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Preparation and Spectral and Electrochemical Characterization of the Tetrakis Eight-Coordinate Molybdenum(IV) and Tungsten(IV) Complexes Containing *tert*-Butyl- and 2-Hydroxy-, 2-Mercapto-, and 2-(Hydroseleno)-Substituted Pyridine and Pyrimidine Ligands

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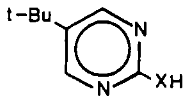
An attempt was made to prepare two series of neutral tetrakis eight-coordinate tungsten(IV) complexes containing the 5-*tert*-butyl-2-chalcopyrimidinato ligands and the 4-*tert*-butyl-2-chalcopyridinato ligands, where 2-chalco = O, S, and Se. Four of the six complexes were isolated and characterized. Two out of three tetrakis eight-coordinate molybdenum(IV) complexes of the 5-*tert*-butyl-2-chalcopyrimidinato ligands have also been prepared. In general, the tungsten(IV) complexes of a given ligand are more stable than the corresponding molybdenum(IV) complexes, the pyrimidinato complexes of a given metal and donor atom are more stable than the corresponding pyridinato complexes, and the 2-mercapto and 2-(hydroseleno) complexes of a given metal and ring system are more stable than the corresponding 2-hydroxy complexes. The ^{1}H NMR and ^{13}C NMR spectra of these complexes have been recorded. Trends in the δ values are noted and discussed. The visible spectrum of these complexes is dominated by an intense ($\epsilon > 10^4$) set of overlapping bands characterized as metal-to-ligand charge-transfer transitions. The contour of these bands is similar in each case, and λ_{max} for these complexes shifts to lower energy when Mo is replaced with W, when the oxygen donor atom is replaced with sulfur and the sulfur donor atom is replaced with selenium, and when the pyridinato ring is replaced with the pyriminidinato ring. Cyclic voltammetric studies of the tungsten(IV) complexes in DMF reveal a quasi-reversible to reversible one-electron oxidation wave, while examination of one of the molybdenum(IV) complexes reveals both a one-electron oxidation and a one-electron reduction wave. The $E_{1/2}$ values for the three tungsten(IV) pyrimidinato complexes span a range of +0.30 to +0.21 V vs SSCE. These values decrease on going from the 2-hydroxy to the 2-mercapto to the 2-(hydroseleno) complexes. The corresponding molybdenum(IV) complexes are more difficult to oxidize. The tetrakis(4-*tert*-butyl-2-mercaptopyridinato)tungsten(IV) complex is more easily oxidized than the corresponding pyrimidinato complex.

Introduction

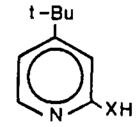
The reports of the preparation and structure determination of the tetrakis(2-mercaptopyrimidinato)tungsten(IV) complex[1] and the tetrakis(2-mercaptopyrimidinato)molybdenum(IV) complex,[2] coupled with our general interest in the chemistry of early-transition-metal eight-coordinate complexes, led us to attempt the preparation of two three-member series of tetrakis eight-coordinate tungsten(IV) complexes and one three-member series of tetrakis eight-coordinate molybdenum(IV) complexes. Preparation of both a series of tungsten(IV) complexes and a series of molybdenum(IV) complexes was attempted from the three ligands 5-*tert*-butyl-2-chalcopyrimidine, where 2-chalco = O, S, and Se, **1a–c**. In addition, a second series of tungsten(IV) complexes was sought from the three ligands 4-*tert*-butyl-2-chalcopyridine, where 2-chalco = O, S, and Se, **2a–c**. Table I summarizes the ligand abbreviations we have adopted. Herein, we report the preparation and characterization of six of the nine targeted complexes. Three of the complexes, W(bhp)$_4$, W(bsp)$_4$, and Mo(bhpm)$_4$, were too air-sensitive to be isolated.



1a, X = O

2a, X = S

3a, X = Se



2a, X = O

2b, X = S

2c, X = Se

We were particularly interested in the relative stability of these eight-coordinate complexes as a guide to the preparation and separation of mixed-ligand eight-coordinate complexes. In fact, we have recently employed one of these ligands, 5-*tert*-butyl-2-mercaptopyrimidine, in a mixed-ligand study.[3] We were also interested in exploring how the stability of these complexes varies as a function of donor atom (O vs S vs Se), metal center (Mo vs W), and heterocyclic ring (pyrimidine vs pyridine).

