leaving **4** (11.8 g) as a viscous orange liquid. Attempted distillation caused elimination of volatile materials (Me_3SiCl and probably HCl) and formation of a complex mixture of unidentified, nonvolatile products.

[Bis(trimethylsilyl)amino][(diphenylphosphino)(trimethylsilyl)-methyl]phosphine (5). A freshly prepared sample of **4** (10.5 g, 21 mmol) was dissolved in Et_2O (50 mL). After the mixture was cooled to 0 °C, $LiAlH_4$ (5.5 mL, 1.0 M in Et_2O, 22 mmol hydride) was added via syringe. The mixture was warmed to room temperature and stirred overnight. Following filtration and solvent removal, distillation through a short-path column gave a high-boiling fraction (bp 140–165 °C (0.03 mm)) that was redistilled through a 10-cm column to give **5** (6.2 g) as an analytically pure, colorless liquid.

[Bis(trimethylsilyl)amino][(diphenylphosphino)(trimethylsilyl)-methyl]methylphosphine (6). By the same procedure as described above for **5**, the P–Cl compound **4** (10.0 g, 20 mmol) in Et_2O (40 mL) was treated at 0 °C with MeMgBr (10 mL, 28.5 mmol, 2.85 M in Et_2O). After the mixture was stirred overnight at room temperature, Me_3SiCl (ca. 2 mL) was added to consume the excess Grignard reagent. The solids were allowed to settle, and the supernatant solution was decanted. After solvent removal, CH_2Cl_2 (20 mL) was added, and the decantation process was repeated. Solvent removal left **6** (8.6 g, 90% yield) as a white wax that was identified by NMR spectroscopy, with only very minor impurities being detectable. Attempts to obtain an analytically pure sample of **6** by either recrystallization or distillation were unsuccessful. Mass spectrum, *m/e* (relative intensity): 478 (0.2) (M^+), 463 (2.6), 390 (4.2), 302 (16.0), 271 (24.2), 262 (11.8), 190 (26.6), 183 (12.4), 135 (51.4), 130 (30.5), 108 (9.9), 73 (100.0).

[Bis(trimethylsilyl)amino][(trimethylsilyl)methyl]iodophosphine (7) A mixture of *t*-BuI (0.80 mL, 6.7 mmol) and **1** (1.70 g, 6.12 mmol) in CH_2Cl_2 (3 mL) was stirred at room temperature with periodic monitoring by ^1H NMR spectroscopy. After 6 days, the signals due to **1** had disappeared and new peaks assignable to **7** and $Me_2C{=}CH_2$ (δ 1.70, 6 H; δ 4.60, 2 H; ^4J = 1.4 Hz) were present. The solvent and other volatile materials were removed under vacuum, and **7** (0.85 g) was isolated by distillation as a yellow liquid. Treatment of **7** with an equimolar quantity of MeLi in Et_2O solution at 0 °C gave the known P–Me derivative **8**[20] (quantitative yield by ^{31}P NMR; 44% distilled yield on 3 mmol scale reaction).

{[Bis(trimethylsilyl)amino][(trimethylsilyl)methylene]phosphine}iron Tetracarbonyl (9). Compound **1** (13.0 g, 46.7 mmol) was added to a slurry of $Fe_2(CO)_9$ (17.0 g, 46.7 mmol) in pentane (200 mL). The mixture was stirred overnight and then filtered to remove a small amount of black solid. Solvent and $Fe(CO)_5$ were removed under vacuum, leaving **9** as an orange liquid of good purity as indicated by NMR spectroscopy. Distillation resulted in partial decomposition, but an analytically pure sample of **9** (8.8 g, 42% yield) was obtained.

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Registry No. **1**, 76173-65-4; **2**, 89982-65-0; **2a**, 96109-86-3; **3**, 96192-48-2; **4**, 89982-64-9; **5** (isomer 1), 96109-84-1; **5** (isomer 2), 96109-87-4; **6**, 96109-85-2; **7**, 89982-63-8; **8**, 90413-57-3; **9**, 89934-22-5; Ph_2PCl, 1079-66-9; $Me_2Si{=}CHCH_2(t\text{-}Bu)$, 79991-59-6.

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Preparation, Separation, and Characterization of Two New Series of Mixed-Ligand Eight-Coordinate Tungsten(IV) Complexes Containing the Pairs of Bidentate Ligands 2-Mercaptopyrimidine–5-*tert*-Butyl-2-mercaptopyrimidine and 5-Methylpicolinic Acid–5-*tert*-Butyl-2-mercaptopyrimidine

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Two new series of mixed-ligand eight-coordinate tungsten(IV) complexes have been prepared, isolated, and characterized. Six $W(bmpd)_n(mpd)_{4-n}$ complexes, where $bmpd^-$ = 5-*tert*-butyl-2-mercaptopyrimidinato and mpd^- = 2-mercaptopyrimidinato, and five $W(bmpd)_n(mpic)_{4-n}$ complexes, where $mpic^-$ = 5-methylpicolinato, have been isolated by thin-layer chromatography on silica gel plates. The pair of bidentate ligands form four-membered chelate rings in the former series, while a four- and a five-membered chelate ring are formed by the pair of bidentate ligands in the latter series. In the $W(bmpd)_n(mpd)_{4-n}$ series a pair of stereoisomers (labeled α and β) are observed for n = 2, while in the $W(bmpd)_n(mpic)_{4-n}$ series only a single stereoisomer is observed for n = 0–4. ^1H NMR studies indicate these complexes are rigid on the NMR time frame. The stereochemistry of these complexes is discussed in terms of their NMR spectrum and Orgel's rule.

Introduction

The study of mixed-chelate complexes is potentially one of the best ways to explore the possibility of stereoisomers in early-transition-metal eight-coordinate complexes. The fruitfulness of this approach has been demonstrated by the study of the $W(mpic)_n(dcq)_{4-n}$ system, where n = 0–4 and $mpic^-$ = 5-methylpicolinato and dcq^- = 5,7-dichloro-8-quinolinolato.[1] Examination of these species revealed that the $W(mpic)_2(dcq)_2$ complex exists in two different stereoisomeric forms (labeled α and β). These two complexes are rigid enough to permit separation by column chromatography but in solution will equilibrate back to a mixture of the two forms in 24 h at 25 °C. An activation energy of 114 kJ/mol was measured for the intramolecular rearrangement process that converts the β form to the α form. The ^1H NMR spectrum of the $W(mpic)_3(dcq)$ complex consists of two methyl signals in a 2:1 ratio and marked the first time rigid behavior was observed on a NMR time frame for an eight-coordinate tetrakis chelate complex at and above room temperature.

We have recently initiated a program to explore further the number and stereochemistry of eight-coordinate complexes that arise when two or more different bidentate ligands are used to form tetrakis chelate complexes. In particular, we are interested in how the following three variables affect the number, stereochemistry, and rigid character of this class of eight-coordinate complexes: (1) the size of the chelate ring; (2) the nature of the donor atoms on the ligand; (3) the nature of the metal center. Because of the substitution inertness observed in the previously characterized tungsten(IV) eight-coordinate complexes $W(q)_4$,[2] $W(pic)_4$,[3] and $W(mpd)_4$[4] and the molybdenum(IV) complex $Mo(pic)_4$,[5] our current efforts are directed toward the synthesis of new mixed-ligand eight-coordinate complexes of molybdenum(IV) and tungsten(IV).

