

signals of $B_3H_8^-$ ion and $H_2B(NH_3)_2^+$ ion. Weak signals of $H_3N \cdot BH_3$ and $H_3N \cdot B_3H_7$ were also detected. When diethyl ether was used as solvent for this reaction instead of dichloromethane, the solution remained clear at all temperatures of spectrum recording. The initial exclusive formation of $B_4H_9^-$ ion and the conversion of the initial product to $H_2B(NH_3)_2^+B_3H_8^-$, which proceeds rapidly at $-40^\circ C$, were evident in the spectra.

The reaction of tetraborane(10) with diethylamine in dichloromethane was studied in the same manner as described immediately above. The reaction began with the initial formation of $B_4H_9^-$ ion and ended with the exclusive formation of $H_2B[(C_2H_5)_2NH]_2^+B_3H_8^-$. The progress of the reaction was also the same as that observed in the dimethylamine reaction. The ^{11}B NMR signal for the $H_2B[(C_2H_5)_2NH]_2^+$ cation appears at -5.0 ppm as a triplet ($J = 115$ Hz). The product is a stable, colorless liquid at room temperature.

(d) **The System of Dimethylamine-Borane(3) and Dimethylamine-Triborane(7).** An equimolar mixture (2.34 mmol each) of $(CH_3)_2NH \cdot BH_3$ and $(CH_3)_2NH \cdot B_3H_7$ in dichloromethane was prepared in a 10 mm o.d. NMR sample tube. The ^{11}B NMR spectra of the sample at temperatures from -80 to $+20^\circ C$ showed no evidence of any change in the original compounds. The mixture remained unchanged even after standing for 5 h at room temperature.

(e) **The System of Diborane(6) and Tetrahydrofuran.** A solution containing 0.30 mmol of B_2H_6 in about 1.5 mL of tetrahydrofuran was prepared in a 10 mm o.d. NMR sample tube at $-80^\circ C$. The solution was never warmed above $-80^\circ C$ before the measurements were initiated. At $-80^\circ C$ a broad band centered at -2.8 ppm was the only signal that could be observed in the proton spin-decoupled spectrum. As the temperature was raised the signal gradually sharpened and shifted slightly downfield. At $+20^\circ C$ a well-defined quartet ($J = 105$ Hz) (or a singlet in the proton-decoupled spectrum) was observed at -1.9 ppm. No other signal could be detected during this whole process. Literature values of the ^{11}B chemical shift for $THF \cdot BH_3$ are -0.8 and -0.9 ppm ($J = 103$ Hz).¹⁷

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Registry No. $H_2B[(CH_3)_2NH]_2^+B_3H_8^-$, 63937-06-4; $H_2B[(CH_3)_2NH]_2^+B_3H_8^-$, 63915-42-4; $H_2B[(C_2H_5)_2NH]_2^+B_3H_8^-$, 63937-10-0; B_4H_{10} , 18283-93-7; $(CH_3)_2NH$, 124-40-3; CH_3NH_2 , 74-89-5; B_2H_6 , 19287-45-7; THF, 109-99-9; $THF \cdot BH_3$, 14044-65-6.

References and Notes

- (1) D. R. Schultz and R. W. Parry, *J. Am. Chem. Soc.*, **80**, 4 (1958).
- (2) S. G. Shore, C. W. Hickam, Jr., and D. Cowles, *J. Am. Chem. Soc.*, **87**, 2755 (1965).
- (3) M. Inoue and G. Kodama, *Inorg. Chem.*, **7**, 430 (1968).
- (4) A. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.*, **59**, 780 (1937).
- (5) (a) D. E. Young and S. G. Shore, *J. Am. Chem. Soc.*, **91**, 3497 (1969); (b) H. D. Johnson, II, and S. G. Shore, *Fortschr. Chem. Forsch.*, **15**, 87 (1970).
- (6) (a) G. Kodama and R. W. Parry, *J. Am. Chem. Soc.*, **82**, 6250 (1960); (b) G. Kodama and R. W. Parry, *Proc. Int. Congr. Pure Appl. Chem.*, **16**, 483 (1958).
- (7) L. J. Edwards, W. V. Hough, and M. D. Ford, *Proc. Int. Congr. Pure Appl. Chem.*, **16**, 475 (1958).
- (8) A. R. Dodds and G. Kodama, *Inorg. Chem.*, **15**, 741 (1976).
- (9) H. D. Johnson, II, and S. G. Shore, *J. Am. Chem. Soc.*, **92**, 7586 (1970).
- (10) R. W. Parry and S. G. Shore, *J. Am. Chem. Soc.*, **80**, 15 (1958).
- (11) H. Nöth, H. Beyer, and H.-J. Vetter, *Chem. Ber.*, **97**, 110 (1964).
- (12) (a) R. Schaeffer, F. Tebbe, and C. Phillips, *Inorg. Chem.*, **3**, 1475 (1964); (b) footnote 12 in ref 14.
- (13) It was reported by E. Mayer, *Inorg. Chem.*, **12**, 1954 (1973), that $H_2B(NH_3)_2^+BH_4^-$ converts to NH_3BH_3 at room temperature in the presence of a catalytic amount of B_2H_6 .
- (14) G. Kodama and D. J. Saturnino, *Inorg. Chem.*, **14**, 2243 (1975).
- (15) E. Mayer, *Inorg. Chem.*, **11**, 866 (1972).
- (16) G. R. Eaton and W. N. Lipscomb, "NMR Studies of Boron Hydrides and Related Compounds", W. A. Benjamin, New York, N.Y., 1969, p 416.
- (17) Reference 16, p 465.

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Transition Metal Eight-Coordination. 9. Tetrakis(picolinato)tungsten(IV) and -(V) Complexes¹

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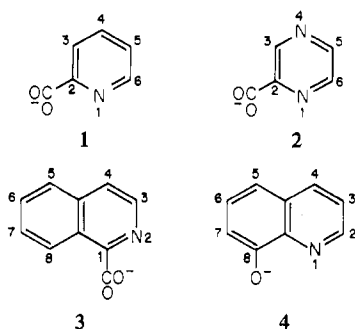
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A series of blue, air and thermally stable, eight-coordinate tungsten(IV) complexes of the type $[WL_4]$ (L = picolinato; 5-methyl-, 5-ethyl-, 3-hydroxy-, and 3,4-benzopicolinato; and 2-pyrazinecarboxylato) has been synthesized anaerobically by high-temperature anhydrous solvent reactions between $W(CO)_6$ and the appropriate ligand. Some were also isolated from sealed-tube melt reactions of the same reactants. These substitution-inert complexes are diamagnetic, and the electronic absorption spectra are dominated by low-energy metal to ligand charge-transfer bands in the range $16\,200$ – $18\,000$ cm^{-1} (ϵ $15\,000$ – $23\,000$), except for tetrakis(1-isoquinolinecarboxylato)tungsten(IV), which has its low-energy maximum at $13\,600$ cm^{-1} ($\epsilon \sim 35\,000$). The more soluble complexes have been studied by 1H NMR and exhibit spectra consistent with eight-coordination. Oxidation of the $[WL_4]$ complexes to $[WL_4]X$ salts was accomplished for L = picolinato (pic^-) and 1-isoquinolinecarboxylato (iqc^-) by treatment with CCl_4 solution of Cl_2 or Br_2 . The golden brown $[W(pic)_4]X$ salts are paramagnetic ($\mu_{eff} = 1.6 \mu_B$) and show moderate stability in air but disproportionate rapidly (<10 min) in solution to WL_4 and a tungstate species. The $[W(iqc)_4]Cl$ salt is considerably more resistant to disproportionation. Liquid nitrogen electron spin resonance studies of $[W(pic)_4]Cl$ suggest a low-symmetry configuration of ligands around the metal in an acetone-glass environment. Anisotropic g values of 1.949, 1.863, and 1.763 were obtained under these conditions.

Introduction

Based on the structural and chemical similarities between 8-quinolinol and picolinic acid and the successful synthesis and characterization of a series of tetrakis(8-quinolinolato)-tungsten(IV)² and -tungsten(V)³ complexes, an investigation of the possible existence of tetrakis(picolinato)tungsten(IV)⁴ and -tungsten(V) complexes was undertaken. In addition to

the picolinato ligand (**1**, pic^-) and its 3-hydroxy ($hpic^-$), 5-methyl ($mpic^-$), and 5-ethyl ($epic^-$) derivatives, the 2-pyrazinecarboxylato (**2**, pzc^-) and the 1-isoquinolinecarboxylato (**3**, iqc^-) ligands have been investigated as potential ligands. Tetrakis-8-quinolinolato (**4**, q^-) tungsten(IV) derivatives have been synthesized² for the 5-bromo (bq^-), the 5,7-dibromo (dbq^-), the 5,7-dichloro (dcq^-), the 7-bromo-



5-methyl (bmq^-), and 5-methyl (mq^-) derivatives in addition to the chelate prepared with the parent ligand. Whereas the tetrakis(picolinato)tungsten(IV) complex (singular) refers to $\text{W}(\text{pic})_4$, the phrase tetrakis(picolinato)tungsten(IV) complexes (plural) refers to all tungsten(IV) derivatives of **1**, **2**, and **3** investigated herein.

Experimental Section

Solvents. Benzene (Fisher, spectrograde) was dried and deoxygenated by heating to reflux conditions over phosphorus pentoxide under prepurified nitrogen for 2 h (5–10 g/L of benzene) followed by distillation. The 79.5–80.5 °C (uncorrected) fraction was collected under nitrogen. Methylene chloride (Fisher, practical grade) was shaken with concentrated sulfuric acid until the acid layer remained colorless and then washed with water, 5% sodium hydroxide solution, and then water again. The methylene chloride was predried with calcium chloride and distilled under prepurified nitrogen from phosphorus pentoxide. The 39.5–40.5 °C (uncorrected) fraction was collected. Pyridine (Eastman, practical grade) and 2,4,6-trimethylpyridine (Eastman, practical grade) were dried and deoxygenated by heating under reflux conditions over potassium hydroxide (50 g/L) under prepurified nitrogen followed by distillation. Fractions collected were 113–114 °C (uncorrected) for pyridine and 164–167 °C (uncorrected) for 2,4,6-trimethylpyridine. Acetone (Fisher, spectrograde), carbon tetrachloride (Mallinckrodt), chloroform (Fisher, spectrograde), dimethyl sulfoxide (Eastman, practical), glacial acetic acid (Mallinckrodt, reagent grade), mesitylene (Eastman), and methanol (Fisher, spectrograde) were used without further purification.