Table I. Ligand Abbreviations

bhp$^-$ = 4-*tert*-butyl-2-hydroxypyridinato
bhpm$^-$ = 5-*tert*-butyl-2-hydroxypyrimidinato
bmp$^-$ = 4-*tert*-butyl-2-mercaptopyridinato
bmpm$^-$ 5-*tert*-butyl-2-mercaptopyrimidinato
bsp$^-$ = 4-*tert*-butyl-2-(hydroseleno)pyridinato
bspm$^-$ = 5-*tert*-butyl-2-(hydroseleno)pyrimidinato

The ability of 2-hydroxy- and 2-mercapto-substituted pyridine and pyrimidine to stabilize transition-metal complexes is well documented. Much of the early work involving these ligands focused on their ambidentate character. The discovery,[4] in the late 1970s, that these ligands could stabilize metal–metal-bonded complexes brought about a renewed interest in these ligands in the past decade. For 2-mercaptopyridine, five distinct modes of coordination have been delineated to date,[5] including 2(1*H*)-pyridinethione as a monodentate ligand that coordinates through the sulfur atom, the conjugate anion pyridine-2-thionate as a monodentate ligand that also coordinates through the sulfur atom, the anion as a bidentate ligand, and the anion as both a doubly and triply bridging ligand. In marked contrast to the attention afforded the 2-hydroxy- and 2-mercapto-substituted pyridine and pyrimidine ligands, we believe this study is the first time 2-(hydroseleno)pyridine and 2-(hydroseleno)pyrimidine have been utilized as ligands.

Experimental Section

N,*N*-Dimethylaniline was vacuum-distilled prior to use and sodium hydrogen sulfide hydrate was dried in vacuo at room temperature for 48 h prior to use. The rest of the solvents and reagents were used without further purification.

Precursors and Ligands. ***tert*-Butylmalononitrile** was prepared by the method of Boldt et al.[6]

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(1) Cotton, F. A.; Ilsley, W. H. *Inorg. Chem.* **1981**, *20*, 614.

(2) Latham, I. A.; Leigh, G. J.; Pickett, C. J.; Huttner, G.; Jibrill, I.; Zubieta, J. *J. Chem. Soc., Dalton Trans.* **1986**, 1181.

(3) Donahue, C. J.; Kosinski, E. C.; Martin, V. A. *Inorg. Chem.* **1985**, *24*, 1997.

(4) Cotton, F. A.; Gage, L. D. *Inorg. Chem.* **1979**, *18*, 1716.

(5) Deeming, A. J.; Hardcastle, K. I.; Meah, M. N.; Bates, P. A.; Dawes, H. M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1988**, 227.

(6) Boldt, P.; Militzer, H.; Thielecke, W.; Schulz, L. *Justus Liebigs Ann. Chem.* **1968**, *718*, 101.

***tert*-Butylmalonodialdehyde** was prepared by the method of Reichardt et al.[7] We have preciously published the ^{1}H NMR spectra of these two precursors.[3]

5-*tert*-Butyl-2-hydroxypyrimidine (1a) was prepared by following the general procedure of Hunt et al.[8] To a warm, stirred solution of urea (1.4 g, 23.3 mmol) in 4.7 mL of concentrated HCl and 15 mL of absolute ethanol was added *tert*-butylmalonodialdehyde (3.1 g, 29.2 mmol). After being stirred at 40–50 °C for 1 h, the solution was cooled to 0 °C whereupon the precipitated 5-*tert*-butyl-2-hydroxypyrimidine hydrochloride (2.23 g) was collected by filtration. Addition of ether (15 mL) yielded a second crop of crystals (0.85 g). The combined crops were dissolved in a minimum amount of an aqueous Na_2CO_3 solution (6 g/100 mL), and the solution was acidified to pH 5 with 5 N sulfuric acid and evaporated to dryness. Sublimation of the residue at 150 °C yielded pure 5-*tert*-butyl-2-hydroxypyrimidine. Yield: 2.41 g, 68%. ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.35 (s, 9 H, *t*-Bu), 8.73 (s, 2 H, H_4 and H_6), 12.43 (s, 1 H, OH).