The previously studied $W(mpic)_n(dcq)_{4-n}$ system employed two bidentate ligands both of which form five-membered chelate rings. Herein, we report the preparation, separation, and characterization of two new series of mixed-ligand eight-coordinate tungsten(IV) complexes. The first of these series contains the two bidentate

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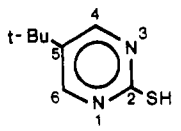
Table I. Ligand Abbreviations

bmpd$^-$	5-*tert*-butyl-2-mercaptopyrimidinato
bq$^-$	5-bromo-8-quinolinato
dcq$^-$	5,7-dichloro-8-quinolinato
mpd$^-$	2-mercaptopyrimidinato
mpic$^-$	5-methylpicolinato
pic$^-$	picolinato = pyridine-2-carboxylato
q$^-$	8-quinolinolato

ligands 2-mercaptopyrimidine (Hmpd) and 5-*tert*-butyl-2-mercaptopyrimidine (Hbmpd), both of which form four-membered chelate rings upon complexation. The second series contains the two bidentate ligands 5-*tert*-butyl-2-mercaptopyrimidine (**1**) and 5-methylpicolinic acid (Hmpic, **2**). This pair of ligands gives rise



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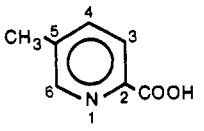

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to four- and five-membered chelate rings, respectively. Like the W(mpic)$_n$(dcq)$_{4-n}$ system, the W(bmpd)$_n$(mpd)$_{4-n}$ series gives rise to six eight-coordinate complexes, one each of the W(bmpd)$_4$, W(bmpd)$_3$(mpd), W(bmpd)(mpd)$_3$, and W(mpd)$_4$ species and a pair of W(bmpd)$_2$(mpd)$_2$ complexes (labeled α and β). Unlike the W(mpic)$_n$(dcq)$_{4-n}$ and W(bmpd)$_n$(mpd)$_{4-n}$ systems, the W(bmpd)$_n$(mpic)$_{4-n}$ series gives rise to only five eight-coordinate complexes: one stereoisomer each for n = 0–4 (Table I).

Experimental Section

Solvents and Reagents. Malononitrile (Aldrich), 2-bromo-2-methylpropane (Aldrich), nitromethane (Aldrich), aluminum chloride (MCB), diisobutylaluminum hydride, 1 M solution in hexane (Aldrich), thiourea (Baker and Adamson), 2,5-lutidene (Aldrich), selenium dioxide (Alfa), pyridine (Fisher), acetonitrile (MCB), bromine (Fisher), mesitylene (Aldrich), Proton Sponge (Aldrich), tungsten hexacarbonyl (Pressure Chemical), and chloroform (Fisher, spectrograde) were used without further purification.

Precursors and Ligands. *tert*-Butylmalononitrile was prepared by the method of Boldt et al.[6] A slurry consisting of anhydrous aluminum chloride (13.4 g, 0.1 mol) and malononitrile (6.6 g, 0.1 mol) in 40 mL of nitromethane was placed in a stoppered flask and cooled to −20 °C. The stirred slurry was added over a 10-min period to a second flask containing 2-bromo-2-methylpropane (14.8 g, 0.16 mol) held at −20 °C. The resulting mixture was stoppered and stored at 0 °C for 24 h. The mixture was transferred to a larger flask and then carefully neutralized at 0 °C with a saturated aqueous solution of $NaHCO_3$. Addition of the $NaHCO_3$ solution was halted prior to formation of aluminum hydroxide. The dark purple organic phase was separated and steam distilled. Nitromethane and 2-bromo-2-methylpropane distilled over first and were discarded. The product, *tert*-butylmalononitrile, separated out in the condenser as white crystals. The crystals were collected, filtered, washed with distilled water, and dried in vacuo. The product was pure enough for use in subsequent reactions but can be purified by recrystallization from hot ethanol: yield 6.6 g (54%); mp 84 °C [lit.[6] mp 84 °C]; ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.20 (s, 9 H, *t*-Bu), 3.50 (s, 1 H, CH).

***tert*-Butylmalonodialdehyde** was prepared by the method of Reichardt et al.[7] A solution of 100 mL of 1 M diisobutylaluminum hydride (DIBAL-H) in hexane was added dropwise from a dropping funnel over a 20-min period to a stirred solution of *tert*-butylmalononitrile (5.33 g, 0.044 mol) in 225 mL of hexane under N_2 at −78 °C. The solution was stirred an additional 1 h at −78 °C and then allowed to stir overnight at room temperature. The resulting clear yellow solution was cooled to 0 °C in an ice bath and 227 mL of 2 N HCl was cautiously added dropwise via the dropping funnel. The resulting solution was stirred 12 h or until the aluminum salts dissolved. The phases were separated, and the aqueous layer was extracted with ether (3 × 60 mL). The original organic layer and the ether extracts were combined and reduced in volume to 150 mL. After addition of 47 mL of 1 N NaOH to the concentrated organic phase, the mixture was stirred rigorously for 15 min and the aqueous phase was separated and acidified with 2 N HCl. The dialdehyde separated out as a clear to light reddish oil and was extracted with ether (3 × 30 mL). The ether extract was dried with $MgSO_4$. Careful removal of the ether by rotary evaporation yielded the clear dialdehyde, which was used immediately after preparation without further purification; yield 3.92 g (70%).

5-*tert*-Butyl-2-mercaptopyrimidine was prepared by the method of Hunt et al.[8] To a hot, stirred solution of thiourea (2.33 g, 0.031 mol) in 20 mL of absolute ethanol and 5 mL of concentrated HCl was added *tert*-butylmalondialdehyde (3.92 g, 0.031 mol). The solution was boiled for 10 min and allowed to cool, and the yellow product was collected by filtration. Addition of ether to the filtrate yielded a second crop of crystals. The product was recrystallized from 95% ethanol; yield 3.76 g (72%).

Anal. Calcd for $C_8H_{12}N_2S$: C, 57.11; H, 7.19; N, 16.65; S, 19.05. Found: C, 57.21; H, 7.07; N, 16.51; S, 18.94.

5-Methylpicolinic acid was prepared by the method of Jerchel et al.[9] Into a 250-mL round-bottom flask was placed 2,5-lutidene (25.0 g, 0.23 mol), selenium dioxide (46.5 g, 0.42 mol), and 75 mL of pyridine. A reflux condenser was attached, and the solution was heated at 115 °C for 2 h. Upon cooling, the gray selenium was filtered off. To the filtrate was added 100 mL of distilled water. The pyridine was removed as the pyridine/water azeotrope by distillation under reduced pressure. When the total volume of the mixture was reduced to 40 mL, the distillation was stopped and the flask was cooled in ice. The crude 5-methylpicolinic acid was collected by filtration and washed with ether. The product was purified by vacuum sublimation at 120 °C: yield 13.5 g (42%); mp 168–169 °C [lit. mp 168–169 °C]; ^{1}H NMR (60 MHz, $CDCl_3$) δ 2.57 (s, 3 H, Me), 8.02 (d, 1 H, J = 8 Hz, H_4), 8.45 (d, 1 H, J = 8 Hz, H_3), 8.93 (s, 1 H, H_6), 12.05 (s, 1 H, COOH).

Anal. Calcd for $C_7H_7NO_2$: C, 61.30; H, 5.15; N, 10.21. Found: C, 61.27; H, 5.07; N, 10.05.

