[a]

	$W(mpic)_4$[b]	$W(mpic)_3(dcq)$[b]	$W(mpic)_2(dcq)_2$[c]	$W(mpic)(dcq)_3$
mpic, 5-methyl	Singlet 2.44	Two singlets [2:1][d] 2.42, 2.47	Two singlets [4:1] 2.41, 2.37	Singlet 2.35
mpic (H_3, H_4) and dcq (H_3, H_4, H_6)	Two doublets 7.62 (8), 7.28 (8)	Two multiplets[e] 7.30, 7.60	Two multiplets 7.25, 7.58	Multiplet 7.40
mpic (H_6)	Singlet 9.21	Two singlets [~2:1][f]	Singlet	g
dcq (H_2)		Singlet 8.95	Singlet 9.08	g

[a] Resonance signals reported in parts per million downfield from tetramethylsilane; J_{H-H} values in parentheses in hertz. [b] See Figure 3. [c] See Figure 4; $W(mpic)_2(dcq)_2$ solution was a mixture of α and β isomers. [d] $W(mpic)_3(mq)$ has singlet resonances at 1.60, 2.37, and 2.43 ppm with 1:2:1 intensity ratios. [e] $W(mpic)_3(mq)$ has multiplets near 7.2 and 7.6 ppm. [f] $W(mpic)_3(mq)$ has a broad unresolved peak at about 9.25 ppm. [g] Unobserved because of low solubility.

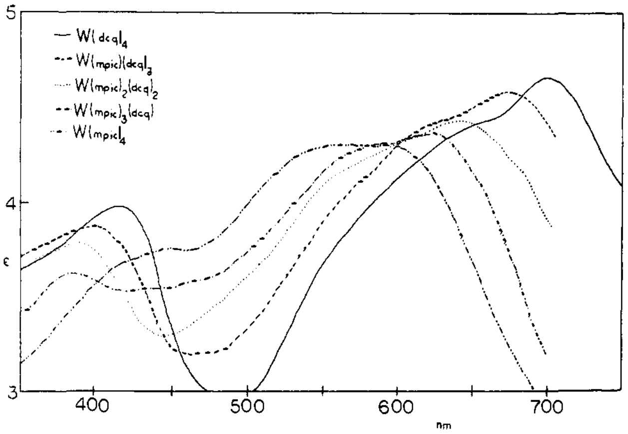

Figure 2. Electronic spectra of the $W(mpic)_n(dcq)_{4-n}$ complexes in chloroform. The $n = 2$ spectrum is for an equilibrium mixture.

complexes $W(mpic)(mq)_3$ and $W(mq)_4$ were oxidized on the column to the corresponding tungsten(V) species during the chromatographic separation process. Once in the +5 state, these cationic complexes could not be eluted from the column even with pure acetone. Initial thin layer chromatographic studies of the $W(mpic)_n(bmq)_{4-n}$ series indicated a similar trend of silica gel induced oxidation as observed for the $W(mpic)_n(mq)_{4-n}$ series.

Magnetic Susceptibility Measurements. The room temperature magnetic measurements on the $W(mpic)_n(dcq)_{4-n}$ series are indicated in Table III. The complexes are diamagnetic or may possess a small paramagnetism ($\leqslant 0.5\ \mu_B$) common in lower valence "diamagnetic" tungsten compounds. This slight paramagnetism has been attributed to temperature-independent paramagnetism.[22]

Electronic Absorption Spectra. The electronic absorption spectra of the $W(mpic)_n(dcq)_{4-n}$ series (Table IV and Figure 2) are characterized by two (or more) overlapping intense absorption bands at the red end of the visible region ($\bar{\nu}$ = 1.42–1.68 μm^{-1}; ϵ 2.0–4.4 × 10^4). The successive replacement of a 5-methylpicolinato ligand by the more highly conjugated 5,7-dichloro-8-quinolinolato ligand results in a 0.06 μm^{-1} energy shift to lower energy per ligand. A less intense band is also observed at the blue end of the visible region ($\bar{\nu}$ = 2.2–2.7 μm^{-1}; ϵ 3–10 × 10^3). The higher energy ultraviolet transitions are typical of the ligands.

Nuclear Magnetic Resonance Studies. The ^1H NMR spectra of the $W(mpic)_n(dcq)_{4-n}$ series at 35 °C in CD_2Cl_2 are given in Table V. The spectrum of the $W(mpic)_4$ complex shows a sharp methyl signal at 2.44 ppm (Figure 3). The aromatic protons of the 5-methylpicolinato ligand in $W(mpic)_4$, H_3 and H_4, are each resolved into a doublet, while the third aromatic

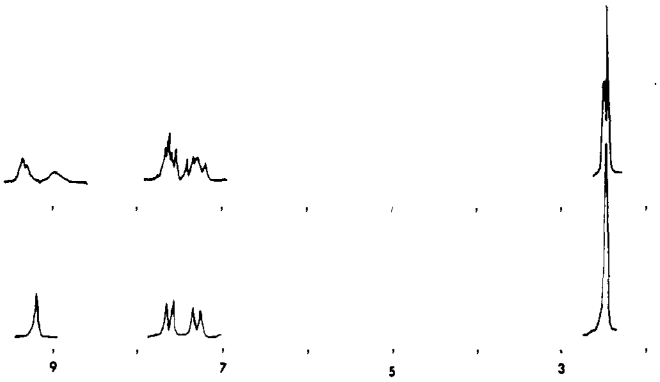

Figure 3. The ^1H NMR spectra of $W(mpic)_4$ and $W(mpic)_3(dcq)$ in CD_2Cl_2 at 35 °C relative to Me_4Si.

Table VI. The $M(AB)_2(AB')_2$ Complexes Which Conform to Orgel's Rule

		IUPAC Nomenclature
	D_{2d} *(mmmm)* Parentage	
I C_{2v} *(m'm'mm)*	mer-D_{2d}	*ae, bf; gc, hd*
II C_2 *(m'm'mm)*	bif-D_{2d}	{*ae, gc; bf, hd* *ae, hd; bf, gc*}
	C_2 *(mmgg)* Parentage	
III C_2 *(mmg'g')*	bif(b)-C_2	{*ac, ge; bf, hd* *ad, he; bf, gc*}
IV C_2 *(m'm'gg)*	bif(b)-C_2	{*ae, gc; bd, hf* *ae, hd; bc, gf*}
V C_1 *(m'mg'g)*	bif(g)-C_2	{*ac, bf; ge, hd* *ad, bf; gc, he*}
VI C_1 *(m'mg'g)*	skew-C_2	{*ac, hd; bf, ge* *ad, gc; bf, he*}
	S_4 *(gggg)* Parentage	
VII C_2 *(g'g'gg)*	bif-S_4	{*ac, bd; gf, he* *ad, bc; ge, hf*}
VIII C_1 *(g'g'gg)*	skew-S_4	{*ac, gf; bd, he* *ad, hf; bc, ge*}
	D_2 *(gggg)* Parentage	
IX C_2 *(g'g'gg)*	bif(a)-D_2	{*ac, bd; ge, hf* *ad, bc; gf, he*}
X C_2 *(g'g'gg)*	skew-D_2	{*ac, hf; bd, ge* *ad, gf; bc, he*}
XI C_2 *(g'g'gg)*	bif(b)-D_2	{*ac, ge; bd, hf* *ad, he; bc, gf*}