Anal. Calcd for $C_8H_{12}N_2O$: C, 63.13; H, 7.95; N, 18.41. Found: C, 62.73; H, 7.71; N, 18.63.

5-*tert*-Butyl-2-mercaptopyrimidine (1b) was prepared by the method of Hunt et al.[8] We have previously reported the synthesis of this compound.[3]

5-*tert*-Butyl-2-(hydroseleno)pyrimidine Hydrochloride (1c). In an argon-filled glovebag, selenourea (4.71 g, 38.3 mmol) was transferred to a 200-mL Schlenk flask and stoppered with a rubber septum. Outside of the glovebag, but under a blanket of argon, was added rapidly, in succession, 20 mL of degassed absolute ethanol, 5 mL of concentrated HCl, and *tert*-butylmalonodialdehyde (5 g, 39.0 mmol). After the reaction mixture was degassed, it was heated to reflux for 5 min. The hot mixture was stirred and allowed to cool gradually back to room temperature over a 30-min period. The ethanol was filtered off by using a cannula. The bright orange product was washed with 20 mL of degassed ethanol, the ethanol removed by using the cannula, and the product dried in vacuo overnight at room temperature. Attempts to recover a second crop of pure product from the filtrate were unsuccessful. Yield: 2.90 g, 30.0%.

Anal. Calcd for $C_8H_{12}N_2Se{\cdot}HCl$: C, 38.19; H, 5.21; N, 11.13. Found: C, 38.43; H, 5.17; N, 11.14.

2-Amino-4-*tert*-butylpyridine was prepared by the Chichibabin reaction.[9] The product was recrystallized from hexanes as plates. Yield: 29.5%. Mp: 75–78 °C. ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.30 (s, 9 H, *t*-Bu), 4.71 (s, 2 H, NH_2), 6.65 (d, 1 H, J = 2 Hz, H_3), 6.83 (dd, 1 H, J = 6 Hz, J' = 2 Hz, H_5), 8.20 (d, 1 H, J = 6 Hz, H_6).

2-Bromo-4-*tert*-butylpyridine was prepared by the method of Allen and Thirtle.[10] Yield: 65%. ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.37 (s, 9 H, *t*-Bu), 7.50 (dd, 1 H, J = 6 Hz, J' = 2 Hz, H_5), 7.70 (d, 1 H, J = 2 Hz, H_3), 8.52 (d, 1 H, J = 6 Hz, H_6).

4-*tert*-Butyl-2-hydroxypyridine (2a) was prepared by the method of Seide.[11] A solution of 2-amino-4-*tert*-butylpyridine (5.00 g, 0.033 mol) in 70 mL of 4 N H_2SO_4 was chilled to 0 °C in an ice bath. To this solution was added dropwise, with stirring, over a 20-min period, a chilled solution of sodium nitrite (3.11 g, 0.045 mol) in water (40 mL). After the ice bath was removed and the mixture was allowed to warm to room temperature, the solution was neutralized to pH 7 with 8 N NaOH, whereupon a light brown precipitate formed. The product was collected by filtration and dried in vacuo to yield 3.74 g of crude product. The crude product was recrystallized from a 1:1 v/v chloroform/hexanes mixture to yield a white powder. Yield: 2.57 g, 51%. Mp: 140–143 °C. ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.28 (s, 9 H, *t*-Bu), 6.51 (dd, 1 H, J = 7 Hz, J' = 2 Hz, H_5), 6.73 (d, 1 H, J = 2 Hz, H_3), 7.51 (d, 1 H, J = 7 Hz, H_6), 13.67 (s, 1 H, OH).

Anal. Calcd for $C_9H_{13}NO$: C, 71.49; H, 8.67; N, 9.26. Found: C, 71.35; H, 8.63; N, 9.44.