Tungsten(IV) Complexes. Bis(acetonitrile)tetrabromotungsten(IV) was made by the method of King and McCarley.[10] Into a 200-mL Schlenk flask were added $W(CO)_6$ (12.5 g, 35.5 mmol), 40 mL of acetonitrile, and a Teflon-coated stir bar. A stoppered pressure-equalizing dropping funnel was attached to the flask, and the whole system was evacuated and back-filled with nitrogen several times. Under a positive pressure of nitrogen, bromine (11.35 g, 3.64 mL, 71.0 mmol) was added to the dropping funnel. The bromine was added dropwise to the stirred solution. The evolution of CO was immediate and vigorous. The flask was stirred at room temperature for 12 h. The crude product was filtered under N_2 and washed with acetonitrile (3 × 40 mL) under N_2. The greenish brown product was dried in vacuo. After drying, a sublimation probe was introduced into the Schlenk flask and the unreacted $W(CO)_6$ was sublimed (80 °C (10 torr)) onto the cold finger. Bis(acetonitrile)-tetrabromotungsten(IV) hydrolyzes in air and must be stored under dry N_2 or in vacuo. No loss of coordinated acetonitrile was observed when the sample was stored in vacuo: yield 12.5 g (60%); IR (KBr, cm^{-1}) ν(CN) 2320 (m), 2285 (s).

Anal. Calcd for $WBr_4(CH_3CN)_2$: C, 8.20; H, 1.03; N, 4.78; Br, 54.58. Found: C, 8.25; H, 1.14; N, 4.87; Br, 54.61.

Tungsten(IV) Mixed-Ligand Complexes. W(bmpd)$_n$(mpic)$_{4-n}$ Complexes. Method 1. To a 200-mL Schlenk flask were added a stir bar, tungsten hexacarbonyl (0.48 g, 1.36 mmol), 5-methylpicolinic acid (0.46 g, 3.35 mmol), 5-*tert*-butyl-2-mercaptopyrimidine (0.57 g, 3.39 mmol), and 75 mL of mesitylene. A condenser equipped with an adapter was added to the flask, and the flask was evacuated and back-filled with nitrogen several times. The mixture was refluxed for 4 h. Upon cooling, the mesitylene was removed by vacuum pump assisted rotary evaporation, leaving a dark blue residue. This procedure also removed any unreacted hexacarbonyl.

Method 2. To a 200-mL Schlenk flask were added bis(acetonitrile)-tetrabromotungsten(IV) (1.21 g, 2.07 mmol), 5-*tert*-butyl-2-mercaptopyrimidine (0.69 g, 4.10 mmol), 5-methylpicolinic acid (0.56 g, 4.08 mmol), and Proton Sponge (1.70 g, 7.93 mmol) along with a stir bar. A rubber septum was added to the flask, and the flask was evacuated and back-filled with nitrogen several times. Degassed chloroform (50 mL) was added to o the flask via a cannula. The reaction was stirred for 3 h at room temperature, the mixture was filtered, and the filtrate was taken to dryness on a rotary evaporator to yield a dark blue residue.

W(bmpd)$_n$(mpd)$_{4-n}$ complexes were prepared by method 1 in an analogous fashion to the W(bmpd)$_n$(mpic)$_{4-n}$ complexes with an equal molar mixture of 2-mercaptopyrimidine and 5-*tert*-butyl-2-mercaptopyrimidine and separated by the procedure described below.

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Table II. Silica Gel TLC R_f Values for the $W(bmpd)_n(mpd)_{4-n}$, $W(bmpd)_n(mpic)_{4-n}$, and $W(dcq)_n(mpic)_{4-n}$[a] Series

n	$W(bmpd)_n(mpd)_{4-n}$[b]	$W(bmpd)_n(mpic)_{4-n}$[b]	$W(dcq)_n(mpic)_{4-n}$[c]
4	0.89	0.90	>0.9
3	0.84	0.81	0.9
2[d]	0.75, 0.72	0.66	0.74, 0.18
1	0.56	0.15	0.13
0	0.34	0.08	0.06

[a] R_f values taken from ref 1. [b] Eluent is 20:1 v/v chloroform/acetone. [c] Eluent is 10:1 v/v chloroform/acetone. [d] The pair of values correspond to the α and β isomers for the $W(bmpd)_2(mpd)_2$ and $W(mpic)_2(dcq)_2$ complexes. The label α is assigned to the species with the higher R_f value.

Chromatographic Separation of the $W(bmpd)_n(mpic)_{4-n}$ Complexes. The blue product mixture was dissolved in a minimum of chloroform and filtered. One edge of a precoated silica gel plate (20 × 20 cm, thickness 2.0 mm or 0.25 mm, E. Merck Anal.) was streaked with the chloroform solution. The plate was developed in a 20:1 v/v chloroform/acetone mixture. The thicker plates were used first to effect a crude separation. The final separation was accomplished, using the thinner plates. Each of the five bands was scraped off the plates separately. The complex was recovered from the silica gel by extracting with acetone, filtering, and taking the filtrate to dryness on the rotary evaporator. The process was repeated several times to ensure the complexes were pure. The purified complexes were dried in vacuo for 24 h at room temperature.

Anal. Calcd for $W(bmpd)_4$: C, 45.06; H, 5.20; N, 13.14; S, 15.04. Found: C, 45.12; H, 5.17; N, 13.07; S, 15.11.

Anal. Calcd for $W(bmpd)_3(mpic)$: C, 45.31; H, 4.79; N, 11.93; S, 11.70. Found: C, 45.16; H, 4.78; N, 11.79; S, 11.59.

Anal. Calcd for $W(bmpd)_2(mpic)_2$: C, 45.58; H, 4.33; N, 10.64; S, 8.22. Found: C, 45.62; H, 4.44; N, 10.60; S, 8.02.

Anal. Calcd for $W(bmpd)(mpic)_3$: C, 45.86; H, 3.85; N, 9.22; S, 4.22. Found: C, 46.16; H, 3.81; N, 8.69; S, 4.42.

Physical Studies. Electronic spectra were recorded on a Cary 118 spectrophotometer with use of a pair of matched 1.000-cm quartz cells. The 60-MHz ^1H NMR spectra were measured on a Varian T-60A spectrometer, and the 360-MHz ^1H NMR spectra were recorded using a Bruker FT spectrometer. All spectra are referenced vs. Me_4Si. Analyses were performed by Spang Microanalytical Laboratories and Galbraith Laboratories.

Results

Synthesis and Separation of the $W(bmpd)_n(mpd)_{4-n}$ and $W(bmpd)_n(mpic)_{4-n}$ Complexes. A total of six and five purple to blue complexes have been isolated from the product mixtures for the $W(bmpd)_n(mpd)_{4-n}$ and $W(bmpd)_n(mpic)_{4-n}$ series, respectively. See Table II for a listing of R_f values. The same mixture of species is produced whether the $W(bmpd)_n(mpic)_{4-n}$ complexes are synthesized by oxidative decarbonylation of $W(CO)_6$ at 160 °C or by reaction of $WBr_4(CH_3CN)_2$ with the ligands in the presence of a strong base in chloroform at room temperature. All of the complexes in these two series are air stable and are unaffected by contact with silica gel.