Ligands, Precursors, and Reagents. Selenium dioxide (Fisher) was used without further purification. The spent selenium dioxide in the form of selenium (red) metal was regenerated by the method of Baker and Maxson.⁵ Concentrated nitric acid was warmed in an evaporating dish and selenium slowly added (4–6 g/10 mL of nitric acid). When dissolution was complete the solution was taken to dryness. Because either sublimation or vacuum sublimation of the crude selenium dioxide resulted in substantial reduction back to selenium, the crude selenium dioxide was dried in vacuo and used without further purification.

2,5-Lutidine (Aldrich) and 5-ethyl-2-methylpyridine (Aldrich) were heated under reflux conditions over potassium hydroxide and then distilled under prepurified nitrogen. Picolinic acid (Eastman), 3-hydroxypicolinic acid (Aldrich), 2-pyrazinecarboxylic acid (Aldrich), and 1-isoquinolinecarboxylic acid (Aldrich) were used without further purification.

5-Ethylpicolinic acid was prepared by the method of Jerchel, Bauer, and Hippchen.⁶ To 43.3 g (0.45 mol) of gently boiling 5-ethyl-2-methylpyridine, 21.9 g (0.20 mol) of selenium dioxide was slowly added in fractions. The solution was heated under reflux conditions for another 30 min after the final addition of selenium dioxide, whereupon 50 mL of water was added to the solution and the solution was steam distilled to remove the unreacted base (5-ethyl-2-methylpyridine). The unreacted selenium dioxide was reduced to selenium by passage of sulfur dioxide through the solution for 2 h. The solution was taken to dryness and the crude product was extracted with benzene. Final purification was achieved by vacuum sublimation of 5-ethylpicolinic acid at a temperature slightly below its melting point: yield 13%, mp 107.5–109 °C, lit.⁷ mp 108 °C.

5-Methylpicolinic acid was prepared and purified following the procedure for the preparation of 5-ethylpicolinic acid.⁶ The reaction of 21.0 g (0.19 mol) of selenium dioxide with 32.0 g (0.30 mol) of 2,5-lutidine yielded 1.25 g of 5-methylpicolinic acid: yield 6%, mp 166–167 °C, lit.⁸ mp 163–164 °C. The ¹H NMR spectra of 5-methylpicolinic acid in D₂O showed three singlets around 8.50 ppm

and a singlet at 2.45 ppm which integrated 1:1:1:3. The carboxylic acid proton was unobserved.

Tungsten hexacarbonyl (Pressure Chemical) was purified by vacuum sublimation at 100 °C onto a cold finger cooled to dry ice temperature.

Tetrakis(picolinato)tungsten(IV). Method 1. Picolinic acid (3.70 g, 30.0 mmol), tungsten hexacarbonyl (1.04 g, 2.96 mmol), and a magnetic stirrer bar were placed in an oven-dried long-necked 50-mL round-bottom flask fitted for nitrogen purging. After purging the system with prepurified nitrogen for several hours the flask was immersed in an oil bath at 150 °C for 3 hours. Immediately upon melting, the ligand began to react with the tungsten hexacarbonyl, evolving carbon monoxide and forming a purplish black solution which remained this color throughout the reaction. The crude product was removed from the reaction flask and subjected to vacuum sublimation at 150 °C for a period of 4 h. A small quantity of a white residue was collected on the dry ice/acetone-cooled cold finger. The complex was then dissolved in methylene chloride, filtered through a sintered glass funnel, and precipitated by the addition of hexane to the methylene chloride solution. The complex was recovered by filtration and dried in vacuo over potassium hydroxide at 100 °C for 24 h.

Anal. Calcd for $\text{W}(\text{C}_6\text{H}_4\text{NO}_2)_4$: C, 42.88; H, 2.40; N, 8.33. Found: C, 42.80; H, 2.60; N, 8.45.

Method 2. Picolinic acid (1.27 g, 16.0 mmol) and tungsten hexacarbonyl (0.77 g, 2.2 mmol) were allowed to react in mesitylene under reflux conditions and a nitrogen atmosphere for 3 h. On cooling, long needle-like black crystals were obtained. The crystals were washed with hexane and dried in vacuo over potassium hydroxide at 100 °C for 24 h, yield 74.2%.

Anal. Calcd for $\text{W}(\text{C}_6\text{H}_4\text{NO}_2)_4$: C, 42.88; H, 2.40. Found: C, 43.20; H, 2.79.

Tetrakis(5-methylpicolinato)tungsten(IV) was prepared by placing 5-methylpicolinic acid (0.41 g, 3.0 mmol) and tungsten hexacarbonyl (0.2 g, 0.6 mmol) in a round-bottom two-neck flask containing 50 mL of dry, deaerated mesitylene. A nitrogen inlet valve was attached to the flask along with a water-cooled reflux condenser fitted with a three-way stopcock. After purging the system with prepurified nitrogen for 10 min the mixture was heated under reflux conditions for 6 h under a back-pressure of nitrogen. The crude product, soluble in mesitylene, was recovered by flask evaporation of the solvent followed by vacuum sublimation at 150 °C for several hours to remove unreacted ligand, tungsten hexacarbonyl, and reduced ligand. The complex was dissolved in methylene chloride, filtered and reprecipitated by the addition of hexane to the methylene chloride solution. The complex was dried in vacuo over potassium hydroxide at 100 °C for 24 h, yield 80.5%.

Anal. Calcd for $\text{W}(\text{C}_7\text{H}_6\text{NO}_2)_4$: C, 46.17; H, 3.32; N, 7.69. Found: C, 45.90; H, 3.88; N, 7.32.

Tetrakis(5-ethylpicolinato)tungsten(IV) was prepared following the procedures described for the preparation of $\text{W}(\text{mpic})_4$. 5-Ethylpicolinic acid (0.61 g, 4.0 mmol) and tungsten hexacarbonyl (0.28 g, 0.8 mmol) were allowed to react in mesitylene under reflux conditions under a nitrogen atmosphere for 6 h. After removing the solvent by flash evaporation and subjecting the crude product to vacuum sublimation at 150 °C, it was dissolved in methylene chloride, filtered, and reprecipitated by the addition of hexane and storage of the solution mixture in a freezer. Reprecipitation was more difficult than for the $\text{W}(\text{pic})_4$ and $\text{W}(\text{mpic})_4$ complexes due to the increased solubility of the $\text{W}(\text{epic})_4$ complex. The complex was dried in vacuo over potassium hydroxide at 100 °C for 24 h, yield 52.8%.

Anal. Calcd for $\text{W}(\text{C}_8\text{H}_8\text{NO}_2)_4$: C, 48.99; H, 4.71; N, 7.14. Found: C, 48.09; H, 4.21; N, 6.78.

Tetrakis(3-hydroxypicolinato)tungsten(IV) was prepared by allowing 3-hydroxypicolinic acid (2.10 g, 15.1 mmol) and tungsten hexacarbonyl (1.05 g, 3.00 mmol) to react in collidine under reflux conditions and a nitrogen atmosphere. The crude product has only slight solubility in all solvents tried; therefore, a Soxhlet extraction was performed on the crude product for 2 days using methylene chloride as the extraction solvent. Hexane was added to the extraction solution, which caused precipitation of the complex, which was then subjected to vacuum sublimation at 150 °C, followed by drying in vacuo over potassium hydroxide at 100 °C for 24 h.

Anal. Calcd for $\text{W}(\text{C}_6\text{H}_4\text{NO}_3)_4$: C, 39.15; H, 2.19; N, 7.61. Found: C, 39.10; H, 2.47; N, 7.32.

Tetrakis(2-pyrazinecarboxylato)tungsten(IV) was prepared by the reaction of 2-pyrazinecarboxylic acid (1.54 g, 12.4 mmol) and tungsten

hexacarbonyl (0.89 g, 2.52 mmol) in 75 mL of mesitylene heated under reflux conditions and a nitrogen atmosphere for 16 h. Upon cooling the crude complex was recovered by filtration. Due to the low solubility of the complex in all solvents tried, it was purified by Soxhlet extraction with methylene chloride under a nitrogen atmosphere for 5 days. The extraction solution was filtered to yield a small quantity of the complex, which was dried in vacuo over potassium hydroxide at 100 °C for 24 h.

Anal. Calcd for $W(C_5H_3N_2O_2)_4$: C, 35.53; H, 1.79; N, 16.57. Found: C, 35.62; H, 1.86; N, 16.56.

Tetrakis(1-isoquinolinecarboxylato)tungsten(IV). 1-Isoquinolinecarboxylic acid (2.60 g, 15.0 mmol) and tungsten hexacarbonyl (1.07 g, 3.04 mmol) reacted in 100 mL of hot collidine under a nitrogen atmosphere for 7 h. The solvent was not heated to the boiling point of collidine, however, to avoid decarboxylation of the ligand. The crude product, blue-green in color, was recovered by flash evaporation of the solvent, followed by vacuum sublimation at 150 °C for several hours. The crude product was then subjected to a Soxhlet extraction by benzene for 2 days, whereupon the solution was taken to dryness. The complex was dried in vacuo over potassium hydroxide for 24 h at 100 °C.

Anal. Calcd for $W(C_{10}H_6NO_2)_4$: C, 55.07; H, 2.77; N, 6.42. Calcd for $W(C_{10}H_6NO_2)_4 \cdot 2.5C_6H_6$: C, 61.85; H, 3.66. Found: C, 61.73; H, 3.92.