4-*tert*-Butyl-2-mercaptopyridine (2b) was prepared by the procedure of Thirtle.[12] To a 100-mL two-neck round-bottom flask equipped with a stoppered dropping funnel and a condenser fitted with a drying tube was added NaSH (16.8 g, 0.30 mol) and 50 mL of 1,2-propanediol. The mixture was brought to reflux and 2-bromo-4-*tert*-butylpyridine (21.7 g, 0.10 mol) was added dropwise at a rate that boiling was maintained. The mixture was refluxed an additional 20 h. Upon cooling, the solvent was stripped off by vacuum-pump-assisted rotary evaporation and heating. The off-white residue was taken up in 100 mL of distilled water. The aqueous solution was acidified with glacial acetic acid until a yellow product precipitated. The product was recovered by filtration, washed with water, and dried in vacuo. The product was recrystallized from 1:1 v/v ethyl acetate/hexanes. Yield: 12.5 g, 74%. Mp: 133–135 °C. ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.32 (s, 9 H, *t*-Bu), 7.03 (dd, 1 H, J = 6 Hz, J' = 2 Hz, H_5), 7.68 (d, 1 H, J = 2 Hz, H_3), 7.81 (d, 1 H, J = 6 Hz, H_6), 14.33 (s, 1 H, SH).

Anal. Calcd for $C_9H_{13}NS$: C, 64.63; H, 7.83; N, 8.37; S, 19.17. Found: C, 64.71; H, 7.73; N, 8.40; S, 19.31.

4-*tert*-Butyl-2-(hydroseleno)pyridine (2c) was prepared by using the procedure outlined by Thirtle[12] and as described above as for 4-*tert*-butyl-2-mercaptopyridine. The sodium hydrogen selenide was generated in situ by following the procedure of Klayman and Griffin.[13] The entire procedure was performed in a well-ventilated hood. All the solvents were degassed prior to use, and all manipulations were performed under nitrogen. Yield: 71%. Mp: 139–142 °C. ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.32 (s, 9 H, *t*-Bu), 7.20 (dd, 1 H, J = 6 Hz, J' = 2 Hz, H_5), 7.92 (d, 1 H, J = 6 Hz, H_6), 8.11 (d, 1 H, J = 2 Hz, H_3), 14.83 (s, 1 H, SeH).

Anal. Calcd for $C_9H_{13}NSe$: C, 50.47; H, 6.12; N, 6.54. Found: C, 50.23; H, 6.13; N, 6.39.

Bis(acetonitrile)tetrabromotungsten(IV) was made by the method of King and McCarley.[14]

Bis(acetonitrile)tetrachloromolybdenum(IV) was prepared by method of Dilworth and Richards.[15]

Molybdenum(IV) and Tungsten(IV) Eight-Coordinate Complexes. The following two general procedures were used to prepare the molybdenum(IV) and tungsten(IV) complexes.

Method 1. To a 200-mL Schlenk flask was added tungsten hexacarbonyl (or molybdenum hexacarbonyl) and the parent ligand in a 1:5 mole ratio. After addition of a stir bar and 50–100 mL of mesitylene a condenser equipped with an adapter was added to the flask and the apparatus 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. This procedure also removed any unreacted hexacarbonyl.

Method 2. To a 200-mL Schlenk flask was added the parent ligand and 1 equiv of sodium methoxide in methanol. Once the sodium salt of the ligand was completely dissolved the methanol was evaporated. To the flask was added enough $WBr_4(CH_3CN)_2)$ (or $MoCl_4(CH_3CN)_2)$ to give a 1:4 mole ratio of metal halide to ligand salt. A rubber septum was added to the flask, and the flask was evacuated and back-filled with nitrogen. Degassed methylene chloride (50 mL) was transferred to the flask via a cannula. The reaction usually occurred immediately. The mixture was stirred for 2 h at room temperature, the solution filtered, and the filtrate evaporated to dryness.

Tetrakis(5-*tert*-butyl-2-hydroxypyrimidinato)tungsten(IV) was prepared by method 1. The complex partially decomposed in air when in contact with silica gel. The complex was purified by column chromatography under a nitrogen atmosphere. A short column (4 cm in diameter × 10 cm in length) was packed with a slurry of silica gel and methylene chloride. The product mixture was loaded on as a methylene chloride solution and the product (the first band) eluted with 10:1 v/v methylene chloride/acetone. The eluent was taken to dryness and then taken up in a minimum of methylene chloride. Hexane was slowly added to this solution, causing the reddish brown product to precipitate. The solid was collected by filtration under N_2 and dried in vacuo at room temperature for 24 h.

Anal. Calcd for $W(C_8H_{11}N_2O)_4$: C, 48.74; H, 5.62; H, 14.21. Found: C, 48.70; H, 5.74; N, 13.69.