A nearly equal distribution of complexes is observed for the $W(bmpd)_n(mpd)_{4-n}$ series. On the other hand, a significantly larger amount of the mixed-ligand complex, $W(bmpd)_2(mpic)_2$, is recovered than the other two mixed-ligand complexes of the same series, $W(bmpd)_3(mpic)$ and $W(bmpd)(mpic)_3$. When either the third or fourth band from the $W(bmpd)_n(mpd)_{4-n}$ series is subjected to a second TLC separation after the recovery process, a pair of complexes are observed, with R_f values corresponding to the third and fourth bands (see Table II). However, a two-dimensional TLC separation of either the third or fourth band does not produce four spots of equal intensity. A set of two spots of nearly equal intensity is observed in the first direction; however, interconversion of the α form to the β form and the β form to the α form is very slight in the second direction.

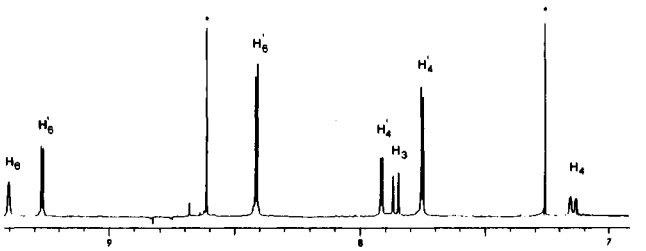


Figure 1. 360-MHz ^1H NMR spectrum, 7–9 ppm, of the $W(bmpd)_3(mpic)$ complex in $CDCl_3$ at 35 °C (* = impurity or $CHCl_3$). The H_4 and H_6 hydrogens of the pyrimidinato ring are designated by a prime.

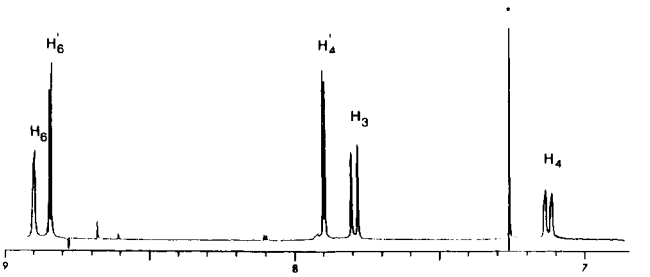


Figure 2. 360-MHz ^1H NMR spectrum, 7–9 ppm, of the $W(bmpd)_2(mpic)_2$ complex in $CDCl_3$ at 35 °C (* = $CHCl_3$). The H_4 and H_6 hydrogens of the pyrimidinato ring are designated by a prime.

Electronic Absorption Spectra. The electronic absorption spectra of the $W(bmpd)_n(mpic)_{4-n}$ complexes are characterized by two or more intense (ϵ (3.5–1.3) × 10^4) absorption bands that overlap and fall within the region of 20 000–16 000 cm^{-1}. See Table III. The two parent complexes $W(bmpd)_4$ and $W(mpic)_4$ define the very narrow boundaries within which the maxima of the other $W(bmpd)_n(mpic)_{4-n}$ complexes fall.

^1H NMR Spectrum of the $W(bmpd)_n(mpic)_{4-n}$ Complexes. The 360-MHz ^1H NMR spectrum of the $W(bmpd)_n(mpic)_{4-n}$ complexes in $CDCl_3$ were recorded at 35 °C, and the results are summarized in Table IV. The ^1H NMR spectrum of the two parent complexes, $W(bmpd)_4$ and $W(mpic)_4$, contain a single *tert*-butyl and a single methyl signal, respectively. The remainder of the ^1H NMR spectrum of $W(bmpd)_4$ consists of a pair of doublets at 7.79 and 8.81 ppm and are assigned to the two hydrogens on the pyrimidine ring, H_4 and H_6. The remainder of the ^1H NMR spectrum of the $W(mpic)_4$ complex consists of a pair of doublets and a singlet at 7.28, 7.65, and 9.30 ppm and are assigned to the H_4, H_3, and H_6 hydrogens of the picolinato ring.

The ^1H NMR spectrum of the $W(bmpd)_3(mpic)$ complex consists of two *tert*-butyl signals present in a 2:1 ratio along with a single methyl signal. The integration of the two *tert*-butyl peaks to the methyl signal is 6:3:1. The splitting pattern in the aromatic region of the $W(bmpd)_3(mpic)$ complex reflects that observed in the alkyl region. Two sets of pyrimidine H_4 and H_6 doublets are present in a 2:1 ratio (Figure 1). The aromatic hydrogens on the picolinato ring are also present in the proper ratio to the aromatic hydrogens of the pyrimidine rings.

The ^1H NMR spectrum of the $W(bmpd)_2(mpic)_2$ complex consists of a single *tert*-butyl signal and a single methyl signal present in a 3:1 ratio. A single set of H_4 and H_6 pyrimidine hydrogens and a single set of H_3, H_4, and H_6 picolinato hydrogens are observed in the aromatic region of the $W(bmpd)_2(mpic)_2$

Table III. Visible Spectrum of the $W(bmpd)_n(mpic)_{4-n}$ Complexes in $CHCl_3$[a]

$W(bmpd)_4$	$W(bmpd)_3(mpic)$	$W(bmpd)_2(mpic)_2$	$W(bmpd)(mpic)_3$	$W(mpic)_4$
17 500 (3.56)	17 900 (2.85)	18 200 (1.68)	17 900 (1.30)	16 000 (2.04)
19 200 (sh, 1.96)	19 600 (sh, 1.80)		16 600 (sh, 1.08)	17 800 (2.00)
				22 400 (sh, 0.61)
				26 600 (sh, 0.27)

[a] Key: λ_{max} in cm^{-1}; extinction coefficient in parentheses (×10^4); sh = shoulder.

Table IV. 360-MHz ^{1}H NMR Spectrum of the W(bmpd)$_n$(mpic)$_{4-n}$ Complexes in $CDCl_3$ at 35 °C[a]

complex	*t*-Bu	Me	pyrimidinato ring[b] H_4	pyrimidinato ring[b] H_6	picolinato ring[c] H_3	picolinato ring[c] H_4	picolinato ring[c] H_6
W(bmpd)$_4$	1.30 s (9)		7.79 d (1)	8.81 d (1)			
W(bmpd)$_3$(mpic)	1.26 s (18)	2.34 s (3)	7.75 d (2)	8.41 d (2)	7.86 d (1)	7.15 d (1)	9.40 s (1)
	1.34 s (9)		7.91 d (1)	9.27 d (1)			
W(bmpd)$_2$(mpic)$_2$	1.31 s (18)	2.32 s (6)	7.90 d (1)	8.84 d (1)	7.79 d (1)	7.13 d (1)	8.90 s (1)
W(bmpd)(mpic)$_3$	1.25 s (9)	2.38 s (3)	7.90 d	8.93 d (1)	7.71 d (1)	7.13 d (2)	8.87 s (1)
		2.41 s (6)			7.73 d (2)	7.26 d (1)	9.24 s (2)
W(mpic)$_4$		2.47 s (3)			7.65 d (1)	7.28 d (1)	9.30 s (1)

[a] Resonance signals reported in ppm downfield from Me_4Si. Key: s, singlet; d, doublet. Relative integrated intensities in parentheses. [b] The *J* value for H_4 and H_6 is 2.80 ± 0.05 Hz for all the complexes containing a 5-*tert*-butyl-2-mercaptopyrimidinato chelate ring. [c] The *J* value for H_3 and H_4 is 7.90 ± 0.2 Hz for all the complexes containing the 5-methylpicolinato chelate ring.