Tetrakis(picolinato)tungsten(V) chloride was prepared by suspending 0.10 g (0.15 mmol) of the tetrakis(picolinato)tungsten(IV) complex, $W(pic)_4$, in 25 mL of CCl_4 and adding 25 mL of a saturated Cl_2/CCl_4 solution. The reaction was run in a 125-mL Erlenmeyer flask and stirred for 30 min by means of a Teflon-coated magnetic stirrer bar. The yellow-brown product was filtered and washed with 100 mL of CCl_4 , followed by drying in vacuo at room temperature for 24 h, yield 80.5%.

Anal. Calcd for $[W(C_6H_4NO_2)_4]Cl$: C, 40.73; H, 2.28, N, 7.91. Found: C, 39.94; H, 2.93.

Tetrakis(picolinato)tungsten(V) bromide was prepared by suspending 0.10 g (0.15 mmol) of the tetrakis(picolinato)tungsten(IV) complex in 25 mL of CCl_4 and adding 25 mL of a Br_2/CCl_4 solution. The solution was stirred for 30 min. The yellow-brown complex was recovered by filtration followed by washing with CCl_4 . The complex was dried in vacuo at room temperature for 24 h, yield ~100%.

Anal. Calcd for $[W(C_6H_4NO_2)_4]Br$: C, 38.32; H, 2.14; N, 7.45. Calcd for $[W(C_6H_4NO_2)_4]Br_3$: C, 31.61; H, 1.76; N, 6.14. Found: C, 30.23; H, 1.88. Because of the instability of the complex, further purification was not attempted.

Physical Studies. Electronic Spectra. The 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 eight-coordinate complexes. $CoHg(SCN)_4$ was used to calibrate the balance. Sample size was ca. 5 mg. The diamagnetism of the ligands was corrected by using Pascal's constant summation method.

Proton Nuclear Magnetic Resonance Spectra. The 1H NMR spectra of the complexes were measured on either 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. Reported temperatures of spectra are accurate to ± 2 °C.

Infrared Spectra. The infrared spectra of the eight-coordinate complexes were recorded on the Perkin-Elmer 180 spectrometer. Using a 1–3-mg sample and approximately 0.25 g of potassium bromide (Harshaw Chemical Co., Infrared Quality reagent), a potassium bromide disk (1.275 cm \times 2 mm) was made with a ram and die under 25 000 psi for several minutes. Samples were run against air.

Electron Spin Resonance Spectra. The ESR spectra were recorded at room and liquid nitrogen temperatures in acetone (Fisher, spectrograde) (10^{-5} – 10^{-2} M) on a Varian E-9 spectrophotometer. The field was referenced against an internally sealed sample of *N,N*-diphenylpicrylhydrazyl.

Thin-Layer Chromatographic Studies. Comparative studies were performed on the eight-coordinate complexes using precoated silica gel plates (20 \times 20 cm, thickness 250 μ , Anal. Tech. Inc. Redi/Plate).

The plates were oven dried at temperatures >100 °C for a period of not less than 1 h.

Thermal Gravimetric Analysis. Thermal gravimetric measurements were recorded on a DuPont 950 thermogravimetric analyzer under a nitrogen atmosphere. Differential scanning calorimetric measurements were recorded on a Perkin-Elmer differential scanning calorimeter. The samples used were of the highest purity obtainable.

Results

Synthesis, Stability, and Solubilities of the Tetrakis(picolinato)tungsten(IV) and -tungsten(V) Complexes. The reaction of tungsten hexacarbonyl with picolinic acid, substituted picolinic acids (with the exception of 1-isoquinolinecarboxylic acid), and 2-pyrazinecarboxylic acid all proceed smoothly by solvent and/or melt reactions to yield complexes consistent with their formulation as discrete tetrakis eight-coordinate complexes of tungsten(IV). The melt reaction of tungsten hexacarbonyl and picolinic acid produces a very small amount of pyridine (detected by its odor) which results from the decarboxylation of some of the picolinic acid under the reaction conditions.

The reaction of 1-isoquinolinecarboxylic acid with tungsten hexacarbonyl is complicated by extensive decarboxylation at high temperatures. The principal products of this reaction at high temperatures appear to be the orange complex $W(CO)_3(\text{isoquinoline})$ and isoquinoline.^{1b} When low-boiling point solvents were used only the desired turquoise blue color was observed, but the reaction is slow and the yields are very low under these conditions. The $W(\text{iq})_4$ complex is the only tungsten(IV) complex which was not obtained in a pure solvent-free state. Solvates of similar complexes are not unknown; e.g., $W(\text{bq})_4 \cdot C_6H_6$ is known to be a solvated eight-coordinate complex.^{2c}

No intermediates were recovered or observed for the $W(\text{pic})_4$ and derivatized Hpic reactions nor were any tungsten(V) complexes isolated with the reactants under the conditions described above. The only color change observed during the course of these reactions was the dramatic change from the original colorless solution to a dark, ink-like blue indicating the formation of the tetrakis species. All complexes in solution are blue. Most have slightly different shades of blue and range from a royal blue for $W(\text{pic})_4$, $W(\text{mpic})_4$, and $W(\text{epic})_4$, which are indistinguishable in color, to a turquoise blue for $W(\text{iq})_4$.

The solubility of these tungsten(IV) complexes varies considerably with the nature of the ligand. Maximum solubility varies over the range of 10^{-4} – 10^{-1} M. The trend in the solubility of these tungsten(IV) complexes in moderately polar to nonpolar solvents (e.g., acetone, chloroform, benzene) is 2-pyrazinecarboxylato \sim 3-hydroxypicolinato $<$ 1-isoquinolinecarboxylato \ll picolinato $<$ 5-methylpicolinato $<$ 5-ethylpicolinato. The 3-hydroxypicolinato- and picolinato-tungsten(IV) complexes are slightly soluble (10^{-4} M) in polar, hydrogen bonding solvents, like methanol or water. The presence of alkyl substituents on the picolinato ligand lowers the solubility of the corresponding tungsten(IV) complexes in protic solvents. Soxhlet extraction of the crude product was necessary to achieve a pure sample for those complexes possessing low solubility.

These complexes appear to be stable in the solid state for years. The solutions of these tungsten(IV) complexes maintain their blue color for many months, but in strong acid or base they are rapidly hydrolyzed.

The synthesis of $[W(\text{pic})_4]X$ was accomplished by treating the tetrakis(picolinato)tungsten(IV), $W(\text{pic})_4$, with Cl_2/CCl_4 or Br_2/CCl_4 solutions, but not with a I_2/CCl_4 solution. The corresponding $[W(\text{iq})_4]Cl$ complex was also synthesized by the above procedure, but the complex was not studied in any detail. The tetrakis(2-pyrazinecarboxylato)tungsten(IV) complex, on the other hand, was unaffected by any of the above oxidizing agents. In several days time the $[W(\text{pic})_4]X$

Table I. Room Temperature Magnetic Moments of the Tetrakis(picolinato)tungsten(IV) and -tungsten(V) Complexes

Complex	$10^6 \chi_g^a$ cgs	$10^6 \chi_M$ (exptl)	$10^6 \chi_M$ (cor) ^b	μ_{eff}
W(pic) ₄	-0.41	-275 ± 100	-50 ± 150	0
W(mpPic) ₄	-0.19	-150 ± 100	140 ± 150	~0.5 ^c
W(epic) ₄	-0.21	-175 ± 100	140 ± 150	~0.5 ^c
W(pzc) ₄	-0.26	-175 ± 100	50 ± 150	~0.3 ^c
[W(pic) ₄]Cl	1.12	850 ± 100	1100 ± 150	~1.65
[W(pic) ₄]Br	1.23	875 ± 100	1100 ± 150	1.65

^a Measured by the Faraday method. ^b Diamagnetic corrections made using Pascal's constants. ^c Zero within experimental error.

complex is reduced to W(pic)₄ when it is left exposed to the atmosphere. In solution this process is accelerated. The color change from yellow (due to the W(pic)₄⁺ cation) to blue (due to the W(pic)₄ complex) occurs between 5 and 20 min after dissolution in spectral grade solvents. The rate depends on the solvent. Of those solvents tested [W(pic)₄]X appears to have maximum solubility in acetone (10⁻²–10⁻³ M). Dissolution of a known amount of the [W(pic)₄]Cl complex in methanol along with the measurement of the absorption spectra of the resulting W(pic)₄ solution indicated a 45 ± 5% conversion of W(pic)₄⁺ back to W(pic)₄. The W(iqc)₄⁺ cation exists in solution for days before disproportionation is complete, indicating it is a more kinetically stable species than the W(pic)₄⁺ complex but still much less stable than the previously characterized W(dcq)₄⁺ cations.

Infrared Spectra. The infrared spectrum of W(pic)₄ has vibrational transitions at 1676 (vs), 1658 (w), 1600 (w), 1500 (w), 1468 (s), 1440 (s), 1318 (s), 1290 (s), 1259 (w), 1152 (s), 1089 (w), 1013 (m), 859 (m), 819 (w), 798 (w), 766 (s), 706 (m), 681 (s), 543 (m), and 471 (m) cm⁻¹. Absent from the spectrum are bands in the C–O stretch region, which indicate that the tungsten hexacarbonyl is completely substituted. The region from 860 to 1000 cm⁻¹ (normally the region where W–O stretches are observed for tungsten oxo complexes⁹) is also devoid of any major bands. The spectrum of W(pic)₄ is dominated by the COO asymmetric stretch at 1676 cm⁻¹, which is typical of other metal picolinato complexes.^{4,10} The absorption bands of the free ligand and the complex generally correspond to within 10–20 cm⁻¹.

The infrared spectrum of the orange product from the Hicq reaction is consistent with the W(CO)₃(isoquinoline) for-

mulation. Carbonyl stretches (2080, 1995, 1970, and 1920 cm⁻¹), a lack of any carboxylate stretches, and the presence of vibrational frequencies similar to nitrogen heterocyclic compounds were observed.