proton (H_6), that α to the nitrogen, is a singlet at 9.21 ppm, which is shifted significantly downfield from the free ligand value of 8.37 ppm. Addition of free ligand to the $W(mpic)_4$ complex in CD_2Cl_2 results in the appearance of two sets of resonance signals, those of the free ligand (H_3 = 8.07, H_4 = 7.85, and H_6 = 8.37 ppm) and those due to the coordinated ligand in $W(mpic)_4$. The methyl signals of free and coordinated ligand both occur at 2.44 ppm, however.

Two 5-methylpicolinato methyl signals are observed for the $W(mpic)_3(dcq)$ complex at 2.47 and 2.42 ppm in a 2:1 ratio (Figure 3). The aromatic protons of the 5-methylpicolinato ligand (H_3, H_4) and the 5,7-dichloro-8-quinolinolato ligand (H_3, H_4, H_6) constitute two multiplets centered around 7.30 and 7.60 ppm. The protons α to the nitrogen in the ligands are distinguishable. The H_6 proton of the 5-methylpicolinato ligands appears as two unresolved singlets in approximately a 2:1 ratio at 9.31 and 9.26 ppm. The corresponding 5,7-dichloro-8-quinolinolato proton, H_2, appears as a broad singlet at 8.95 ppm.

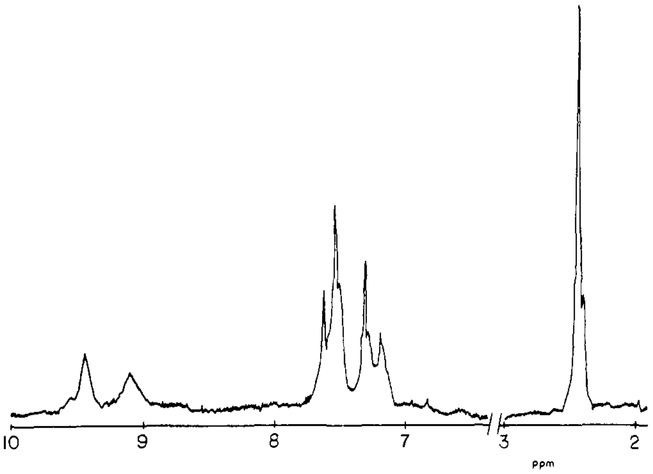

Figure 4. The ^1H NMR spectrum of equilibrated $W(mpic)_2(dcq)_2$ in CD_2Cl_2 at 35 °C relative to Me_4Si.

The $W(mpic)_2(dcq)_2$ ^1H NMR spectrum was recorded of an equilibrium mixture of the α and β isomers. The 5-methylpicolinato methyl protons are only partially resolved into what appears to be two singlets of ~4:1 intensity at 2.41 and 2.37 ppm, respectively (Figure 4). Again, with the exception of the protons α to the nitrogen, the picolinato and quinolinolato aromatic protons appear as multiplets centered around 7.25 and 7.58 ppm. The protons α to the nitrogens are again distinct for the two ligands, occurring as broad resonances in a 1:1 ratio at 9.43 ppm for the picolinato ligands and 9.08 ppm for the quinolinolato ligands.

The $W(mpic)(dcq)_3$ complex is only soluble enough to raise the stronger resonances above the noise level. The 5-methylpicolinato methyl signal is a singlet occurring at 2.35 ppm. The protons α to the nitrogen were not observed while the remainder of the aromatic protons were grouped around 7.40 ppm. For $W(dcq)_4$ no resonance signals could be observed because of low solubility.

The variable temperature ^1H NMR spectra of $W(mpic)_3(dcq)$ and of $W(mpic)_2(dcq)_2$ were recorded in CD_2Cl_2 down to −50 °C and in $CDCl_3$ at 55 °C. The $W(mpic)_3(dcq)$ complex yielded the same methyl splitting pattern for the entire temperature range explored. The ^1H NMR spectra of the $W(mpic)_2(dcq)_2$ mixture did not change at 55 °C in $CDCl_3$ compared to the 35 °C spectra in CD_2Cl_2, but at 0 °C and below, the weaker methyl signal of the $W(mpic)_2(dcq)_2$ mixture was not resolved. At 0 °C it appears as a shoulder at the base of the stronger methyl signal, while at −25 and −50 °C it was unobserved. This change is the result of broadening due to solution viscosity increases: $\nu_{1/2}$ (35 °C) = 2.5, $\nu_{1/2}$ (0 °C) = 3.5, $\nu_{1/2}$ (−25 °C) = 4.5, $\nu_{1/2}$ (−50 °C) = 6.5 Hz. On warming this sample to 35 °C both methyl signals were again observed.

Photochemistry. The relative photochemical sensitivity of the $W(mpic)_n(dcq)_{4-n}$ complexes was graphically illustrated by their behavior (color changes) as separated spots when a TLC plate was left exposed to the fluorescent lights in the laboratory. Within minutes the $W(dcq)_4$ complex on silica gel would turn from blue-green to pink. A fine spray of Cl_2 gas produced the same pink color instantaneously and a drop of alcoholic KOH added to the pink spot would return the $W(dcq)_4$ complex back to its original color. The members of the $W(mpic)_n(dcq)_{4-n}$ series all behaved in an analogous fashion. The rate of the photochemical color change decreases as n increases. Covering the plates or storing the plates in the dark preserves the original color of the complexes much longer, but not indefinitely. Quantum yield studies have not been performed for these complexes to date.

Isomerization. As noted above, either of the two isomers of $W(mpic)_2(dcq)_2$ undergo some isomerization to approach the equilibrium

$$\beta\text{-W(mpic)}_2\text{(dcq)}_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \alpha\text{-W(mpic)}_2\text{(dcq)}_2 \qquad (1)$$

A comparison of the electronic spectra of the α and β isomers directly after chromatographic separation of an equilibrium mixture of the two isomers together with the extinction coefficients of the two isomers at 648 and 662 nm produced a value of 5 ± 1 for the equilibrium constant of eq 1. The infinite time spectra show that the equilibrium constant does not change appreciably over the temperature range studied. The equilibrium constant had been estimated as 4 from the NMR results.