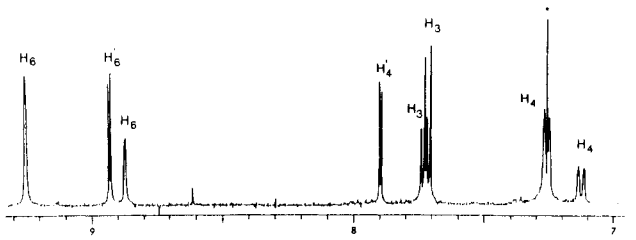


Figure 3. 360-MHz ^{1}H NMR spectrum, 7–9 ppm, of the W(bmpd)(mpic)$_3$ complex in $CDCl_3$ at 35 °C (* = $CHCl_3$). The H_4 and H_6 hydrogens of the pyrimidinato ring are designated by a prime.

complex (Figure 2). Variable-temperature ^{1}H NMR studies of the W(bmpd)$_2$(mpic)$_2$ complex in $CDCl_3$ over a temperature range of −30 to +50 °C reveal little or no change in the spectrum. Only one *tert*-butyl and one methyl signal are detectable over the temperature range examined.

The ^{1}H NMR spectrum of the W(bmpd)(mpic)$_3$ complex consists of a single *tert*-butyl signal and a pair of methyl signals present in a 2:1 ratio. The integration of the *tert*-butyl peak to that of the methyl signals is 3:2:1. The aromatic region of the W(bmpd)(mpic)$_3$ complex reflects the splitting pattern observed in the alkyl region of the spectrum as is the case for the W(bmpd)$_3$(mpic) complex. Two sets of picolinato ring hydrogens H_3, H_4, and H_6 are observed in a 2:1 ratio in this spectrum (Figure 3). In addition, a single set of H_4 and H_6 pyrimidinato ring hydrogens is observed.

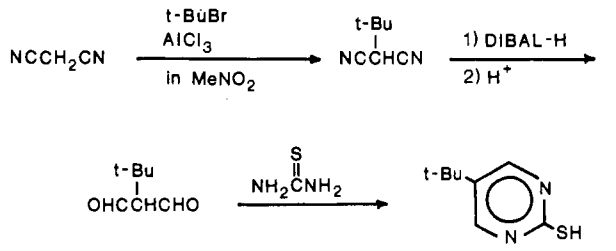
^{1}H NMR Spectrum of the W(bmpd)$_n$(mpd)$_{4-n}$ Complexes. Even at 360 MHz the resolution of the different alkyl and aromatic hydrogens in the W(bmpd)$_n$(mpd)$_{4-n}$ series of complexes is poor. While the *tert*-butyl peaks are just barely resolved, the peaks in aromatic region cannot be properly assigned because of the overlapping between signals. In $CDCl_3$ the ^{1}H NMR spectrum of the W(bmpd)$_3$(mpd) complex consists of two *tert*-butyl signals in a 2:1 ratio at 1.296 and 1.301 ppm. The ^{1}H NMR spectrum of an equilibrium mixture of the α- and β-W(bmpd)$_2$(mpd)$_2$ complexes consists of two *tert*-butyl signals at 1.299 and 1.295 ppm. The relative intensities of the peaks is approximately 2:1. The ^{1}H NMR spectrum of W(bmpd)(mpd)$_3$ contains only a single *tert*-butyl signal at 1.296 ppm.

Discussion

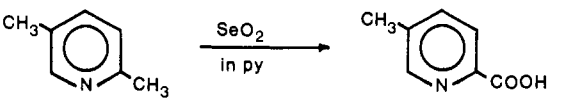
Selection and Synthesis of Ligands for Mixed-Ligand Studies. Because of synthetic constraints, it is unlikely that a single tetrakis mixed-chelate eight-coordinate complex can be prepared without also synthesizing the rest of the eight-coordinate complexes in that series. Consequently, some means of separation is likely to be necessary in order to isolate an individual eight-coordinate complex from the rest of the product mixture. Chromatography is probably the only separation technique that will permit one to isolate all of the products in the aforementioned system. Selecting the right combination of ligands is therefore crucial to the success of this type of project.

The suitability of a bidentate ligand as a component in a mixed-chelate eight-coordinate complex is governed by a number of practical considerations. Ideally, the resulting mixed-chelate eight-coordinate complexes should be air stable, substitution inert, and resistant to oxidation when in contact with silica gel or some other support. They should also be moderately soluble in organic solvents and should possess R_f values sufficiently different from one another to effect a separation.

Scheme I



Scheme II



The preparation and study of the single-ligand tetrakis eight-coordinate tungsten(IV) complex are the best guides to the selection of a ligand for use in a mixed-ligand system. Both the tetrakis(picolinato)tungsten(IV) complex[3] and the tetrakis(2-mercaptopyrimidinato)tungsten(IV) complex[4] have been previously prepared. Both complexes are air stable, substitution inert, and resistant to oxidation when in contact with silica gel.

In order to ensure the resulting mixed-chelate complexes possessed adequate solubility in organic solvents and in order to have a simple set of handles by which to probe the stereochemistry of the complexes by ^{1}H NMR, we chose to utilize alkylated forms of 2-mercaptopyrimidine and picolinic acid. Schemes I and II were used, respectively, to synthesize 5-*tert*-butyl-2-mercaptopyrimidine and 5-methylpicolinic acid.

Synthesis of the Mixed-Chelate Tungsten(IV) Complexes. Two different synthetic approaches have been employed to prepare the W(bmpd)$_n$(mpic)$_{4-n}$ complexes. The first method involves oxidative decarbonylation of tungsten hexacarbonyl by the ligands. The second method involves the reaction of bis(acetonitrile)tetrabromotungsten(IV) with the two ligands in the presence of 1,8-bis(dimethylamino)naphthalene (Proton Sponge). Both methods have been previously utilized in the preparation of other group 6[23] metal eight-coordinate complexes. Oxidative decarbonylation of the group 6 hexacarbonyls has been used to prepare W(dcq)$_4$,[2] W(pic)$_4$,[3] W(mpd)$_4$,[4] and Mo(pic)$_4$.[5] The six-coordinate Mo(pic)$_3$ complex[3a] has also been prepared via this approach. The tetrakis(dialkyldithiocarbamate) complexes of tungsten(IV) have been made by both of these procedures.[11] Both methods offer advantages and disadvantages.

The advantage of oxidative decarbonylation as a synthetic route is that the tungsten starting material is commercially available and air stable. There are three potential disadvantages to this approach, however. First, the reaction must be run at high temperatures where ligand decomposition is possible. Second, since the ligand is also the oxidizing agent in these reactions, it must be used in excess of the stoichiometrically required amount. Third,

because this is a redox reaction, the product mixture may be more complex than that obtained for a straight substitution reaction. The advantage of using a tungsten(IV) halide complex as the starting material is that reactions can be run at room temperature and are likely to yield product mixtures that are less complex than those obtained by oxidative decarbonylation. The two disadvantages of this approach are that the starting material is air sensitive and not commercially available.

^{1}H NMR Spectra of the W(bmpd)$_n$(mpic)$_{4-n}$ Complexes. The ^{1}H NMR spectra of the W(bmpd)$_n$(mpic)$_{4-n}$ complexes are consistent with their assignment as neutral, diamagnetic, substitution-inert, tetrakis eight-coordinate tungsten(IV) complexes.