Magnetic Susceptibility Measurements. The room temperature magnetic moments of the tungsten(IV) and tungsten(V) complexes are indicated in Table I. Within experimental error, the tungsten(V) complexes have magnetic moments of zero. These complexes are diamagnetic, although the tungsten may possess a small amount of paramagnetism, which is normally attributed to temperature-independent paramagnetism.¹¹ The room temperature magnetic moments of the tungsten(V) salts, 1.65 μ_B, are near the spin-only value for a d¹ species.

Electronic Absorption Spectra. The electronic absorption spectra of the tungsten(IV) complexes, excepting W(iqc)₄, are characterized by two (or more) overlapping bands in the red end of the visible region (16 600–18 500 cm⁻¹; ε (15–23) × 10³) and, in the case of the W(pic)₄, W(mpPic)₄, and W(epic)₄ complexes, by a less intense transition at a higher energy (22 000–26 000 cm⁻¹; ε (5–7) × 10³). See Table II. The even higher energy bands of the tungsten(IV) complexes in the ultraviolet (33 000–38 000 cm⁻¹; ε (22–33) × 10³) coincide with the maxima of the corresponding free ligand in the same solvent. Shifts in the absorption maxima of the tetrakis(picolinato)tungsten(IV) complex in various solvents (Table III) indicate varying degrees of solvent–complex interaction. Polar solvents cause a shift in the maxima to higher energy with polar hydrogen-bonding solvents (water, glacial acetic acid) causing the largest shift. This shift is visibly noticeable as the color of the solution changes from blue to purple.

The electronic absorption spectrum of the W(iqc)₄ complex resembles the spectrum of W(dcq)₄ more closely than that of the tetrakis(picolinato)tungsten(IV) complexes. Only semi-quantitative results have been obtained. The W(iqc)₄ complex has a maximum at 13 600 cm⁻¹ (ε ~ 35 000) and a second weaker maximum at 24 400 cm⁻¹ (ε ~ 10 000). The 13 600-cm⁻¹ maximum is at a lower energy than any of the other tetrakis(picolinato)tungsten(IV) and tetrakis(8-quinolinato)tungsten(IV) complexes observed to date.

The electronic spectrum of the tetrakis(picolinato)tungsten(V) chloride complex in acetone shows bands at 23 400, 25 000, 27 800, and 29 400 cm⁻¹ with slightly increasing absorbances to the 29 400-cm⁻¹ maximum. A band at 38 900

Table II. Electronic Spectra of Tetrakis(picolinato)tungsten(IV) Complexes in Chloroform^a

W(pic) ₄	W(mpPic) ₄	W(epic) ₄	W(hpic) ₄	W(pzc) ₄
16 600 (18400)	16 900 (20400)	16 900 (23650)	16 900 (15100)	16 200 (19400)
17 500 (18000)	17 800 (20000)	17 800 (23000)	18 200 (sh, 13800)	17 700 (sh, 15000)
22 700 (sh, 5500)	22 400 (sh, 6100)	22 400 (sh, 7200)	<i>e</i>	<i>e</i>
26 600 (sh, 2850)	26 600 (sh, 2700)	26 600 (sh, 3050)	25 900 (sh, 1500)	<i>e</i>
33 900 (sh, 17450)	34 800 (sh, 17450)	34 800 (sh, 21050)	<i>e</i>	<i>e</i>
37 800 (24550)	37 100 (28000)	37 100 (33350)	33 300 (22100)	36 900 (25250)
[37 700 (3500)]	[37 000 (4850)]	[37 200 (5200)]	[33 100 (5750)]	[37 200 (7600)]

^a The values given are in cm⁻¹; the numbers in parentheses are ε values; sh = shoulder; the ultraviolet maximum for the uncomplexed protonated ligand is indicated in brackets.

Table III. Solvent Dependence of the W(pic)₄ Spectra^a

Solvent	Low-energy envelope ^b		Second (blue) region maxima
	Maxima	Shoulder	
Benzene	16 700 (21 200)	17 500 (20 900)	22 300 (5800)
Pyridine	17 100 (13 400)	16 400 (13 000)	22 200 (4400)
Dimethyl sulfoxide	17 200 (15 300)	16 400 (14 500)	22 200 (4600)
Dichloromethane	17 500 (17 800)	16 700 (17 600)	22 600 (5400)
Methanol	17 700 (17 200)	16 700 (15 500)	22 700 (5700)
Glacial acetic acid	17 700 (12 000)	16 700 (11 200)	23 500 (4700)
Water	17 900 (12 800)	17 000 (11 700)	23 400 (4600)

^a Absorption values given in cm⁻¹ with ε values in parentheses. ^b Note that in solvents such as benzene and dichloromethane the low-energy band is approximately a flat top curve; see Figure 2.

Table IV. The ^1H NMR Spectra of Tetrakis(picolinato)tungsten(IV) Complexes at 35 °C^a

Complex	H ₃	H ₄	H ₅	H ₆	CH ₂	CH ₃
W(pic) ₄ ^{b,c}	(7.50 mult)			9.45 d (6)	<i>d</i>	<i>d</i>
W(mpico) ₄ ^{c,e,f}	7.62 d (8)	7.28 d (8)	<i>d</i>	9.21 s	<i>d</i>	2.44 s
W(mpico) ₄ ^{e,g}	7.81 d (8)	7.55 d (8)	<i>d</i>	9.33 s	<i>d</i>	2.54 s
W(mpico) ₄ ^{c,e,h}	7.61 d (8)	8.09 d (8)	<i>d</i>	10.93 s	<i>d</i>	2.14 s
W(mpico) ₄ ^{c,e,i}	(6.85 mult)		<i>d</i>	7.90 s	<i>d</i>	2.11 s
W(epico) ₄ ^{c,e}	7.63 d (8)	7.27 d (8)	<i>d</i>	9.24 s	2.76 q (7)	1.27 t (8)

^a Resonance signals reported in ppm downfield from tetramethylsilane. $J_{\text{H-H}}$ values in parentheses in units of Hz. Key: s, singlet; d, doublet; t, triplet; q, quartet; mult, multiplet. ^b A 90-MHz spectrum. ^c CD₂Cl₂ solvent. ^d Not applicable. ^e A 60 MHz spectrum. ^f Figure 1. ^g CD₃COOD solvent. ^h Eu(C₁₁H₁₉O₂)₃ shift reagent. ⁱ Pr(C₁₁H₁₉O₂)₃ shift reagent.

Table V. Electron Spin Resonance Parameters for [W(pic)₄]Cl and W(dcq)₄]Cl^a

Complex	Solvent	Temp, K	$\langle g \rangle$	g_1	g_2	g_3	$\langle A \rangle^b$	A^b	B^b	C^b
[W(pic) ₄]Cl	CH ₂ COCH ₃	298	1.855				69			
[W(pic) ₄]Cl	CH ₃ COCH ₃	77	(1.858)	1.949	1.863	1.763	(69)	55	62	90
[W(dcq) ₄]Cl	CH ₂ Cl ₂	298	1.872				74			
[W(dcq) ₄]Cl	CH ₂ Cl ₂	77	(1.875)	1.956	1.893	1.775	(78)	80	67	86

^a Solution and glass matrices; g values ± 0.001 ; hyperfine values $\pm 4 \times 10^{-4} \text{ cm}^{-1}$; calculated values in parentheses. ^b $\text{cm}^{-1} \times 10^4$.

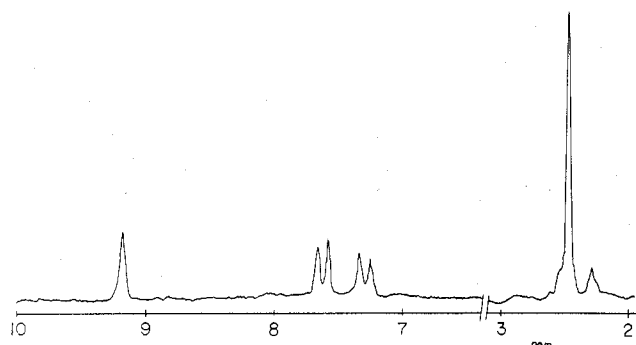


Figure 1. ^1H NMR spectrum of W(mpico)₄, in ppm downfield from tetramethylsilane in CD₂Cl₂ at 35 °C.

cm^{-1} can be seen in CH₂Cl₂ with shoulders at 36 800 and 32 300 cm^{-1} . Quantitative measurements were precluded because of the rapid decomposition of the W(pic)₄⁺ complex in solution. The visible and near-infrared regions are almost totally barren of maxima for the W(pic)₄⁺ species.

Nuclear Magnetic Resonance Spectra. Only the picolinato-, 5-methylpicolinato-, and 5-ethylpicolinatotungsten(IV) complexes are soluble enough to obtain normal ^1H NMR spectra. The resonances and their assignments are tabulated in Table IV. The 90-MHz ^1H NMR spectrum of W(mpico)₄ is shown in Figure 1. The assignments are based on spectral assignments made for picolinic acid and for 5-methylpicolinato esters, where the H₃, H₄, and H₆ methyl ester resonances occur at 8.04, 7.63, and 8.67 ppm, respectively.¹²

The ^1H NMR spectrum of W(mpico)₄ at 35 °C in CD₃C-OD was also investigated and is tabulated in Table IV. Upon aging for 1 week the sample's ^1H NMR spectrum had several new small peaks. One at 2.65 ppm at the base of the methyl protons appeared along with two singlets at 8.75 and 8.52 ppm. Some slow decomposition in CD₃COOD was evident.

The qualitative effect of two lanthanide shift reagents on the ^1H NMR spectrum of W(mpico)₄ in CD₂Cl₂ at 35 °C resulted in better separation but no further resolution of the peaks.

A variable-temperature ^1H NMR study of W(pic)₄ in CD₂Cl₂ down to -90 °C produced no change in the spectra attributable to structural changes in the W(pic)₄ complex. The resolution of the aromatic signals decreased slightly due to broadening of the signals by the increased viscosity of the solution.