Tetrakis(5-*tert*-butyl-2-mercaptopyrimidinato)tungsten(IV) was prepared by method 1. The complex was purified by preparative TLC using silica gel plates and 20:1 v/v chloroform/acetone as the eluent. The purified complex was recrystallized from hexanes to yield a purple powder, which was dried overnight in vacuo.

Anal. Calcd for $W(C_8H_{11}N_2S)_4$: 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.

Tetrakis(5-*tert*-butyl-2-(hydroseleno)pyrimidinato)tungsten(IV) was prepared by method 2. Since 5-*tert*-butyl-2-(hydroseleno)pyrimidine was best handled as the hydrochloride, 2 equiv of sodium methoxide was used to form the sodium salt. The crude product was purified by preparative TLC using silica gel plates and 20:1 v/v chloroform/acetone as the eluent. The purified blue complex was dried 24 h in vacuo at room temperature.

Anal. Calcd for $W(C_8H_{11}N_2Se)_4$: C, 36.99; H, 4.26; N, 10.77. Found: C, 36.34; H, 4.12; N, 10.09.

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(7) Reichardt, C.; Wurthwein, E. U. *Chem. Ber.* **1974**, *107*, 3454.

(8) Hunt, R. R.; McOmie, J. F. W.; Sayer, E. R. *J. Chem. Soc.* **1959**, 525.

(9) (a) Chichibabin, C.; Seide, O. *J. Russ. Phys.-Chem. Soc.* **1914**, *46*, 1216. (b) Leffler, M. T. *Org. React.* **1942**, *1*, 91.

(10) Allen, C. F. H., Thirtle, J. R. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 136.

(11) Seide, O. *Ber. Dtsch. Chem. Ges.* **1924**, *57*, 493.

(12) Thirtle, J. R. *J. Am. Chem. Soc.* **1946**, *68*, 342.

(13) Klayman, D. L.; Griffin, T. S. *J. Am. Chem. Soc.* **1973**, *95*, 197.

(14) King, M. A. S.; McCarley, R. E. *Inorg. Chem.* **1973**, *12*, 1972.

(15) Dilworth, J. R.; Richards, R. L. *Inorg. Synth.* **1980**, *20*, 119.

Tetrakis(5-*tert*-butyl-2-hydroxypyrimidinato)molybdenum(IV) was prepared by method 2 to give a purplish brown residue. This complex was very air-sensitive. All attempts to isolate the pure complex by using inert-atmosphere techniques have failed thus far.

Tetrakis(5-*tert*-butyl-2-mercaptopyrimidinato)molybdenum(IV) was prepared by method 1. However, an argon atmosphere was found to be necessary in place of a nitrogen atmosphere to prevent decomposition of the complex during the reaction. The crude product was purified by preparative TLC using silica gel plates and 20:1 v/v chloroform/acetone as the eluent. The purified brown product was dried overnight in vacuo at room temperature.

Anal. Calcd for $Mo(C_8H_{11}N_2S)_4$: C, 50.25; H, 5.80; N, 14.65; S, 16.77. Found: C, 49.32; H, 5.65; N, 13.73; S, 15.80.

Tetrakis(5-*tert*-butyl-2-(hydroseleno)pyrimidinato)molybdenum(IV) was prepared by method 2. Since 5-*tert*-butyl-2-(hydroseleno)pyrimidine was best handled as the hydrochloride, 2 equiv of sodium methoxide was used to form the sodium salt. The crude product was purified by preparative TLC using silica gel plates and 20:1 v/v chloroform/acetone as the eluent. The purified brownish purple complex was dried in vacuo overnight.

Anal. Calcd for $Mo(C_8H_{11}N_2Se)_4$: C, 40.35; H, 4.66; N, 11.76. Found: C, 40.72; H, 4.84; N, 11.69.

Tetrakis(4-*tert*-butyl-2-hydroxypyridinato)tungsten(IV) was prepared by method 1 to give a reddish brown residue. All attempts to purify this very air-sensitive complex have failed to date.