In the previously characterized W(mpic)$_4$ complex it was observed that the chemical shift of the 5-methylpicolinato H_6 hydrogen changes from 8.93 ppm for the free ligand to 9.30 ppm upon complexation. Assuming the same trend occurs on complexation of the 5-*tert*-butyl-2-mercaptopyrimidinato ligand, the H_6 hydrogen of bmpd$^-$ in the W(bmpd)$_4$ complex was assigned to the doublet at 8.81 ppm. The free ligand, Hbmpd, has very low solubility in chloroform, but the chemical shift of the H_4 and H_6 hydrogens appears to be 8.61 ppm in $CDCl_3$. A downfield shift in the H_6 signal upon complexation of the picolinato and pyrimidinato rings is not always observed in the mixed-ligand complexes. In one instance, i.e. for the W(bmpd)(mpic)$_3$ complex, the chemical shift of one of the two H_6 picolinato signals occurs upfield rather than downfield of the free-ligand value. In another instance, the W(bmpd)$_2$(mpic)$_2$ complex, the value of the H_6 picolinato signal almost exactly equals the free-ligand value for H_6. For the W(bmpd)$_3$(mpic) complex the pair of H_6 signals for the bmpd$^-$ rings show considerable deviation from the values observed in the other complexes. While the other complexes containing the bmpd$^-$ ligand have an H_6 value of 8.87 ± 0.06 ppm, the two H_6 signals in W(bmpd)$_3$(mpic) occur at 8.41 and 9.27 ppm. These variations in the H_6 signals of the mixed-ligand complexes may reflect some variation in the strength of the W–N bonds as compared to the same interactions in the parent complexes. On the other hand, these anomalous shifts in the H_6 resonances might be due to ring currents from the adjacent ligands.

Stereochemistry of the Mixed-Ligand Complexes—General Considerations. The following list of previously accumulated results and observations is the foundation for our conclusions about the stereochemistry of the newly prepared and characterized series of eight-coordinate mixed-ligand complexes W(bmpd)$_n$(mpd)$_{4-n}$ and W(bmpd)$_n$(mpic)$_{4-n}$. A single-crystal X-ray diffraction study has shown that the W(bq)$_4$ complex[12] possesses dodecahedral geometry, with the 5-bromo-8-quinolinolato ligands spanning the *m* edges to give rise to almost perfect D_{2d} symmetry. The 2-mercaptopyrimidinato ligand has also been found to span the dodecahedral *m* edges in the W(mpd)$_4$ complex.[4] In both instances these complexes conform to Orgel's rule.[13]

Orgel's rule states that for eight-coordinate complexes containing a d^2 metal ion and two distinctly different sets of donor atoms, one set a π-acceptor set (the unsaturated pyridine or pyrimidine nitrogen atoms) and the other set a π-donor set (the anionic oxygen and sulfur atoms), the complex will adopt dodecahedral geometry, with the π-acceptor atoms occupying the dodecahedral B sites and the π-donor atoms occupying the dodecahedral A sites. The A and B positions and the *a*, *b*, *g*, and *m* edges are the designations of Hoard and Silverton[14] (Figure 4). For the generalized eight-coordinate complex, M(XY)$_4$, compliance to Orgel's rule eliminates the 42 possible square-antiprismatic isomers from consideration and reduces the 93 possible dodecahedral isomers to only four ground-state isomers[15] (Figure 5). Steric considerations can reduce this number still further.[16] We have assumed that all the eight-coordinate mixed-ligand complexes belonging to these two new series will also conform to

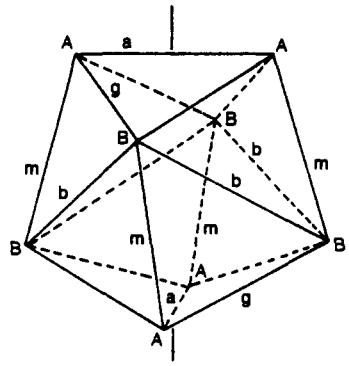


Figure 4. D_{2d} dodecahedron. The two sets of nonequivalent sites are labeled A and B. The four different edges are labeled *a* (2), *b* (4), *g* (8), and *m* (4) in accordance with the standard Hoard–Silverton nomenclature. See ref 14.

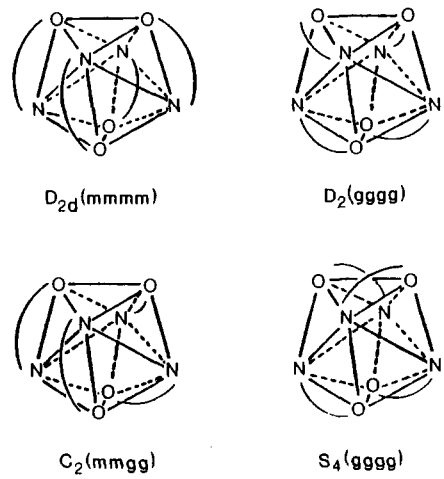


Figure 5. Four dodecahedral M(XY)$_4$ isomers consistent with Orgel's[13] rule that π acceptors should occupy the B positions (occupied by the N atoms) in d^2 eight-coordinate species.

Orgel's rule. That is, these complexes will possess dodecahedral geometry, with the nitrogen donor atoms occupying the B sites and the sulfur or oxygen atoms occupying the A sites.

Figures 6 and 7 catalog those dodecahedral isomers that conform to Orgel's rule for a d^2 metal ion for the general complexes M(XY)$_3$(XY′) and M(XY)$_2$(XY′)$_2$. For the M(XY)$_3$(XY′) case a total of five isomers are possible—one of each arising from the M(XY)$_4$ D_{2d}(*mmmm*), D_2(*gggg*), and S_4(*gggg*) parent complexes. The remaining two complexes arise from the M(XY)$_4$ C_s(*mmgg*) parent complex. Eleven M(XY)$_2$(XY′)$_2$ isomers conform to Orgel's rule: two each of M(XY)$_4$ D_{2d}(*mmmm*) and S_4(*gggg*) parentage, three of M(XY)$_4$ D_2(*gggg*) parentage, and four of M(XY)$_4$ C_2(*mmgg*) parentage.

In evaluation of the W(mpic)$_n$(dcq)$_{4-n}$ series of complexes,[1] it was concluded that the mpic$^-$ and dcq$^-$ ligands always spanned the *m* edge of a dodecahedron in a manner consistent with Orgel's rule. This was the only explanation that accounted for the observed ^{1}H NMR spectra and the distribution of stereoisomers. One stereoisomer each was recovered for the W(mpic)$_4$, W(mpic)$_3$(dcq), W(mpic)(dcq)$_3$, and W(dcq)$_4$ complexes, while a pair of stereoisomers (labeled α and β) were recovered for the W(mpic)$_2$(dcq)$_2$ complex. However, which structure (I or II in Figure 7) goes with the α isomer and which goes with the β isomer was not elucidated.