Electron Spin Resonance Studies. The room and liquid nitrogen temperature ESR spectra of [W(pic)₄]Cl were ex-

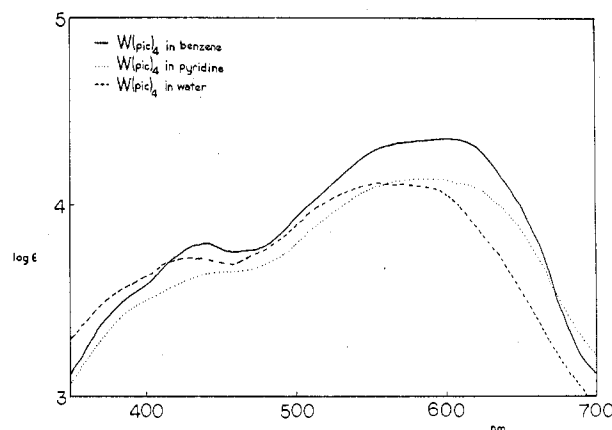


Figure 2. Visible electronic spectra of W(pic)₄ in three solvents; cf. Table III.

amined using acetone as the solvent or glass matrix. The spectrum at 25 °C indicates an isotropic g tensor of 1.855 ± 0.001 . The shoulder observed on the main resonance represents an isotropic hyperfine splitting of $80 \pm 5 \text{ G}$ due to ^{183}W (14.28% abundance, $I_{\text{nuclear}} = 1/2$).

The frozen acetone glass spectrum of [W(pic)₄]Cl (Table V) resembles in detail the frozen CH₂Cl₂ glass spectra of [W(dcq)₄]Cl. Anisotropic g values of 1.949, 1.863, and 1.763 are found for the liquid N₂ spectrum with corresponding hyperfine values of 60, 71, and 110 G. These values give $\langle g \rangle = 1.858$ and $\langle A \rangle = 80 \text{ G}$, which are well within the experimental and interpretational error of the room temperature isotropic values.

Thermal Studies. Thermogravimetric analysis of W(pic)₄ under a nitrogen atmosphere at a heating rate of 10 °C/min indicates a constant weight to 260 °C. At 300 °C approximately 20% loss in weight had been sustained and by 400 °C a 45% loss in weight had occurred. Differential scanning calorimetric measurements on an encapsulated sample of W(pic)₄ indicate only a slight and gradual decomposition prior to melting at 335 °C. Melting was immediately followed by rapid decomposition.

Chromatographic Behavior of Tungsten(IV) Complexes. In order to investigate the feasibility of separating a series of mixed-ligand eight-coordinate tetrakis tungsten(IV) complexes from one another the relative interactions of a number of tungsten(IV) single ligand eight-coordinate complexes were explored by determining R_f values on silica gel with thin-layer chromatography. Concentrating on the picolinato-, 5-

Table VI. Silica Gel TLC R_f Values of the Tetrakis(picolinato)tungsten(IV) Complexes

Complex	1:1 v/v $\text{CHCl}_3/\text{CH}_3\text{COCH}_3$
$\text{W}(\text{pic})_4$	0.21
$\text{W}(\text{mpic})_4$	0.40
$\text{W}(\text{mpic})_n(\text{pic})_{4-n}^a$	0.39, 0.31, 0.25
$\text{W}(\text{epic})_4$	0.70
$\text{W}(\text{hpic})_4$	<0.05
$\text{W}(\text{pzc})_4^b$	~0.1

^a Prepared from the reaction of $\text{W}(\text{CO})_6$, Hmpic, and Hpic. A 3:1 molar ratio of Hmpic to Hpic was used; therefore only $n \geq 2$ complexes were observed. ^b Spot was elongated.

methylpicolinato-, and 5-ethylpicolinatotungsten(IV) complexes, of the numerous solvent systems tried, a one to one volume to volume chloroform/acetone mixture was found to give the largest separation in R_f values for these three complexes. Table VI gives the R_f values of these and other complexes in the above-mentioned solvent system.

Discussion

The tetrakis(picolinato)tungsten(IV) and -tungsten(V) complexes constitute a new series of eight-coordinate complexes in which the same metal is capable of stabilizing two oxidation states. Until this past decade the molybdenum(V)- and -(IV)- and tungsten(V)- and -(IV)-octacyano complexes¹³ and the rhenium(V)- and -(VI)-octacyano complexes¹⁴ were the only known eight-coordinate complexes capable of such behavior. As Table VII indicates, this list has begun to grow quite rapidly.

The group 6 metals, molybdenum and tungsten, the group 7 metal rhenium (and undoubtedly technetium as well), and the group 5 metals, niobium and tantalum, possess the capacity to stabilize eight-coordinate complexes in two oxidation states with common unidentate or chelating ligands of normal ring size. The achievement of stable eight-coordination is facilitated by a large, highly charged metal ion with d^0 , d^1 or d^2 configurations.¹⁵ Requirements of large size and two stable oxidation states tend to exclude the group 5 metal, vanadium, the group 6 metal, chromium, and the group 4 metals from achieving stable complexes of coordination number eight in two different oxidation states.

These tungsten(IV)- and -(V)-picolinato complexes appear to be the first reported tetrakis eight-coordinate complexes containing these ligands.¹⁶ Given the chemical similarities between the various picolinato ligands (including iqc^-) and the 8-quinolinol series and the fact that numerous $\text{M}(\text{quinolinolato})_4^n$ complexes are known (where $\text{M} = \text{Sn},^{18} \text{Th},^{19} \text{U},^{20} \text{Ti},^{21} \text{Zr},^{22} \text{Hf},^{22} \text{Nb},^{23} \text{Mo},^{24}$ and $\text{W}^{2,3}$), there is little reason to suppose that $\text{M}(\text{picolinolato})_4$ complexes for the same and

related metals cannot be synthesized unless some of the metal ions catalyze decarboxylation. Our related work with molybdenum¹⁶ appears to substantiate this proposition, but molybdenum can stop at $\text{Mo}(\text{pic})_3$ under some conditions.⁴

A number of early transition-metal complexes have been reported which contain either the picolinato or the 2-pyrazinecarboxylato ligand. This group of complexes generally falls into one of two categories, either lower valence (and lower coordination number) complexes or oxo-metal complexes. Those lower valence complexes reported include picolinato complexes of chromium(III),²⁵ vanadium(II) and -(III),²⁶ titanium(III),²⁷ and molybdenum(III),⁴ while the latter category includes picolinato (and in one case 2-pyrazinecarboxylato) complexes of the zirconyl ion²⁸ and the vanadyl ion²⁹ and molybdenum-oxo complexes.^{17,30}

Synthesis. The tetrakis(8-quinolinolato)tungsten(IV)² and the tetrakis(picolinato)tungsten(IV) complexes can be synthesized by analogous procedures. However, unlike the 8-quinolinolato tungsten(V) complexes,³ the $\text{W}(\text{pic})_4^+$ complex cannot be synthesized directly. This is not surprising in view of the instability of the $\text{W}(\text{pic})_4^+$ complex and the inability to achieve $\text{W}(\text{pzc})_4^+$. Although the $\text{W}_2\text{Cl}_9^{3-}$ salt was not investigated as a starting material for the preparation of the tetrakis(picolinato)tungsten(IV) complexes, the evidence from the 8-quinolinol studies^{2b} indicates that the $\text{W}_2\text{Cl}_9^{3-}$ salt is a more universal starting material than $\text{W}(\text{CO})_6$, the former already being in the plus three oxidation state. Another subtle difference between the two ligands and their reaction with $\text{W}(\text{CO})_6$ is that the picolinato ligand is subject to decarboxylation, as the formation of pyridine in the melt reaction of $\text{W}(\text{CO})_6$ and picolinic acid attests. When rhenium carbonyl was allowed to react with picolinic acid via a melt reaction, an air-stable crystalline complex, $\text{Re}(\text{CO})_3(\text{py})(\text{pic})$, where $\text{py} = \text{pyridine}$,³¹ was formed.

The mechanisms for the formation of WQ_4 , $\text{W}(\text{pic})_4$, and $\text{W}(\text{pzc})_4$ complexes are probably similar. In neither study were intermediate tungsten complexes observed or isolated in spite of the fact that tungsten is initially in the zero oxidation state. The characterization of a reduced ligand species in the reaction between $\text{W}(\text{CO})_6$ and 8-quinolinol indicates that the ligand also functions as the oxidizing agent in these reactions.³

Dorsett and Walton⁴ have recently reported the synthesis of the parent compound tetrakis(picolinato)tungsten(IV) from the same reactants used in this study ($\text{W}(\text{CO})_6$ and picolinic acid) but in lower boiling solvents (methanol, ethanol, and acetonitrile). They report the evolution of both CO and H_2 and postulate a tungsten(I) intermediate, $[\{\text{W}(\text{CO})_3(\text{pic})\}_n]$, also formulated as $\text{W}_2(\text{CO})_6(\text{pic})_2$ on the basis of its diamagnetism ($\chi_g = 0.18 \times 10^{-6}$ cgsu), an oxidation state titration (0.95 ± 0.1), and the infrared spectra which showed an absence

Table VII. Eight-Coordinate Complexes Existing in Two Oxidation States^a

d^0	Ref	d^1	Ref	d^2	Ref
		$\text{Re}(\text{CN})_8^{2-}$	14	$\text{Re}(\text{CN})_8^{3-}$	14
		$\text{Mo}[\text{W}](\text{CN})_8^{3-}$	13	$\text{Mo}[\text{W}](\text{CN})_8^{4-}$	13
		$\text{W}(\text{dcq})_4^+$	3	$\text{W}(\text{dcq})_4$	2
		$\text{W}(\text{pic})_4^+$	This study	$\text{W}(\text{pic})_4$	This study
		$\text{Mo}[\text{W}](\text{S}_2\text{CNR}_2)_4^+$	b	$\text{Mo}[\text{W}](\text{S}_2\text{CNR}_2)_4$	c, 32
		$\text{Nb}(\text{CN})_8^{4-}$	d	$\text{Nb}(\text{CN})_8^{5-}$	d
$\text{Nb}[\text{Ta}](\text{diars})_2\text{Cl}_4^+$	e	$\text{Nb}[\text{Ta}](\text{diars})_2\text{Cl}_4$	f		
NbT_4^+	g	NbT_4	23		