First-order specific rate constants were determined from the slope from the ln $[(\Delta A_\infty - \Delta A_t)/(\Delta A_\infty - \Delta A_0)]$ vs. time plots and a value of 5 ± 1 for the equilibrium constant. The calculated k_1 values are 8.8 (±0.4) × 10^{-6}, 3.4 (±0.2) × 10^{-5}, and 1.19 (±0.05) × 10^{-4} s^{-1} at 23.0, 31.0, and 40.5 °C for the conversion of the β isomer to the α isomer, where the numbers in parentheses are the standard deviations, including both the errors from the time plots and the estimated errors in K. Since k_1 is proportional to $K/K + 1$, the range from 4 to 6 for K gives only a 7% range in k_1 values. An Arrhenius plot gives an activation energy of 27.3 (±1.1) kcal/mol (114 kJ/mol). The transition state activation parameters are $\Delta G^{\ddagger} = 24.1$ (±1.1) kcal/mol (101 kJ/mol), $\Delta H^{\ddagger} = 26.5$ (±1.1) kcal/mol (111 kJ/mol) and $\Delta S^{\ddagger} = 8.4$ (±10) cal mol^{-1} deg^{-1} (35 J mol^{-1} deg^{-1}) at 25 °C.

Discussion

Synthesis of the $W(mpic)_n(dcq)_{4-n}$ Complexes. The synthesis of the series $W(mpic)_n(dcq)_{4-n}$ from tungsten hexacarbonyl, 5-methylpicolinic acid, and 5,7-dichloro-8-quinolinol was modeled after the successful synthesis of the parent complexes, $W(pic)_4$[2a] and $W(dcq)_4$,[5] which were previously reported. Tungsten hexacarbonyl was used rather than $W_2Cl_9^{3-}$ or other tungsten species because of its ready availability and convenience and rather than molybdenum because of the all-around greater stability of the tungsten complexes. The observation[2a] that the $W(pic)_4$ complexes could not be synthesized by a melt reaction of the tungsten hexacarbonyl and picolinic acid without some decarboxylation of the ligand to pyridine prompted the use of a high-boiling, inert solvent as a reaction medium for the tungsten hexacarbonyl/ligand mixture. Five moles of the ligands was used because they also function as the oxidizing agents, taking the tungsten from a formal oxidation state of zero to four, for the tetrakis chelate complexes. The predominance of the complexes $W(mpic)_n(dcq)_{4-n}$ where n = 2, 3, and 4 over the complexes where n = 0 and 1 indicates that 5,7-dichloro-8-quinolinol is the stronger oxidizing agent.

Chromatographic Separation of the $W(mpic)_n(dcq)_{4-n}$ Series. The chromatographic behavior of the $W(mpic)_n(dcq)_{4-n}$ series coupled with the electronic spectral evidence and the elemental analyses clearly points to the existence of an equilibrium mixture of two geometrical isomers of $W(mpic)_2(dcq)_2$. Equally remarkable is the observation that isomers are found only for the 2:2 ligand combination. The other ligand combinations [where $n \neq 2$ for the series $W(mpic)_n(dcq)_{4-n}$] produce a single stereoisomer each.

Scrutiny of the R_f values of the $W(mpic)_n(dcq)_{4-n}$ series (Table II) obtained by thin layer chromatographic separation with a 4:1 v/v chloroform/acetone mixture reveals that $W(mpic)(dcq)_3$ and α-$W(mpic)_2(dcq)_2$ have similar R_f values (0.32 and 0.39) and that β-$W(mpic)_2(dcq)_2$ and $W(mpic)_3(dcq)$ complexes also have similar R_f values (0.83 and >0.9). The similarity in the R_f values suggests that $W(mpic)(dcq)_3$ and α-$W(mpic)_2(dcq)_2$ have some closely related structural feature as do the β-$W(mpic)_2(dcq)_2$ and $W(mpic)_3(dcq)$ complexes. These values also imply that the α and β isomers have at least one structural feature which is somewhat different. The lack of a center of symmetry for all logical eight coordinate isomers does not help in the assignments of the α and β isomers. The elution order of the $W(mpic)_n(dcq)_{4-n}$ series indicates that the 5,7-dichloro-8-quinolinato group interacts less strongly with the Si-O-H groups of the silica gel than does the 5-methylpicolinato group. The marked difference is probably due to the presence of the carbonyl oxygen of the carboxylic acid group on the 5-methylpicolinato ligand which can hydrogen bond to the hydroxyl groups on the silica gel and bind its complexes more tightly to the silica gel than those complexes containing more 5,7-dichloro-8-quinolinolato ligands. The assignment of the α and β isomers to definite structures cannot be made on this information either.

Magnetic Moments of the $W(mpic)_n(dcq)_{4-n}$. All of the complexes in the $W(mpic)_n(dcq)_{4-n}$ series can logically be assumed to be spin-paired d^2 complexes of tungsten(IV). The magnetic moments of these complexes, zero within experimental error, are consistent with those found previously for the octacyano species,[24] the tetrakis(8-quinolinolato)tungsten(IV) species,[3,5,25] and the tetrakis(picolinato)tungsten(IV) species.[2] The χ_g of $W(pic)_4$ was recently reported[2b] to be −0.25 × 10^6 cgs in good agreement with the value of −0.36 × 10^6 cgs determined for $W(mpic)_4$ in this study.

The chemical inertness of this class of compounds is apparently due to the placement of the two d electrons in the lowest lying b_1 level (or the $d_{x^2-y^2}$ orbital), which is orthogonal to the σ-bonding matrix, but capable of π bonding.[8a] The relative chemical inertness toward base of the tetrakis(picolinato)tungsten(IV) complexes is such as to fall closer to the octacyano species than the tetrakis(quinolinolato)tungsten(IV) complexes.

Electronic Spectra of the $W(mpic)_n(dcq)_{4-n}$ Series. By virtue of their intensities ($\epsilon > 10^4$) the low energy (14 200–17 800 cm^{-1}) bands observed for the $W(mpic)_n(dcq)_{4-n}$ series are assigned as charge-transfer bands rather than as d–d transitions. The transitions would appear to be metal to ligand[8a] ($\pi^* \leftarrow d$) rather than ligand to metal ($d \leftarrow n$ or π) type transitions based on the two following experimental observations. First there is a shift to higher energies for the $W(pic)_4^+$ and WQ_4^+-type tungsten(V) species relative to the corresponding tungsten(IV) complexes, which is in line with metal to ligand type transitions but is the reverse trend to that expected for ligand to metal type transitions. Second, a comparison of the electronic spectra of $Mo(pic)_4$[2a] to the more easily oxidizable $W(pic)_4$ indicates a shift from high to low energy, which is the proper trend for a metal to ligand charge-transfer transition, but is again contrary to that expected for a ligand to metal transition.