Stereochemistry of the W(bmpd)$_n$(mpd)$_{4-n}$ Complexes. Although well-resolved ^{1}H NMR spectra of the W(bmpd)$_n$(mpd)$_{4-n}$ complexes were not obtained, it is nonetheless clear that the distribution of these complexes is identical with that previously observed for the W(mpic)$_n$(dcq)$_{4-n}$ series. Furthermore, since the structure of the W(mpd)$_4$ complex has previously been shown to possess D_{2d}(*mmmm*) dodecahedral geometry, we conclude this series of eight-coordinate mixed-ligand complexes all adopt do-

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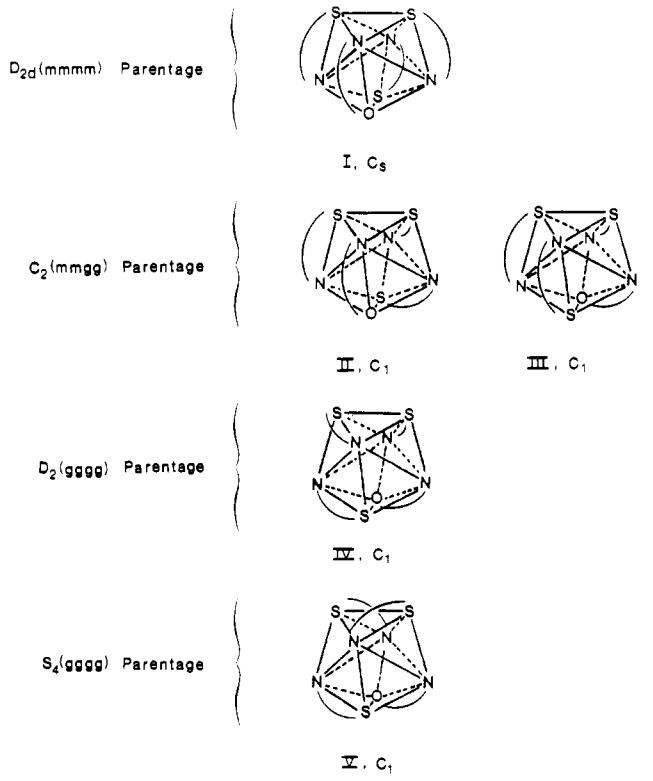

Figure 6. $M(XY)_3(XY')$ complexes that conform to Orgel's rule for a d^2 metal ion.

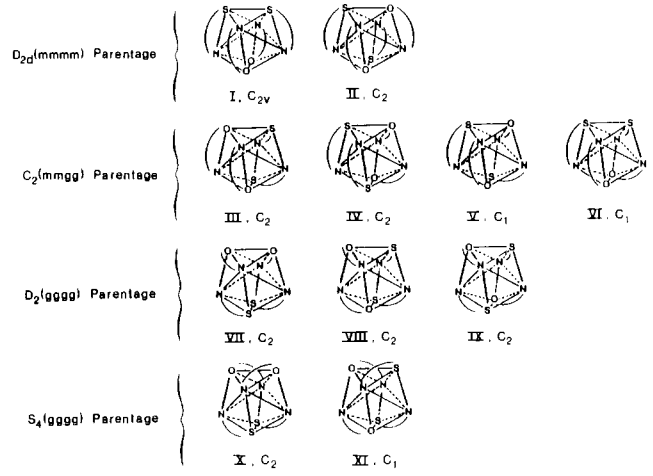

Figure 7. $M(XY)_2(XY')_2$ complexes that conform to Orgel's rule for a d^2 metal ion.

decahedral geometry, with the bmpd$^-$ and mpd$^-$ ligands spanning the *m* edges in accord with Orgel's rule. The expected pair of $W(bmpd)_2(mpd)_2$ stereoisomers are observed. The equilibrium constant for the $\beta \rightleftarrows \alpha$ system appears to be approximately 2. The rate of interconversion between α and β for this pair of stereoisomers appears to be somewhat slower than that observed between the α- and β-$W(mpic)_2(dcq)_2$ complexes.

Stereochemistry of the $W(bmpd)_n(mpic)_{4-n}$ Complexes. Assuming Orgel's rule is obeyed, the only stereoisomer consistent with the ^{1}H NMR spectrum of the $W(bmpd)_3(mpic)$ and $W(bmpd)(mpic)_3$ complexes is the $C_s(m'mmm)$ stereoisomer (Figure 6). The ^{1}H NMR spectrum of both these complexes clearly shows that a pair of bmpd$^-$ ligands (in the case of the $W(bmpd)_3(mpic)$ complex) or a pair of mpic$^-$ ligands (in the case of the $W(bmpd)(mpic)_3$ complex) are in equivalent environments. For the $C_s(m'mmm)$ stereoisomer the pair of bmpd$^-$ or mpic$^-$ ligands on opposite *m* edges are equivalent. The 2:1 ratio observed for the alkyl peaks is also observed in the aromatic hydrogens of these complexes. The $C_s(m'mmm)$ stereoisomer is the only structure out of the five that has symmetry higher than C_1 (Figure 6). The ^{1}H NMR spectrum of a $W(bmpd)_3(mpic)$ or $W(bmpd)(mpic)_3$ complex possessing any of the other stereochemistries would contain three distinct *tert*-butyl or methyl signals. The same assignment was also made for the $W(mpic)_3(dcq)$ and $W(mpic)(dcq)_3$ complexes.[1]

Only one stereoisomeric form of the $W(bmpd)_2(mpic)_2$ complex appears to exist. The ^{1}H NMR spectrum of this complex contains a single *tert*-butyl signal and a single methyl signal along with a single set of H_4 and H_6 pyrimidinato hydrogen signals and a single set of H_3, H_4, and H_6 picolinato hydrogen signals. These results indicate that the two bmpd$^-$ ligands are in equivalent environments, as are the two mpic$^-$ ligands. Of the 11 $M(XY)_2(XY')_2$ complexes pictured in Figure 7 only structures V, VI, and XI can be ruled out solely on the gounds of symmetry considerations. All eight of the remaining structures have C_2 symmetry or higher and are therefore plausible structures solely on the basis of consideration of the observed ^{1}H NMR spectrum of the $W(bmpd)_2(mpic)_2$ complex.

Of the three eight-coordinate $M(XY)_2(XY')_2$ complexes, $[Nb(O_2)_2(ox)_2]^{3-}$,[17] $Mn(NO_3)_2(dppn)_2$,[18] and $Zr(acac)_2(NO_3)_2$,[19] that have been structurally characterized, all have been found to adopt the $C_2(m'mm'm)$ stereochemistry (II in Figure 7). The rationale for this preference is that the two different ligands with unequal size bites are better accommodated by placing one each along the two *m* edges of a single trapezoid than by placing one set of identical ligands along the two *m* edges of one trapezoid and the other set of identical ligands along the other two *m* edges of the second trapezoid. The occurrence of only a single stereoisomer for the $W(bmpd)_2(mpd)_2$ complex might be another example of this same phenomenon. This would imply a sizable difference in stability between the $C_2(m'mm'm)$ stereoisomer and all the other possible structures, so much so that the equilibrium between the $C_{2v}(m'm'mm)$ stereoisomer and the $C_2(m'mm'm)$ stereoisomer observed for $n = 2$ in the $W(mpic)_n(dcq)_{4-n}$ and the $W(bmpd)_n(mpd)_{4-n}$ complexes is so lopsided as to be undetectable, if it exists at all in the $W(bmpd)_2(mpic)_2$ case.