^a $\text{R} = \text{Me}, \text{Et}, \text{Ph}$; $\text{R}_2 = (-\text{CH}_2)_2$; diars = *o*-phenylenebis(dimethylarsine); T = tropolonate. ^b A. Nieuwpoort, J. H. E. Moonen, and J. A. Cras, *Recl. Trav. Chim. Pays-Bas*, **92**, 1086 (1973); A. Nieuwpoort, *J. Less-Common Metals*, **36**, 271 (1974); A. Nieuwpoort, H. M. Claessen, and J. G. M. van der Linden, *Inorg. Nucl. Chem. Lett.*, **11**, 869 (1975); A. Nieuwpoort and J. J. Steggerda, *Recl. Trav. Chim. Pays-Bas*, **95**, 250, 289 (1976). ^c R. N. Jowitt and P. C. H. Mitchell, *Inorg. Nucl. Chem. Lett.*, **4**, 39 (1968); D. C. Bradley and M. H. Gitlitz, *J. Chem. Soc. A*, 1152 (1969); J. N. Smith and T. M. Brown, *Inorg. Nucl. Chem. Lett.*, **6**, 441 (1970); J. F. Rowbottom and G. Wilkinson, *ibid.*, **9**, 675 (1973); T. M. Brown and J. N. Smith, *J. Chem. Soc., Dalton Trans.*, 1614 (1972). ^d P. M. Kiernan, J. F. Gibson, and W. P. Griffith, *J. Chem. Soc., Chem. Commun.*, 816 (1973). ^e J. C. Dewan, D. L. Kepert, C. L. Raston, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 2031 (1975). ^f R. J. H. Clark, D. L. Kepert, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 2865 (1965); R. L. Deutscher and D. L. Kepert, *Inorg. Chem.*, **9**, 2305 (1970). ^g A. R. Davis and F. W. B. Einstein, *ibid.*, **14**, 3030 (1975).

of bridging carbonyl groups. Unfortunately the details of the titration were not given. Could the complex be $W(CO)_3\pi\text{-picH}$? The reaction times for their syntheses were 1–4 days. The use of solvents with much higher boiling points and the use of an excess of the ligand may account for the absence of any intermediates in our study and the previous study using the 8-quinolinato ligand. The important role that the reaction conditions play in the products obtained is illustrated by the complexes recovered for the reaction of $Mo(CO)_6$ and picolinic acid. In low-boiling solvents and a stoichiometric mixture of the two reactants $Mo(\text{pic})_3$ is produced,⁴ whereas with an excess of the ligand and a high-boiling solvent $Mo(\text{pic})_4$ is produced.¹

The observation by Dorsett and Walton⁴ that hydrogen is a product of these reactions is also previously unobserved and poses the question as to whether its evolution is dependent on the reaction solvent chosen. Recently, the reaction of “[$W(CO)_3(\text{pic})_n$]” with several tertiary phosphines in refluxing methanol was reported to yield the tungsten(II)-hydride complexes $HW(CO)_2(PR_3)_2(\text{pic})$.³¹ If the same complex had not also been prepared in refluxing benzene, the solvent would seem the most likely source of hydrogen. Hydrogen abstraction from the phosphine would be an alternative mechanism.

Although attempts to isolate $W(\text{iqc})_4$ in the pure state failed, all of its chemical and physical behavior is consistent with its formulation as a tetrakis eight-coordinate complex. The orange side product of the $W(CO)_6$, 1-isoquinolinecarboxylic acid reaction has not been fully characterized but on the basis of the elemental analysis results and the infrared spectra, the complex is probably $W(CO)_3(\text{isoquinoline})$. This is consistent with the partial substitution found by Dorsett and Walton.⁴

Magnetic Moments and Chemical Inertness. The magnetic moments for the tetrakis(picolinato)tungsten(IV) complexes, 0–0.6 μ_B , are consistent with those reported for the corresponding tetrakis(8-quinolinolato)tungsten(IV)^{2b} complexes. The value of -0.25×10^6 cgs reported⁴ for the χ_g of $W(\text{pic})_4$ is in good agreement with the value obtained in this study. The value of 1.65 μ_B for $W(\text{pic})_4^+$ is likewise in good agreement with the value reported for the $[W(\text{dcq})_4]^+$ species.³

A rather large range values have been reported for the magnetic moments of d^1 and d^2 second- and third-row early transition metal complexes. See Table VIII. A variety of reasons may account for such large variations in these moments: (1) given the redox properties of most of these complexes, a sample may very easily be contaminated by complexes of a lower or higher oxidation state,³² (2) a change in the stereochemical configuration from one complex to another can alter the positioning of energy levels,³³ (3) the paramagnetism of a complex may include a temperature-independent paramagnetism term, (4) the nature of the ligand's bonding capabilities may cause significant changes in the spin-orbit coupling constant of the complexes, and lastly (5) the inherent limitations in the techniques for determining the magnetic moments of diamagnetic and of low-paramagnetic species and the uncertainty in the diamagnetic corrections associated with these measurements means a significant experimental error is associated with these values.

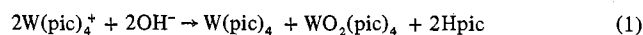
The ability of these eight-coordinate complexes to stabilize the tungsten(V) state and also their ability to resist attack by strong base is dependent on the nature of the ligand. Of the three ligands examined to date which contain nitrogen and oxygen donor atoms, 8-quinolinol, 2-pyrazinecarboxylic acid, and picolinic acid, only the complex containing the first of these three ligands can both stabilize the tungsten(V) state and resist decomposition by strong base. The $W(\text{pic})_4$ complex is not resistant to alcoholic KOH, but can be oxidized to the plus five state. However, the resulting complex, $W(\text{pic})_4^+$, has

Table VIII. Magnetic Moments of Some d^1 and d^2 Early Transition Metal Complexes

Complex	μ_{eff}, μ_B	Ref
I. d^2 Configuration		
$W(\text{dcq})_4$	0–0.5	2a
$W(\text{pic})_4$	0–0.6	This study
$Mo(S_2CR)_4$	0.5–0.6	a
$Mo[W](S_2CNPh_2)_4$	0.8	b
$W(S_2CN(CH_2)_4)_4$	0.98	c
$Mo(S_2CNEt_2)_4$	0.4	32
$W(S_2CNEt_2)_4$	1.17	d
$Mo(S_2CN(CN_2)_4)_4$	0.7 ^e	32
II. d^1 Configuration		
$Nb(S_2CNEt_2)_4$	0.55	f
NbT_4	0.74	23
$Nb(NCS)_4(\text{py})_2$	0.95	33a
$Nb(S_2CNMe_2)_4$	1.32	f
$[W(OC_2H_5)_2Cl_2]^-$	1.36	g
$Nb(\text{acac})_4$	1.47	23
$[W(OC_2H_5)_2Cl_2]^-$	1.53	g
$Nb(\text{diars})_2Cl_4$	1.60	h
NbQ_4	1.60	23
$W(\text{dcq})_4^+$	1.60	3
$W(\text{pic})_4$	1.65	This study
$Mo(S_2CNEt_2)_4^+$	1.70	i
$Nb(NCS)_4(C_{10}H_8N_2)_2$	1.72	33a

^a O. Piovesana and L. Sestili, *Inorg. Chem.*, **13**, 2745 (1974).
^b A. Nieuwpoort, H. M. Claessen, and J. G. M. van der Linden, *Inorg. Nucl. Chem. Lett.*, **11**, 869 (1975). ^c T. M. Brown and J. N. Smith, *J. Chem. Soc., Dalton Trans.*, 1614 (1972). ^d J. N. Smith and T. M. Brown, *Inorg. Nucl. Chem. Lett.*, **6**, 441 (1970).
^e An earlier study^c had indicated 2.11 μ_B . ^f D. C. Bradley and M. H. Gitlitz, *J. Chem. Soc. A*, 1152 (1969). ^g D. P. Rillema and C. H. Brubaker, Jr., *Inorg. Chem.*, **9**, 397 (1970). ^h R. L. Deutscher and D. L. Kepert, *ibid.*, **9**, 2305 (1970). ⁱ A. Nieuwpoort, *J. Less-Common Metals*, **36**, 271 (1974).

limited stability. Recovery of approximately 50% $W(\text{pic})_4$ when $W(\text{pic})_4^+$ is placed in solution suggests, as was previously observed for the $W(\text{dcq})_4^+$ complex,³ that $W(\text{pic})_4^+$ disproportionates to give $W(\text{pic})_4$ and a tungstate complex; i.e.



The $W(\text{pzc})_4$ complex is neither stable to alcoholic KOH nor able to stabilize the plus five oxidation state.

Delocalization of the electron density onto the ligand moiety ought to enhance the ease of oxidation, as the greater ease of oxidation of the $W(\text{dcq})_4$ complex over the $W(\text{pic})_4$ and $W(\text{pzc})_4$ complexes attests. The presence of the carbonyl group in the picolinato and 2-pyrazinecarboxylato complexes should make them susceptible to nucleophilic attack by bases which would in turn cause the decomposition of these complexes.

Electronic Spectra. By virtue of their intensities ($\epsilon > 10^4$), the low-energy (13 600–18 500 cm^{-1}) bands observed for the $W(\text{pic})_4$, $W(\text{hpic})_4$, $W(\text{mpic})_4$, $W(\text{epic})_4$, $W(\text{pzc})_4$, and $W(\text{iqc})_4$ complexes are assigned as charge-transfer bands rather than as d–d transitions.³⁴ The transitions appear to be metal to ligand ($\pi^* \leftarrow d$) type transitions based on the shift to higher energy for the transitions of $W(\text{pic})_4^+$ and the observation that a comparison of the electronic spectra of $Mo(\text{pic})_4$ and the more easily oxidizable $W(\text{pic})_4$ complex indicates a shift to lower energy on going from $Mo(\text{pic})_4$ to $W(\text{pic})_4$. A maximum around 22 500 cm^{-1} , $\epsilon (5.5\text{--}7.2) \times 10^3$, is also observed for the $W(\text{pic})_4$, $W(\text{mpic})_4$, and $W(\text{epic})_4$ complexes and is probably too intense to be assigned as a simple d–d transition.