The stepwise trend in the low energy (14 200–17 800 cm^{-1}) bands of the $W(mpic)_n(dcq)_{4-n}$ series, which maintain approximately the same contour, lends further support to the conclusion that the entire series are tetrakis eight-coordinate complexes. The trend toward lower energy with increasing conjugation [$W(mpic)_4$ to $W(dcq)_4$] for this transition is consistent with the metal to ligand charge-transfer suggestion noted above; i.e., to a first approximation, an electron moves to the ligand system in the excited state.

The change in the maxima of the electronic spectra of the α and β isomers of $W(mpic)_2(dcq)_2$, not only in the 15 000-cm^{-1} region but also in the 26 000-cm^{-1} region, suggests that these latter transitions are also charge-transfer transitions (or less likely d–d transitions) rather than ligand transitions. The differences in the extinction coefficients of the two isomers in

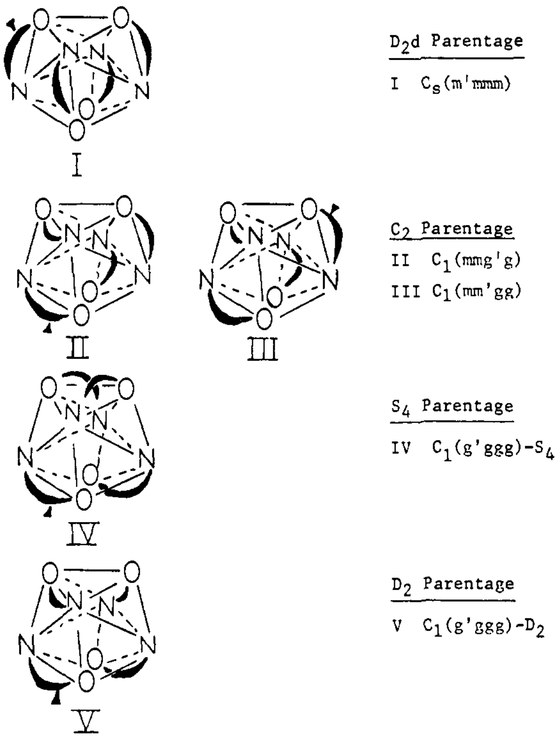

Figure 5. The $M(AB)_3(AB')$ complexes which conform to Orgel s rule.

both the 26 000-cm^{-1} and 15 000-cm^{-1} energy regions are measurable but small and therefore nothing conclusive can be asserted about the relative symmetry of the two molecules. The similarity in the extinction coefficients of the two isomers is consistent with the two molecules having similar point group symmetries. Unfortunately, none of the logical eight-coordinate isomers possess a center of symmetry.

This appears to be the first well-documented evidence for the existence of eight-coordinate geometrical isomers in solution,[13] although eight-coordinate geometrical isomers are known in the solid state.[16,17]

Stereochemistry of the $W(mpic)_n(dcq)_{4-n}$ Complexes. The $W(bq)_4$ complex[8a] possesses dodecahedral geometry with the quinolinolato ligands spanning the *m* edges to give almost perfect D_{2d} symmetry. The four quinolinol nitrogens occupy the dodecahedral B sites and the four phenolic oxygens occupy the dodecahedral A sites[8a] in accord with Orgel's rule.[9] Comparison of reported quinolinolato and picolinato structures reveals the bites of the two ligands to be approximately equal for the same metal center; e.g., copper(II).[26] It was anticipated on the basis of this bite similarity and the x-ray results[8] that the stereochemistry of the $W(mpic)_n(dcq)_{4-n}$ complexes would conform to Orgel's rule.

Figures 5 and 6 catalog those dodecahedral isomers which conform to Orgel's rule for the general complexes, $M(AB)_3(AB')$ and $M(AB)_2(AB')_2$. For the $M(AB)_3(AB')$ complexes one isomer arises from each of the $M(AB)_4$-D_{2d} (*mmmm*), -S_4 (*gggg*), and -D_2 (*gggg*) parentages and two from the $M(AB)_4$-C_2 (*mmgg*) parentage.

Eleven $M(AB)_2(AB')_2$ isomers conform to Orgel's rule, two each of $M(AB)_4$-D_{2d} (*mmmm*) and -S_4 (*gggg*) parentage, three of $M(AB)_4$-D_2 (*gggg*) parentage, and four of $M(AB)_4$-C_2 (*mmgg*) parentage. In order to identify each member of this class uniquely (with one exception) the following nomenclature has been adopted. The abbreviation *bif* is for bifacial and any letter following *bif* signifies the edge joining the two faces connecting the AB ligands. The abbreviation *mer* is for meridonal and the term *skew* is used to designate the remaining low symmetry complexes. Lastly these designations are appended with the point group symmetry of the $M(AB)_4$ complex from which they arose. This nomenclature uniquely identifies all but a pair, C_2 (*m'm'gg*) and C_2 (*mmg'g'*), of the $M(AB)_2(AB')_2$ complexes. An alternative approach, that adopted by the IUPAC, is to label each of the eight positions *a* through *h* and to specify the edge which each of the ligands spans by a two-letter combination. This method uniquely defines all possible wrapping patterns but is very cumbersome.

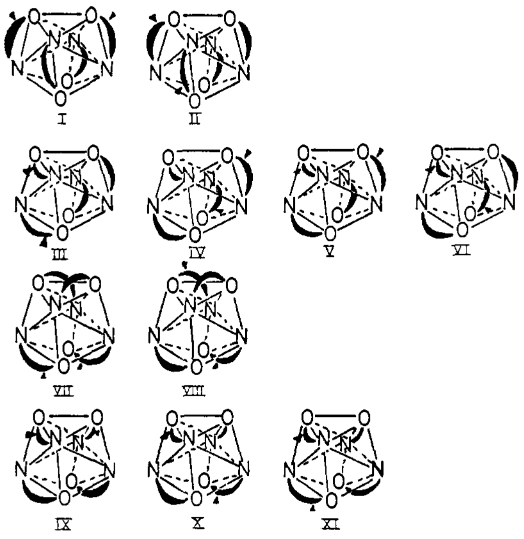

Figure 6. The $M(AB)_2(AB')_2$ complexes which conform to Orgel's rule. See Table VI.