An alternative explanation for the existence of only one isomeric form of the $W(bmpd)_2(mpic)_2$ complex is that because two different size chelate rings are being formed, two different types of dodecahedral edges are being spanned. Stereoisomers derived from $C_2(mmgg)$ parentage would accommodate this arrangement. In particular, either structure III or IV (Figure 7) would permit one set of ligands to span one edge and the other set of ligands to span a different edge. The bite of the bmpd$^-$ ligand should be shorter than that of the mpic$^-$ ligand, since the former forms a four-membered chelate ring and the latter a five-membered chelate ring. Provided the *m* edges are shorter than the *g* edges, structure IV, with the bmpd$^-$ ligands spanning the *m* edges, should be more likely than structure III. In the "most favorable" dodecahedron for identical donor atoms described by Hoard and Silverton[14] the *g* edge is slightly longer than the *m* edge. The same trend in edge lengths is also observed in almost all the actual dodecahedral eight-coordinate complexes that have been structurally characterized.[20] There is precedent for this suggestion that the $W(bmpd)_2(mpic)_2$ complex adopts a geometry arising from $C_2(mmgg)$ parentage. Fanfani et al. reported that the tetrakis(dithioacetato)vanadium(IV) complex existed in the solid state in two different isomeric forms—the $D_{2d}(mmm)$ stereoisomer and the $C_2(mmgg)$ stereoisomer.[21]

Unfortunately, ^{1}H NMR and TLC studies alone are insufficient evidence on which to elucidate the stereochemistry of the $W(bmpd)_2(mpic)_2$ complex. Nor can these results be used to rule out stereoisomers arising from $D_2(gggg)$ parentage or $S_4(gggg)$

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parentage and having C_2 symmetry as possible structures for the $W(bmpd)_2(mpic)_2$ complex. It is clear, however, that these new mixed-ligand eight-coordinate tungsten(IV) complexes are rigid on the NMR time frame as were the previously studied $W(mpic)_n(dcq)_{4-n}$ complexes.[1]

Future Studies. As yet, no single-crystal X-ray diffraction studies have been performed on group 6 mixed-ligand eight-coordinate complexes containing two different bidentate ligands. If suitable crystals of the $W(bmpd)_2(mpic)_2$ complex can be obtained, such a study is planned. In addition, since the interconversion of the α and β forms of the $W(bmpd)_2(mpd)_2$ complex appears to be a relatively slow process, attempts will be made to isolate single crystals of the two forms and perform X-ray diffraction studies on these complexes as well.

Because the visible spectrum of the α and β forms of the $W(bmpd)_2(mpd)_2$ complex are virtually identical, we were unable to conduct spectrophotometric kinetic studies on their interconversion. Recent studies in our laboratory indicate that 5-*tert*-butyl-2-hydroxypyrimidine (Hbhpd) and 5-*tert*-butyl-2-selenopyrimidine (Hbspd) also can be used to form tetrakis eight-coordinate tungsten(IV) complexes.[22] The preparation and isolation of the α and β forms of $W(bhpd)_2(bmpd)_2$, $W(bmpd)_2(bspd)_2$, and/or $W(bhpd)_2(bspd)_2$ would provide series better suited for spectrophotometric kinetic studies. Kinetic studies on all three of these series of complexes would provide information on the influence of the donor atom on the rate of interconversion. At least one such study is planned.

Finally, we plan to continue our efforts to synthesize a stable tungsten(IV) eight-coordinate complex containing a bidentate ligand that forms a six-membered chelate ring. This would permit us to explore the number, stereochemistry, and rigid character of mixed-ligand eight-coordinate tungsten(IV) complexes containing a four- and a six-membered chelate ring and a five- and a six-membered ring, in addition to a mixed-ligand system containing two different bidentate ligands both of which formed six-membered chelate rings.

Acknowledgment. Support of this work by the Office of Vice President for Graduate Studies and Research of the University of Michigan is gratefully acknowledged.

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(23) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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Magnetic Resonance Studies of Trifluoperazine–Calmodulin Solutions: ^{43}Ca, ^{25}Mg, ^{67}Zn, and ^{39}K Nuclear Magnetic Resonance

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Interactions of calmodulin (CaM) with Ca^{2+}, Mg^{2+}, Zn^{2+}, K^+, and an antagonist were studied with metal NMR methods. Line widths of ^{43}Ca, ^{25}Mg, ^{67}Zn, and ^{39}K NMR of free Ca^{2+}, Mg^{2+}, Zn^{2+}, and K^+ were markedly increased by adding CaM. However, the ^{43}Ca NMR line width of the Ca^{2+}–CaM solution was markedly decreased by adding trifluoperazine (TFP), probably due to the reduction of the Ca^{2+}-exchange rate. The line width of the ^{25}Mg NMR of the Mg^{2+}–CaM solution was remarkably decreased by adding $CaCl_2$. Adding TFP to the Mg^{2+}–CaM solution also decreased the line width of the ^{25}Mg NMR of the solution. However, the decrease in line width observed for ^{25}Mg NMR of the Mg^{2+}–CaM solution by adding TFP was smaller than that observed for ^{43}Ca NMR of the Ca^{2+}–CaM solution. The increase in line width of the ^{67}Zn NMR of free Zn^{2+} by adding CaM in *N*-(2-hydroxyethyl)piperazine-*N'*-2-ethenesulfonic acid (HEPES)–Na^+ solution was larger than that in HEPES–K^+ solution. The line width shown by the Zn^{2+}–CaM solution containing HEPES–Na^+ was not changed by adding excess Ca^{2+}, while that in HEPES–K^+ solution was markedly decreased by adding excess Ca^{2+}. The line width of the ^{39}K NMR of the K^+–CaM solution was decreased by adding Ca^{2+}. From these and other spectral findings, the following suggestions were given: (1) The environment of the Ca^{2+} low-affinity site in CaM is markedly changed by TFP. (2) Mg^{2+} binds exactly to the Ca^{2+} binding site in CaM. (3) Mg^{2+} does not cause a specific conformational change of CaM, which is necessary for the specific TFP–CaM interaction. (4) K^+ binds to the Zn^{2+} binding site in CaM. (5) Zn^{2+} binds to the Ca^{2+} binding site of CaM in the HEPES–K^+ soluion, while this is not true in the HEPES–Na^+ solution. Therefore, the high utility of diamagnetic metal NMR has been demonstrated.

Introduction

Calmodulin (CaM)[1] is a ubiquitous and multifunctional regulatory protein and plays the central role in th regulation of cellular functions.[2-4] Ca^{2+} is essential for CaM–dependent functions. CaM has four Ca^{2+} binding sites, probably two of which are Ca^{2+} high-affinity sites and the others are Ca^{2+} low-affinity sites.[2-4] The structure of CaM is changed by Ca^{2+}, but a detailed conformational change of CaM caused by Ca^{2+} has not been shown yet. Bivalent metal cations other than Ca^{2+} such as Mg^{2+}, Mn^{2+}, or Zn^{2+} are known to activate the CaM functions or to bind to CaM.[5-10] It has been controversial whether Mg^{2+} binds exactly to the Ca^{2+} binding sites of CaM or not.[5-10] It was also suggested from CD and absorption spectroscopies that alkanine monovalent metal cations such as K^+, Na^+, etc., markedly change the conformation of CaM.[5-8] Thus, it will be necessary to study the exact binding sites of these monovalent and bivalent metal cations on CaM to understand their roles in physiological functions.

An antipsychotic drug, trifluoperazine (TFP), is a potent antagonist of CaM functions.[11,12] TFP will tightly bind to CaM,

(1) Abbreviations: CaM, calmodulin; TFP, trifluoperazine; K_d, dissociation constant; CD, circular dichroism; UV, ultraviolet; NMR, nuclear magnetic resonance; Tris, tris(hydroxymethyl)aminomethane; HEPES, *N*-(2-hydroxyethyl)piperazine-*N'*-2-ethenesulfonic acid.

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