Tetrakis(4-*tert*-butyl-2-mercaptopyridinato)tungsten(IV) was prepared by method 1. Upon slow cooling of the mesitylene solution, purple crystals of the product were recovered. The crystals were collected by filtration, washed with hexanes, and dried in vacuo. Examination of a chloroform solution of this complex by TLC revealed only a single species, which decomposed as the plate was developed. Anal. Calcd for $W(C_9H_{12}NS)_4\cdot{}^1/_2C_9H_{12}$: C, 53.51; H, 5.99; N, 6.16; S, 14.11. Found: C, 53.62; H, 6.19; N, 5.86; S, 13.62.

Tetrakis(4-*tert*-butyl-2-(hydroseleno)pyridinato)tungsten(IV) was prepared by method 2. All attempts to isolate this very air-sensitive complex by using inert-atmosphere techniques have failed thus far.

Physical Studies. Electronic spectra were recorded on a Cary 118 spectrophotometer using a pair of matching 1.000-cm quartz cells. The 60-MHz ^1H NMR spectra were measured on a Varian T-60A spectrometer, and the 90 MHz ^{13}C NMR spectra were recorded with a Brucher FT spectrometer. All spectra are referenced versus TMS. Analyses were performed by Spang Microanalytical Laboratories and Gailbraith Laboratories.

Electrochemical experiments were carried out with a Princeton Applied Research Model 173 potentiostat/galvanostat equipped with a PAR Model 179 digital coulometer and Model 175 universal programmer. All electrochemical measurements were made in Omnisolv (MCB) *N*,*N*-dimethylformamide (DMF) that was used without further purification. The supporting electrolyte, tetraethylammonium perchlorate (TEAP), was purified chromatographically.[16] The solutions were deoxygenated with ultrahigh-purity N_2 that had been passed through a chromous perchloric acid scrubber, a $CaSO_4$ drying column, and a DMF-TEAP solution. A three-electrode cell with a saturated NaCl calomel reference electrode (SSCE), at Pt-wire counter electrode, and Brinkmann Model EA290 hanging mercury drop (HMDE) or a Tacussel Pt-disk working electrode was used for the cyclic voltammetry experiments. The reference electrode was separated from the sample chamber by two salt bridges. The bridge adjacent to the reference electrode contained a 0.13 M TEAP aqueous solution, and the one adjacent to the sample chamber contained a 0.1 M TEAP in DMF solution.

Results

Synthesis and Relative Stability of the Tetrakis Eight-Coordinate Complexes. The title complexes have been synthesized by either oxidative decarbonylation of the molybdenum or tungsten hexacarbonyl at an elevated temperature or by the reaction of the sodium salt of the ligand with the bis(acetonitrile)tetrahalometal(IV) complex at room temperature.

Table II summarizes the colors, relative stabilities, and R_f values for the title complexes.

Table II. R_f Values, Colors, and Relative Stabilities of the Tetrakis(5-*tert*-butyl-2-chalcopyrimidinato)tungsten(IV) and -molybdenum(IV) Complexes and the Tetrakis(4-*tert*-butyl-2-chalcopyridinato)tungsten(IV) Complexes

complex	R_f[a]	color	stability
$Mo(bhpm)_4$		brown	very air-sensitive
$Mo(bmpm)_4$	0.84	reddish brown	air-stable
$Mo(bspm)_4$	0.86	brownish purple	air-stable
$W(bhpm)_4$	0.14	reddish brown	moderately air-stable; air-sensitive in solution, partially decomposed on silica gel
$W(bmpm)_4$	0.83	purple	air-stable
$W(bspm)_4$	0.85	blue	air-stable
$W(bhp)_4$		brown	very air-sensitive
$W(bmp)_4$		purple	moderately air-stable; air-sensitive in solution, decomposed on contact with silica gel
$W(bsp)_4$		purple	air-sensitive

[a] E. Merck "Silica Gel 60" TLC Plates, 0.25-mm thickness, were used; eluent was 40:1 v/v chloroform/acetone.