Nuclear Magnetic Resonance Spectra as a Nonrigidity Probe. NMR spectroscopy has been the primary technique used to examine the potentially nonrigid behavior of molecules. Several possibilities must be considered, and as many as possible eliminated, when relying on equivalent or nonequivalent NMR resonance signals to interpret the stereochemical nature of molecules in solution. Equivalent NMR resonance signals can result from a number of possible structural situations including (1) *rigid* molecules in the NMR time frame (where the rigid connotation implies only normal vibrations, translations, and rotations) provided that (a) the molecule has sufficient symmetry such that only one signal is expected, or (b) the molecule possesses properties such that the nonequivalence is unresolved or accidently superimposed; (2) *nonrigid* molecules undergoing rapid polytopal conversions with (a) cycles scrambling all positions (regardless of molecular symmetry) or (b) cycles not scrambling all of the positions, but with a single signal for the high symmetry or nonresolution reasons noted above for a rigid molecule.

Nonequivalent NMR signals may result from (1) a single rigid structure with low symmetry; (2) a mixture of rigid and/or nonrigid structures; (3) an association or dissociation of the species in solution; (4) a "freezing out" of normally free rotations; and (5) *pseudorigid* species undergoing rapid polytopal conversions but not scrambling all positions. Such rapid but nonscrambling cycling can allow a stereochemical integrity sufficient for the isolation of geometrical isomers (as in this study) even though analogous scrambling cycles would produce nonrigidity on an NMR time scale. Theoretical and prior experimental evidence suggests that eight-coordinate species, including bidentate ligand complexes, should undergo rapid polytopal cycling, which normally leads to experimental nonrigidity when viewed via NMR.

^1H NMR Spectra of the $W(mpic)_n(dcq)_{4-n}$ Complexes. Taken without the ^1H NMR results for the rest of the $W(mpic)_n$-$(dcq)_{4-n}$ series, the ^1H NMR results for $W(mpic)_4$ (Figure 3 and Table V) are ambiguous. The single methyl signal at 2.44 ppm is consistent with numerous possibilities: (1) the rigid dodecahedra D_{2d} (*mmmm*), S_4 (*gggg*) or D_2 (*gggg*), (2) the rigid square antiprisms C_4 (*llll*), D_2 (*llll*), or D_2 (*ssss*), (3) a dodecahedral or square antiprismatic isomer of lower symmetry which is spectrally unresolved, (4) a mixture of isomers which is spectrally unresolved, and (5) a nonrigid structure cycling by either a scrambling or a nonscrambling mechanism [provided that the ground-state configuration in the latter case is identical with one of the six configurations mentioned in (1) and (2)].

The attempt to clarify the nature of the tetrakis homochelate eight-coordinate complexes in solution led to a preparation of the mixed-ligand tetrakis heterochelate series W(mpic)$_n$(dcq)$_{4-n}$. The ^{1}H NMR spectra of W(mpic)$_3$(dcq) show two methyl signals at 2.42 and 2.47 ppm of 2:1 intensity (Figure 3). The α aromatic protons show analogous signals further downfield. The methyl and α aromatic splitting patterns and intensity ratios of the mpic ligands in the W(mpic)$_3$(dcq) dodecahedra which conform to Orgel's rule (Figure 5) should all have intensities of 1:1:1 except for the C_s (*m′mmm*) isomer for which these signals should be 2:1 as observed Thus the only one consistent with the experimental results is the C_s (*m′mmm*) complex. Naturally, accidental partial degeneracy cannot be ruled out.

Even if Orgel's rule were ignored and all possible dodecahedral and square antiprismatic structures were considered, the 2:1 intensity list would still only include dodecahedral complexes with the *mmmm* wrapping pattern. These additional structures would simply have some or all ligands chelating contrary to the predictions of Orgel's rule. However, the single crystal x-ray structure determination of W(bq)$_4$[8a] showed the complex to have D_{2d} (*mmmm*) dodecahedral geometry with the ligands chelated so as to confirm Orgel's predictions, which clearly makes these latter W(mpic)$_3$(dcq) structures inferior.

The ^{1}H NMR spectrum of W(mpic)$_3$(mq) methyl signals at 1.60, 2.37, and 2.43 ppm with intensity ratios of 1:2:1 have been assigned to the 5-methyl peaks of the mq ligand, two equivalent mpic ligands, and one nonequivalent mpic ligand, respectively. And whereas the α aromatic protons are unresolved in this complex, the results are again completely consistent with a C_s (*m′mmm*) structure.

The diamagnetic nature of these complexes, their chemical inertness, the single sharp methyl resonance of the W(mpic)$_4$ complex, and the two sets of signals which occur when 5-methylpicolinic acid is added to a CD_2Cl_2 solution of W(mpic)$_4$, all strongly counter the possibility that the splitting patterns of the W(mpic)$_3$(dcq) and W(mpic)$_3$(mq) complexes are due to an "arm off" type dissociation of one or more of the ligands on the complexes.

The ^{1}H NMR spectra of the mixture of α- and β-W(mpic)$_2$(dcq)$_2$ show two methyl signals with approximately 4:1 intensity. For the W(mpic)$_2$(dcq)$_2$ dodecahedra which conform to Orgel's rule, one of two possible methyl resonance patterns are expected. For those complexes with C_2 or C_{2v} symmetry the methyl groups are expected to appear as a singlet and for those complexes with C_1 symmetry as two singlets of 1:1 intensity. If the spectrum of the W(mpic)$_2$(dcq)$_2$ mixture is completely resolved, it is most plausibly interpreted as two molecules each producing a single methyl resonance.

The 4:1 intensity of the methyl signals is not consistent with the pattern for a single molecule of C_1 symmetry. It is consistent, however, with the presence of two molecules both with at least C_2 symmetry. (The room temperature equilibrium constant calculated for a 4:1 v/v chloroform/acetone solution mixture of α and β of 5 ± 2 is in good agreement with the approximate 4:1 ratio of ^{1}H NMR methyl signals.) Eight out of the 11 possible structures in Figure 6 have C_2 or C_{2v} symmetry, which is necessary to give the ^{1}H NMR methyl splitting pattern discussed above. Of these eight complexes, the two arising from D_{2d} (*mmmm*) parentage appear to be the most plausible structures for the α and β isomers of W(mpic)$_2$(dcq)$_2$, based on the W(bq)$_4$ structure[8a] and consistent with the most plausible structure for the W(mpic)$_3$(dcq) and W(mpic)$_3$(mq) complexes, as noted above. Furthermore, a comparison of known complexes of 8-quinolinol and picolinic acid indicates that two ligands should have very similar bites.[1a]

The observation that the weaker of the two methyl signals appears to vanish at 0 °C down to −50 °C is not consistent with the electronic spectral evidence gathered for the equilibrium behavior of the α and β isomers. However, broadening due to the increased viscosity of the solution at lower temperatures obscured this second peak, which was only partially resolved at higher temperatures.