The change in the maxima of the low-energy transitions of the $W(\text{pic})_4$ complex as the solvent was varied indicates differing degrees of interaction between the solvent and the complex. The carboxylic acid carbonyl group is probably

responsible for the strong interaction between the solvent and complex. Protic solvents (H₂O, methanol, and glacial acetic acid) capable of hydrogen bonding to the carbonyl groups cause the most dramatic shift in the maxima, a shift to higher energy. This shift in the maxima could be indicative of a change in the configuration of the complex.

The maxima of the tetrakis(picolinato)tungsten(IV) complexes occur at higher energy than in the tetrakis(8-quinolinolato)tungsten(IV) complexes.² This trend is repeated in the tetrakis(picolinato)tungsten(V) complex vs. the tetrakis(8-quinolinolato)tungsten(V) complexes,³ that is, the maxima for the W(pic)₄⁺ complex occur at higher energy than for the corresponding W(dcq)₄⁺ complex. Interpretation of the more intense transitions in the visible spectra as transitions to the metal d level from the oxygen lone pairs of π symmetry for the WQ₄⁺ complexes was based on shifts to higher energy as the substituents on the 8-quinolinolato ligand were changed from 5,7-dihalo to 7-chloro-5-nitro to 5-acetyl.³ Given the electron-withdrawing nature of the carboxyl group, the significant shifts to higher energy on going from W(pic)₄ to W(pic)₄⁺ and from W(dcq)₄⁺ to W(pic)₄⁺ are consistent with the earlier assignments.

¹H NMR Spectra. The ¹H NMR spectra of W(pic)₄, W(mpic)₄, and W(epic)₄ are consistent with the formation of these complexes as discrete eight-coordinate molecules. The single sharp methyl resonance of the W(mpic)₄ complex is attributable to a variety of structures and stereochemical states as is discussed elsewhere.^{35,36}

Electron Spin Resonance Spectra. McGarvey³⁸ has derived equations for the spin-Hamiltonian parameters for the dodecahedral and square antiprismatic geometries for a d¹ metal ion, using first- and second-order perturbation theory. For the dodecahedral complex having a ²B ground state the equations for g_⊥ and g_∥ indicate g_⊥ > g_∥ and |A_∥| > |B_⊥| assuming reasonable values for the spin-orbit coupling constant and the d orbital energy separations. Just the reverse trend is predicted for a d¹ complex possessing square antiprismatic geometry, i.e., g_∥ > g_⊥ and |B_⊥| > |A_∥| for a ²A₁ ground state. This analysis indicates that provided the complex has either D_{2d} or D_{4d} symmetry, i.e., is axially symmetric and contains a single unpaired electron, two ESR signals are expected.

The liquid nitrogen spectrum of [W(pic)₄]⁺ clearly reveals that the symmetry of this complex must be lower than D_{2d} or D_{4d}. The spectrum of [W(pic)₄]⁺ is consistent with the complex being a low-symmetry pseudododecahedral isomer of either D₂-gggg or C₂-mmgg symmetry. Since the lone d electron is expected to occupy the b₁ d-like energy level which corresponds to the d_{x²-y²} orbitals, the g_x and g_y values are expected to be closer to the free electron value of 2.0023. On the basis of this argument g₃ is logically assigned as the g_z component while the g₁ and g₂ values are regarded as g_x and g_y or g_y and g_x. These conclusions are based on the analysis of the ESR spectra of [W(dcq)₄]⁺³ and the close similarities in the ESR spectra of [W(dcq)₄]⁺ and [W(pic)₄]⁺.

Other interpretations of the liquid nitrogen spectra are also possible. The results are consistent with significant electronic perturbations by the counterion and a higher pseudosymmetry, such as D_{2d}. Another interpretation is that the spectra could result from two isomers of similar energy in the well of the potential energy surface. However, since intramolecular rearrangement is not anticipated in the solid state and since the ratio of the intensities of the g₁, g₂, and g₃ components are nearly constant for all the derivatives of the tungsten(V)-quinolinolato and -picolinato complexes which have been examined, such an interpretation has been ruled out.

The g values, both isotropic and anisotropic for [W(pic)₄]⁺, are consistently further from the free electron value of 2.0023 than the corresponding g values of the [W(dcq)₄]⁺ complex.

The results are consistent with less electron delocalization in the single ring pic⁻ complexes.

Based on the structure determination of the tetrakis(5-bromo-8-quinolinato)tungsten(IV) complex,^{2c} in which it was found that the complex possessed D_{2d}(mmmm) dodecahedral geometry, and the similarity in the bites of the 8-quinolinato and the picolinato ligands in all probability the W(pic)₄ complex also exists as the D_{2d}(mmmm) dodecahedral stereoisomer. This conclusion plus the results from the ESR studies suggests, as was the conclusion for the W(dcq)₄, [W(dcq)₄]⁺ complexes,² that the W(pic)₄ complex undergoes a change in configuration on oxidation to [W(pic)₄]⁺, although the possibility of tight ion-pair perturbation in solid solutions cannot be completely disregarded.

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Registry No. W(pic)₄, 59368-37-5; W(mpic)₄, 61805-72-9; W(epic)₄, 63956-88-7; W(pzc)₄, 63950-71-0; [W(pic)₄]Cl, 63956-87-6; [W(pic)₄]Br, 63950-72-1; W(hpic)₄, 63950-73-2; [W(dcq)₄]Cl, 37473-84-0; W(iqc)₄, 63950-74-3; W(CO)₆, 14040-11-0.

References and Notes

- (1) (a) The tungsten(IV) complexes were initially reported by R. D. Archer and C. J. Donahue, Abstracts, 169th National Meeting of the American Chemical Society, Philadelphia, Pa., 1975, INOR 056. (b) Taken in part from C. J. Donahue, Ph.D. Dissertation, University of Massachusetts, Dec 1976. (c) Part 8: C. J. Donahue and R. D. Archer, *J. Am. Chem. Soc.*, **99**, 6613 (1977).
- (2) (a) R. D. Archer and W. D. Bonds, Jr., *J. Am. Chem. Soc.*, **89**, 2236 (1967); (b) W. D. Bonds, Jr., and R. D. Archer, *Inorg. Chem.*, **10**, 2057 (1971); (c) W. D. Bonds, Jr., R. D. Archer, and W. C. Hamilton, *ibid.*, **10**, 1764 (1971); (d) R. A. Pribush, Ph.D. Dissertation, University of Massachusetts, 1972.
- (3) R. D. Archer, W. D. Bonds, Jr., and R. A. Pribush, *Inorg. Chem.*, **11**, 1550 (1972).
- (4) Subsequent to our initial report (ref 1a), the tungsten(IV) picolinate complex was reported by T. E. Dorsett and R. A. Walton, *J. Chem. Soc., Dalton Trans.*, 347 (1976).
- (5) R. H. Baker and R. N. Maxson, *Inorg. Synth.*, **1**, 117 (1939).
- (6) D. Jerchel, E. Bauer, and H. Hippchen, *Chem. Ber.*, **88**, 156 (1955).
- (7) N. A. Hughes and H. Rapoport, *J. Am. Chem. Soc.*, **80**, 1604 (1958).
- (8) N. H. Cantwell and E. J. Brown, *J. Am. Chem. Soc.*, **74**, 5967 (1952).
- (9) D. M. Adams, "Metal-Ligand and Related Vibrations", Edward Arnold, London, 1967.
- (10) A. Kleinstein and G. A. Webb, *J. Inorg. Nucl. Chem.*, **33**, 405 (1971).
- (11) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry", J. Lewis and R. G. Wilkins, Ed., Interscience, New York, N.Y., 1962, Chapter 6.
- (12) L. W. Deady, D. M. Harrison, and R. D. Topson, *Org. Magn. Reson.*, **7**, 41 (1975).
- (13) (a) Z. Stasicka, *Zesz. Nauk. Univ. Jagiellon., Pr. Chem.*, **18**, 39 (1973); (b) W. P. Griffith, *Coord. Chem. Rev.*, **17**, 177 (1975); (c) S. J. Lippard, *Prog. Inorg. Chem.*, **8**, 109 (1967); (d) R. A. Pribush and R. D. Archer, *Inorg. Chem.*, **13**, 2556 (1974).
- (14) (a) R. Colton, R. D. Peacock, and G. Wilkinson, *Nature (London)*, **182**, 393 (1958); (b) *J. Chem. Soc.*, 1374 (1960).
- (15) Eight-coordination in the solid state is also obtained with small bite ligands (NO₃⁻, 1,8-naphthyridine, etc.) with other smaller transition metal ions, too.
- (16) We have also synthesized the molybdenum(IV) species, ref 1. Although the Chemical Abstracts Eighth Collective Index, 19654S, 9135F (1973), indexed an earlier molybdenum(IV) picolinate complex as a tetrakis(picolinato)molybdenum(IV) complex, the abstract itself [*Chem. Abstr.*, **66**, 91250h (1967)] only notes a molybdenum(IV) picolinate and the original paper by Gunduz¹⁷ actually discusses a mixed-ligand species or mixture of species with only one picolinato ligand per molybdenum.
- (17) T. Gunduz, *Commun. Fac. Sci. Univ. Ankara, Ser. B*, **11**, 21 (1963-1964).
- (18) K. Ramaiah and D. F. Martin, *J. Chem. Soc., Chem. Commun.*, 130 (1965).
- (19) G. R. Horton and W. W. Wendlandt, *J. Inorg. Nucl. Chem.*, **25**, 247 (1963).
- (20) W. W. Wendlandt and G. R. Horton, *J. Inorg. Nucl. Chem.*, **19**, 272 (1961).
- (21) D. Cunningham, I. Douck, M. J. Frazer, W. E. Newton, and B. Rimmer, *J. Chem. Soc. A*, 2133 (1969).
- (22) M. J. Frazer and B. Rimmer, *J. Chem. Soc., A*, 2273 (1968).
- (23) (a) R. L. Deutscher and D. L. Kepert, *Inorg. Chim. Acta*, **4**, 645 (1970); (b) *Chem. Commun.*, 121 (1969).
- (24) D. C. Bradley, private communication.
- (25) (a) M. Nakahara, *Bull. Chem. Soc. Jpn.*, **35**, 782 (1962); (b) N. Matsuoka, Y. Shimura, and R. Tsuchida, *Nippon Kagaku Zasshi*, **82**,