The ^{1}H NMR spectra of W(mpic)(dcq)$_3$ yields no additional insights into the nature of these complexes in solution because of the poor quality of the spectra (owing to the low solubility of the complex) and because any rigid dodecahedral or square antiprismatic structure would be consistent with the spectra.

Comparison with Previous NMR Studies of Eight-Coordinate Complexes. As noted in the introduction, eight-coordinate tetrakis chelates are typically nonrigid, with position equivalence shown at very low temperatures. The previously most rigid behavior for a tetrakis chelate on an NMR time frame was for the cation $Ta[S_2CNMe_2]_4^+$, whose structure in the solid state was determined to be D_{2d} (*mmmm*).[4a,b] The single, time-averaged methyl resonance signal for this dodecahedral cation split into two lines of equal intensity at −62 °C, with line-shape analysis indicating $\Delta H^{\ddagger} = 44$ kJ/mol, $\Delta S^{\ddagger} = -13$ J/mol deg, and $\Delta G^{\ddagger}(-62\ ^\circ C) = 46$ kJ/mol. Neutral chelates with eight equal donor atoms appear to have very low barriers to nonrigidity, so the cation's relatively slow exchange was attributed to its charge. The rate of rearrangement appears to slow down as a result of the increased nuclear charge. The ion-pair interactions would be extensive in the low temperature region. If the ion-pair dissociation rate were slow enough, low symmetry NMR signals could result from this effect.

Cyanide carbon-13 resonances of various tetraalkylammonium salts of $Mo(CN)_8^{4-}$ and $W(CN)_8^{4-}$ consist of single resonances down to about −150 °C,[4d] even though solution spectral data[27] suggest that dodecahedral geometry predominates for these d^2 ions, which should possess nonequivalent A and B sites. Anticipating resolved signals, these results suggest a barrier to rearrangement of ≤25 kJ/mol for eight equivalent donors.

The first class of eight-coordinate complexes for which limiting slow-exchange NMR spectra were reported is the class of metal hydrides of the type $H_4M(PR_3)_4$ (where M = Mo or W)[7] and $H_5Re(Y(C_6H_5)_2C_2H_5)_3$[28] (where Y = P or As). For the $H_4M(PR_3)_4$ series, the barrier to intramolecular rearrangement increases as the atomic number of the central metal increases. The apparent rigid to nonrigid transition on an NMR time scale occurs at −15 °C for the molybdenum complexes and 28 °C for the corresponding tungsten complexes. Replacing the four monodentate phosphine ligands with two bidentate phosphine ligands raised the coalescence temperature to 60 °C for the tungsten hydride complexes. The estimated free energies of activation for the metal-centered exchange process of these tetrahydrides ranged from 59–61 kJ/mol for the monodentate phosphine complexes of tungsten to 69 kJ/mol for the corresponding bidentate complexes. Incidentally, the P_4H_4 donor set obeys Orgel's rule in the solid state, too.

For our W(mpic)$_n$(dcq)$_{4-n}$ complexes, the interconversion of positions is too slow to be observed via NMR, even at elevated temperatures. Hence, we resorted to classic isomer separation for the $n = 2$ set. The activation energy of 114 kJ/mol obtained for the conversion of the β isomer of

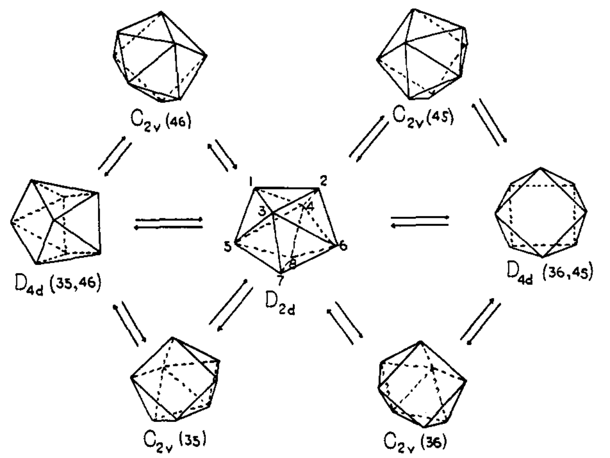

Figure 7. Polytopal cycles which should result in stereochemical integrity and cause pseudorigidity. The *b* edges which are opened in the intermediates are indicated in parentheses.

$W(mpic)_2(dcq)_2$ to the α isomer is consistent with this process being a slow, moderately high energy scrambling mechanism. Because the value of the equilibrium constant for this process is not accurately known for any of the three temperatures, the activation energy may be in error by several kJ/mol. Fortunately, the value of the activation energy is fairly insensitive to changes in K.

Taking all of the relevant studies carried out to date, the observed activation energies (enthalpies and/or free energies) appear to increase with chelation, with nonequivalent donors, with changes in electronic configuration (from d^0 to d^2), and with increasing electron density about the metal as exemplified by the cationic and d^2 complexes.

Rigid or Pseudorigid Structures. Although the ^1H NMR results suggest "rigid" behavior for the $W(mpic)_3(dcq)$ and $W(mpic)_2(dcq)_2$ complexes on the NMR time frame, this is not the only interpretation consistent with the results. Theoretical calculations[29] do not imply appreciable nonrigidity barriers. However, if a single ground state configuration is favored over all others, metal-centered rearrangements can cycle through various polytopes without a scrambling of ligand donor sites, and therefore not appear nonrigid on the NMR time scale.[7b] Such a process can be described by the series of closed cycles shown in Figure 7. For an eight-coordinate dodecahedral ground state, the anticipated low-energy pathways are those which expand and contract the *b* edges of the dodecahedron. The *b* edge is the longest of the dodecahedral edges and rearrangement via these edges would presumably involve the least amount of distortion on going from one polytope to another. The expansion of *b* edges may occur in two steps or simultaneously. The opening of one dodecahedral *b* edge results in the formation of the C_{2v} bicapped trigonal prism. The opening of the *b* edge opposite the square face of the bicapped trigonal prism yields the square antiprismatic polyhedron. Of course, the simultaneous opening of opposite *b* edges produces the square antiprism directly.

Figure 7 is only a small piece of a potentially much larger reaction scheme. The closing of the two square faces of the two square antiprisms in Figure 7 to give the original dodecahedral configuration is only one of four dodecahedra that could be generated by each of these square antiprisms. This one dodecahedral configuration is distinguished from all others by its positioning of all the π-acceptor atoms in dodecahedral B sites and all the π-donor atoms in dodecahedral A sites in agreement with Orgel's rule and the experimental findings of this study. In the six other dodecahedra generated from the two square antiprisms, *at least two* of the ligands have the π-donor and π-acceptor atoms reversed relative to the desirable A and B site positionings. These latter six dodecahedra constitute configurations energetically less favorable than the original dodecahedra. Through a series of dodecahedral-square antiprismatic transformations it is possible to arrive back at the original dodecahedron as in Figure 8. However, such a process requires passage through several scrambled higher energy dodecahedral configurations. The select cycles which constitute Figure 7 involve intermediates which can all collapse back to the original dodecahedron without ever having scrambled the ligands. Such cycles maintain the stereochemical integrity of the unique ligand positioning of Orgel's dodecahedra,[9] i.e., a process of *pseudorigidity*.

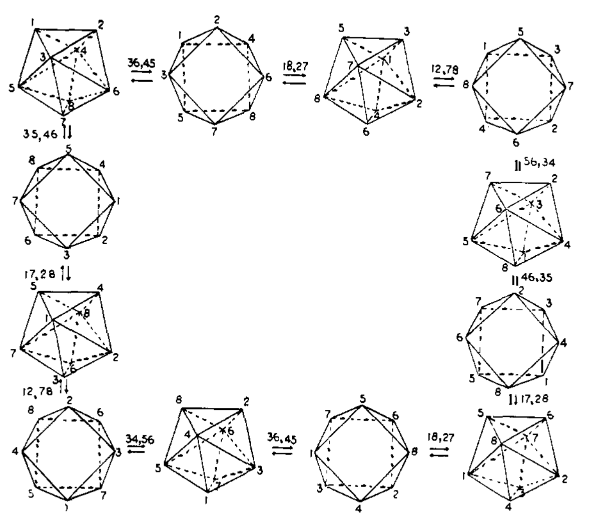

Figure 8. A rearrangement cycle via dodecahedral *b* edge opening. (The full cycle is sterically impossible for an *mmmm* complex with ligands of the type used in this study.)

If all of the complexes of the $W(mpic)_n(dcq)_{4-n}$ series belong to the (*mmmm*) dodecahedral class as the experimental evidence suggests, then it becomes very clear why isomers were observed for only the $W(mpic)_2(dcq)_2$ complex and also why only two were observed. On a molecular level, the complexes' normal cycle of rearrangement would coincide with the maintenance of stereochemical integrity. Only occasionally would a $W(mpic)_n(dcq)_{4-n}$ molecule leave the potential energy well which Figure 7 represents and traverse a high-energy path which would eventually place it in a second potential energy well. The resulting configuration is different only for the $W(mpic)_2(dcq)_2$ complex. The acceptance of such a picture for the solution behavior of the $W(mpic)_n(dcq)_{4-n}$ complexes requires that the terms rigid and nonrigid be interpreted very carefully. What appears rigid experimentally may be only *pseudorigid* in fact.

Scrambling Pathways. A number of criteria can be used in evaluating the merit of different pathways in regard to the $W(mpic)_n(dcq)_{4-n}$ complexes. First, any proposed mechanism must be consistent with the experimental findings. The slow exchange appears most consistent with a ground state configuration which has dodecahedral geometry and which obeys Orgel's rule. Therefore, a qualitative measure of instability in an intermediate dodecahedron is the number of ligands inverted relative to Orgel's prediction. The larger this number, presumably, the less stable the configuration.

Minimization of ligand-ligand repulsions is also important. The dodecahedral, the bicapped trigonal prism, and the square antiprismatic geometry minimize ligand-ligand repulsions most effectively; thus, any other proposed polyhedra must be assumed to be energetically unfavorable. Sterically, inverted ligands along the *m* edge as opposed to the *g* edge would constitute a large strain.[8,12] Obviously, when dealing with chelated complexes, intermediate structures cannot be proposed which would require the ligand to drastically alter the size of its bite.

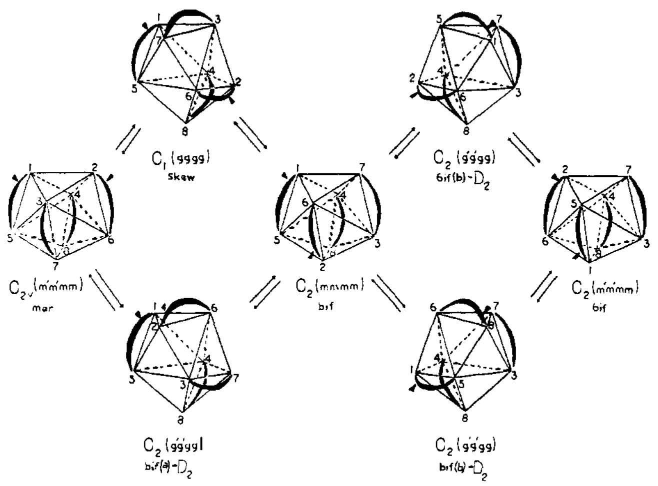

Figure 9. The C_2 (*b*) twist mechanism for α- and β-W(mpic)$_2$(dcq)$_2$.

A ligand, for example, cannot be expected to bridge the diagonal of a square face. Logical pathways would also presumedly conform to the normal modes of vibration[30] of the molecule. Lastly, small distortions in the ground state configuration should constitute lower energy pathways than large distortions. Such a notation is embodied in the common suggestion that dodecahedra will open along the longest of its edges, the *b* edge, to yield the square antiprism.[3]

One such multistep scrambling process is illustrated in Figure 8. This process involves opening and closing along dodecahedral *b* edges only. The dodecahedra in this scheme fall into one of two classes: (1) dodecahedra with the donor atoms placed at the A and B sites in accord with Orgel's rule for a d^2 metal ion and (2) dodecahedra with all donors improperly placed for a d^2 metal ion by Orgel's rule. In addition to violating Orgel's rule, this and all analogous *b* edge modification cycles which we can find to interconvert isomers (for example, D_{2d} (*mmmm*) and D_2 (*gggg*) or S_4 (*gggg*) and C_2 (*mmgg*) for Figure 8) do *not* interconvert the *mer* and *bif* D_{2d} (*mmmm*) isomers of W(mpic)$_2$(dcq)$_2$. Examination of models of the W(mpic)$_n$(dcq)$_{4-n}$ complexes also indicates that this cycle is sterically unlikely for an *mmmm* isomer.