- 1637 (1961); (c) A. J. Saraceno and B. F. Block, *Inorg. Chem.*, **2**, 864 (1963); (d) M. Ban and J. Csaszar, *Acta Chim. Acad. Sci. Hung.*, **54**, 133 (1967).
- (26) R. C. Mercier and M. R. Paris, *C. R. Hebd. Seances Acad. Sci.*, **259**, 2445 (1964).
- (27) M. Paris, *Chim. Mod.*, **8**, 228 (1963).
- (28) R. C. Paul, S. K. Gupta, S. S. Parmar, and S. K. Vasisht, *Z. Anorg. Allg. Chem.*, **423**, 91 (1976).
- (29) (a) R. L. Dutta and S. Ghosh, *J. Indian Chem. Soc.*, **44**, 273 (1967); (b) *ibid.*, **44**, 290 (1967); (c) *ibid.*, **44**, 296 (1967); (d) M. Paris and J. C. Merlin, *Bull. Soc. Chim., Fr.*, 800 (1962); (e) R. L. Dutta, S. Ghosh, and S. Lahiry, *Sci. Cult.*, **30**, 551 (1964); (f) S. P. Singh and J. P. Tandon, *Indian J. Chem.*, **13**, 1221 (1975).
- (30) (a) R. G. Beiles and E. M. Beiles, *Zh. Neorg. Khim.*, **12**, 884 (1967); (b) P. C. H. Mitchell, *J. Chem. Soc.*, **4**, 146 (1969); (c) R. L. Dutta and B. Chatterjee, *J. Indian Chem. Soc.*, **46**, 228 (1969); (d) M. K. Alyariya and M. K. Kasymov, *Zh. Neorg. Khim.*, **15**, 3015 (1970).
- (31) T. E. Dorsett and R. A. Walton, *J. Organomet. Chem.*, **114**, 127 (1976).
- (32) A. Nieuwpoort and J. J. Steggerda, *Recl. Trav. Chim. Pays-Bas*, **95**, 294 (1976).
- (33) (a) J. N. Smith and T. M. Brown, *Inorg. Chem.*, **11**, 2697 (1972); (b) D. W. Smith, *J. Chem. Soc. A*, 1024 (1971).
- (34) A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, New York, N.Y., 1968, Chapter 8.
- (35) Cf. ref 1b and 1c.
- (36) Nonrigidity would give one sharp methyl resonance; but as noted by mixed-ligand studies,^{16,37} resolution of the methyl signals does exist in these species when nonequivalent environments exist.
- (37) R. D. Archer and C. J. Donahue, *J. Am. Chem. Soc.*, **99**, 269 (1977).
- (38) B. R. McGarvey, *Inorg. Chem.*, **5**, 476 (1966).

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Chemistry of Molybdenum and Tungsten. 10.¹ Oxotungsten(V) and Oxotungsten(IV) Complexes of Diphosphine and Diarsine Ligands

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The reaction of oxotrichlorobis(tetrahydrofuran)tungsten(V) [$WOCl_3(THF)_2$] with bidentate ligands [L-L = $Ph_2PCH_2CH_2PPh_2$ (dpe), $o-C_6H_4(PPh_2)_2$ (pp), $cis-Ph_2PCH=CHPPh_2$ (VPP), $cis-Ph_2AsCH=CHAsPh_2$ (VAA), $Me_2PCH_2CH_2CH_2PMe_2$ (dmp), $Me_2PCH_2CH_2CH_2AsMe_2$ (dmpa), $Me_2AsCH_2CH_2CH_2AsMe_2$ (dma), $o-C_6H_4(PMe_2)_2$ (mpp), $o-C_6H_4(AsMe_2)_2$ (das), $o-C_6H_4(AsMe_2)(SbMe_2)$ (stars)] has led to the isolation of [$WOCl_3(L-L)$] complexes. The phenyl-substituted arsines [L-L = $Ph_2AsCH_2CH_2AsPh_2$ (dae), $Ph_2PCH_2CH_2AsPh_2$ (ape), and $o-C_6H_4(AsPh_2)_2$ (aa)] react with [$WOCl_3(THF)_2$] to produce blue, diamagnetic powders " $W_2O_4Cl_4(L-L)$ " which contain both terminal $W=O$ and bridging $W-O-W$ moieties. The possible nature of these products is discussed. Reactions of [$WOCl_3(THF)_2$] with PPh_3 and $PMePh_2(L)$ yield [$WOCl_3L_2$], while $P(C_6H_{11})_3$ produces $\{WOCl_3[P(C_6H_{11})_3]THF\}$. Bis(diphenylphosphino)methane (dpm) and [$MOCl_3(THF)_2$] ($M = Mo, W$) produce the novel [$MOCl_2(dpm)_2$]⁺[$MOCl_4$]⁻, containing five-coordinate trigonal-bipyramidal cations and monodentate dpm. The complexes have been characterized by the use of IR, electronic absorption and EPR spectroscopy. The EPR spectra suggest that the [$WOCl_3(L-L)$] species have a *fac* structure and that the [$WOCl_3L_2$] are the *mer* isomers. Refluxing the [$WOCl_3(L-L)$] (L-L = dpe, pp, VPP) with excess L-L and $NaBPh_4$ in ethanol resulted in reduction to [$WOCl(L-L)_2$]BPh₄, which have trans structures on the basis of their IR and ³¹P NMR spectra.

The preparation and properties of a range of oxomolybdenum(V) complexes of mono-³ and bidentate^{1,4-7} group 5B donor ligands have been reported. In previous parts of this series, we have described systematic studies on alkyl-¹ and aryl-substituted⁴ bidentate complexes [$MoOCl_3(L-L)$] and their reduction to oxomolybdenum(IV) [$MoOCl(L-L)_2$]⁷. In marked contrast no oxotungsten(V) complexes of group 5B donor ligands have been reported; indeed few complexes of the types [$WOCl_3L_2$] or [$WOCl_3(L-L)$] are known at all — examples are L-L = bipyridyl, $Et_4P_2S_2$; L = THF, MeCN, pyridine.⁸⁻¹¹ Butcher et al.¹² obtained [$W^{IV}OCl_2(PR_3)_3$] [$R_3 = Me_2Ph, MePh_2, Et_2Ph$] by reaction of WCl_6 , $WOCl_4$, or [NEt_4] $[WCl_6]$ with the phosphines in wet ethanol. Here we report on a systematic study of the reaction of [$WOCl_3(THF)_2$] with a range of monodentate (L) and bidentate (L-L) group 5B donor ligands, which have resulted in [$WOCl_3L_2$] and [$WOCl_3(L-L)$] complexes, and the reduction of several of the latter to [$WOCl(L-L)_2$]BPh₄.

Experimental Section

Tetrahydrofuran, *n*-pentane, toluene, and cyclohexane were dried by distillation from sodium benzophenone ketyl, dichloromethane was dried over molecular sieves, and absolute ethanol was dried by distillation from magnesium ethoxide. All preparations were conducted under a dry nitrogen atmosphere using standard Schlenk tube and drybox techniques. Physical measurements were made as described previously.⁴ EPR spectra were obtained on a Varian E9 EPR spectrometer using the dual cavity mode and were run in the X-band

(~9.3 GHz) in dichloromethane solution at various temperatures +35 to -160 °C. The ligands were prepared by literature methods^{1,4} except for *o*-phenylenebis(dimethylphosphine), the preparation of which will be described elsewhere.

Oxotrichlorobis(tetrahydrofuran)tungsten(V), [$WOCl_3(THF)_2$]. Tungsten hexachloride (RIC, Kirby and Co., Liverpool) (25 g) was treated with cyclohexane (100 cm³) and THF (50 cm³) and the mixture stirred. After 30–60 min an exothermic reaction developed and a turbid dark green solution formed. The mixture was stirred for a further 4 h and then filtered. The blue solid was rinsed with cyclohexane (~8 × 5 cm³) until the washings were no longer green and then with *n*-pentane (10 cm³) and dried in vacuo. The product was sealed in small ampoules (~1–1.5 g/ampoule) under nitrogen. The product will keep for about 4 weeks, but then decomposition sets in yielding a blue oil.

Oxotrichloro(*o*-phenylenebis(diphenylphosphine))tungsten(V), [$WOCl_3(pp)$]. [$WOCl_3(THF)_2$] (0.91 g, 2.0 mmol) was suspended in toluene (40 cm³), pp (0.9 g, 2.0 mmol) in dichloromethane (20 cm³) added, and the mixture stirred for 18 h. *n*-Pentane (30 cm³) was added and the mixture stirred for a further 1 h. The greenish solid was filtered off, rinsed with 1:1 toluene:CH₂Cl₂ (10 cm³) and *n*-pentane (2 × 10 cm³), and dried in vacuo (yield 80%).

The same general method was used to prepare the other complexes, with the exceptions noted below.

Oxotrichloro(*cis*-1,2-bis(diphenylarsino)ethylene)tungsten(V), [$WOCl_3(VAA)$]. The ligand (0.95 g, 2.0 mmol) was dried at 60 °C (10⁻¹ Torr) for 1 h, dissolved in dichloromethane (20 cm³), and added to a suspension of [$WOCl_3(THF)_2$] (0.91 g, 2.0 mmol) in toluene (40 cm³). After 24 h of stirring, *n*-pentane (20 cm³) was added, resulting in the precipitation of a sticky green solid. The solvent was decanted