An alternative method to rearrange the coordination sites around dodecahedra is shown in Figure 9. This process involves the concerted movement of four sites (two A and two B) around one of the C_2 axes which bisect opposite *b* edges. The highest energy intermediate, which is a distorted cube, is not shown. It occurs between the D_{2d} (*mmmm*) and D_2 (*gggg*) dodecahedra on the reaction pathways. The D_2 (*gggg*) intermediates, which are shown between the two D_{2d} (*mmmm*) ground state dodecahedra, should be low energy intermediates if Orgel's rule is used as a criterion. That is, the A and B positions are occupied by π-donor and π-acceptor ligands, respectively, for a d^2 metal ion. Therefore, this process is limited by the distorted cubic intermediates. The most notable fact about this process is that it accounts, where the *b* edge expansion processes do not, for the conversion of the meridonal isomer of the W(mpic)$_2$(dcq)$_2$ complex to the corresponding bifacial isomer. Any of the W(mpic)$_n$(dcq)$_{4-n}$ complexes can undergo this rearrangement, but, with the exception of the W(mpic)$_2$(dcq)$_2$ complex, both *mmmm* structures in the scheme are the same isomer.

Two other previously proposed mechanisms warrant examination. The Hoard–Silverton[10] concerted rearrangement permutes A and B sites by elongation and compression of complementary *b* edges in the dodecahedron. However, this mechanism gives results which are no different than one of the mechanisms previously discussed (Figure 8). The only difference is that the Hoard–Silverton mechanism does not consider the square antiprism as an intermediate. Therefore, for the same reasons discussed previously, the Hoard–Silverton mechanism is an unsuitable pathway for these unsymmetrical tetrakis chelate eight-coordinate complexes.

Meakin et al.[7b] proposed a mechanism which starts with a dodecahedron and involves the inversion of the flattened B site tetrahedron and the simultaneous twisting of the elongated A site tetrahedron. In the transition state intermediate, having S_4 symmetry, the four B site atoms are coplanar with the central atom, and A site tetrahedron is twisted through 45° with respect to the B site tetrahedron. Although this mechanism cannot be eliminated for tetrakis chelate eight-coordinate complexes, the integrity of the ligand greatly restricts the results. By starting with a D_{2d} (*mmmm*) configuration a new configuration, S_4 (*gggg*), can be generated, but the two W(mpic)$_2$(dcq)$_2$ isomers cannot be interconverted. If one configuration (C_{2v} or C_2) is preferred to the exclusion of the other, this mechanism would also explain the appearance of two isomers for the W(mpic)$_2$(dcq)$_2$ complex, but not the absence of isomers for the other members of the W(mpic)$_n$(dcq)$_{4-n}$ series. Thus this mechanism also fails to explain in its entirety the experimental results obtained for the W(mpic)$_n$(dcq)$_{4-n}$ series.

Finally, the slow isomerization could be the result of a slow dissociative or semidissociative mechanism. We have not studied the exchange rates of ligands under comparable conditions. Even if we had, the possibility of "end off" rearrangements could not be excluded.

Summary

It must be concluded that the W(mpic)$_n$(dcq)$_{4-n}$ series of complexes, which are tetrakis bidentate complexes containing a d^2 metal ion with asymmetric ligands capable of achieving both metal to ligand and ligand to metal π bonding and which appear to span the *m* edges of a dodecahedron, constitute a system highly resistant to scrambling rearrangement mechanisms. This is probably accomplished (1) by achieving a very stable ground state configuration in comparison to other early transition metal eight-coordinate complexes whose stereochemistry has been studied by variable temperature NMR techniques, and (2) by the steric constraints imposed by the chelating ligands and the nonequivalent donors, which make fewer rearrangement pathways accessible. These observations are reflected in the activation parameters determined relative to other eight-coordinate systems. Further studies are in progress.

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Mixed Valence Interactions in Di-μ-oxo Bridged Manganese Complexes

Stephen R. Cooper* and Melvin Calvin

Contribution from the Department of Chemistry and Laboratory of Chemical Biodynamics, Lawrence Berkeley Laboratory, University of California, Berkeley, Berkeley, California 94720. *Received January 2, 1976*

Abstract: The complexes $[(L)_2MnO_2Mn(L)_2]^{3+}$ where L = 2,2′-bipyridine or 1,10-phenanthroline, have been examined, in addition to the corresponding (IV, IV) complex of phenanthroline. The crystal structure of the mixed valence (III, IV) compound with L = 2,2′-bipyridine demonstrated that this complex has deeply trapped valences, corresponding to class II in the classification of Robin and Day since the bond lengths differ considerably about the manganese ions. We have examined the electronic spectrum of the (III, IV) complexes and observed broad bands in the near infrared which we have assigned to the mixed valence band expected for a class II system. No comparable band is observed for the phenanthroline(IV, IV) complex. Lowering the pH of (III, IV) dimer solutions reversibly cleaves the antiferromagnetically coupled (III, IV) dimers as determined by the increase in solution magnetic susceptibility; loss of the near infrared band occurs with dimer cleavage, although the remainder of the visible spectrum is substantially unaltered. Both absorbance and solution magnetic susceptibility changes with pH are reversible. The solvent dependence of the near infrared band is small but apparently opposite to that predicted by Hush's theory. However, the bandwidths agree well with those predicted from Hush's treatment (e.g., 0.53 μm^{-1} predicted, 0.46 μm^{-1} observed). A band at 688 cm^{-1} in the infrared spectrum of the bipyridyl(III, IV) dimer is shifted by isotopic substitution with ^{18}O, and has been assigned to one of the stretching modes of the Mn_2O_2 bridge; analogous bands are found for the phenanthroline(III, IV) and -(IV, IV) complexes. Pertinent aspects of the electrochemistry are also discussed.

In 1972 Plaksin et al.[1] reported the crystal structure of di-μ-oxo-tetrakis(2,2′-bipyridyl)dimanganese(III, IV) perchlorate (hereafter termed the bipyridyl(III, IV) dimer) which was originally synthesized by Nyholm and Turco[2] in 1960. This complex, which Nyholm and Turco had formulated as a Mn(III)–Mn(IV) compound, was found by Plaksin et al. to have discrete Mn(III) and Mn(IV) ions from the inequivalence of the bond lengths about the ions. The electronic structure of such complexes with mixed oxidation states has excited considerable interest since the 1967 reviews of Robin and Day,[3] Hush,[4] and Allen and Hush.[5]

Robin and Day[3] have classified mixed valence complexes into three categories. Class I compounds exhibit essentially no interaction between the ions, while class III ions are fully delocalized, resonance stabilized compounds. The electronic spectra of class I ions are the sum of the spectra of the constituent ions; those of class III are due to transitions between molecular orbitals and bear no necessary relation to the spectra of the components. Class II ions have weak but nonnegligible interactions between the ions; thus, in addition to contributions typical of both constituent ions, the electronic spectrum of a class II ion is expected to exhibit a new absorption due to a photon-driven electron transfer between the ions. Such electron transfer bands, termed mixed valence or intervalence transfer absorption bands, are typically broad and low in energy. In addition to the optical process, an associated thermally acti-