Table III. 60-MHz ^1H NMR Spectral Data for the Tetrakis(5-*tert*-butyl-2-chalcopyrimidinato)molybdenum(IV) and -tungsten(IV) Complexes in $CDCl_3$ at 35 °C

complex	*t*-Bu	H_4	H_6
$Mo(bmpm)_4$	1.34 s (9)	8.40 d (1)	9.42 d (1)
$Mo(bspm)_4$	1.35 s (9)	8.33 d (1)	10.00 d (1)
$W(bhpm)_4$	1.32 s (9)	8.17 d (1)	8.31 d (1)
$W(bmpm)_4$	1.33 s (9)	8.00 d (1)	9.10 d (1)
$W(bspm)_4$	1.35 s (9)	8.08 d (1)	9.97 d (1)

Table IV. 90-MHz ^{13}C NMR Spectral Data for the Tetrakis(5-*tert*-butyl-2-chalcopyrimidinato)molybdenum(IV) and -tungsten(IV) Complexes in $CDCl_3$

	Mo(IV) complexes		W(IV) complexes		
	S	Se	O	S	Se
$-C(CH_3)_3$	30.52	30.45	30.74	30.41	30.23
$-C(CH_3)_3$	32.92	33.00	32.71	33.03	33.09
C-2	167.40	163.43	154.70	165.42	161.92
C-4	157.15	156.78	152.71	156.18	155.85
C-5	138.16	138.62	134.97	137.91	138.11
C-6	160.03	164.30	158.58	160.17	164.61

^1H NMR and ^{13}C NMR Spectra. With the exception of the $Mo(bhpm)_4$ complex, the 60-MHz ^1H NMR spectrum and the 90-MHz ^{13}C NMR spectrum of the tetrakis 5-*tert*-butyl-2-chalcopyrimidinato eight-coordinate complexes have been obtained. These results are summarized in Tables III and IV. The ^1H NMR spectrum of each of these complexes exhibits a single, sharp *tert*-butyl signal at 1.34 ± 0.02 ppm along with a pair of doublets of equal intensity, which are assigned to the H_4 and H_6 hydrogens on the pyrimidine ring. While the chemical shift value of the H_4 hydrogen varies only slightly in these complexes, 8.20 ± 0.20 ppm, the chemical shift values of the H_6 hydrogen span a range of 8.31 to 10.00 ppm. The δ value for the H_6 hydrogen varies with the chalcogen atom in the 2-position of the pyrimidinato ring. This doublet is shifted further downfield as oxygen is replaced with sulfur and sulfur is replaced with selenium. For the pair of mercapto complexes, $Mo(bmpm)_4$ and $W(bmpm)_4$, and for the pair of hydroseleno complexes, $Mo(bspm)_4$ and $W(bspm)_4$, the separation between the H_4 and H_6 doublets remains nearly constant at 1.05 ± 0.05 and 1.78 ± 0.11 ppm, respectively. On the other hand, the separation between the H_4 and H_6 doublets in the $W(bhpm)_4$ complex is only 0.14 ppm.

The 90-MHz ^{13}C NMR spectrum of each of the five pyrimidinato complexes consists of six lines. For each complex the four sets of *tert*-butyl methyl carbons and *tert*-butyl quaternary carbons give rise to single peaks at 30.50 ± 0.25 and 32.90 ± 0.20 ppm, respectively. Of the four pyrimidine ring carbons two are quaternary, C-2 and C-5, and their signals can be readily distinguished from the other two ring carbons, C-4 and C-6. The signal of one of the two quaternary carbons is considerably upfield of the rest of the aromatic carbon signals and is assigned to the C-5 carbon.

Electronic Absorption Spectra. The electronic absorption spectra of the five isolable 5-*tert*-butyl-2-chalcopyrimidinato complexes and the $W(bmp)_4$ complex are all dominated by an

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[16] Handy, R. F. Ph.D. Thesis, Wayne State University, 1972.

Table V. Electronic Absorption Spectral Data for the Isolable Tetrakis(5-*tert*-butyl-2-chalcopyrimidinato)molybdenum(IV) and -tungsten(IV) Complexes in $CHCl_3$[a]

$Mo(bmpm)_4$	$Mo(bspm)_4$	$W(bhpm)_4$	$W(bmpm)_4$	$W(bspm)_4$
19 700 (1.84)	18 500 (1.79)	19 700 (2.88)	17 600 (3.56)	16 800 (5.15)
21 300 (sh, 1.42)	19 800 (sh, 1.37)	21 100 (sh, 2.19)	19 400 (sh, 1.96)	17 900 (sh, 3.16)

[a] The values given are in cm^{-1}; numbers in parentheses are ϵ values × 10^4 with units of M^{-1} cm^{-1}; sh = shoulder.

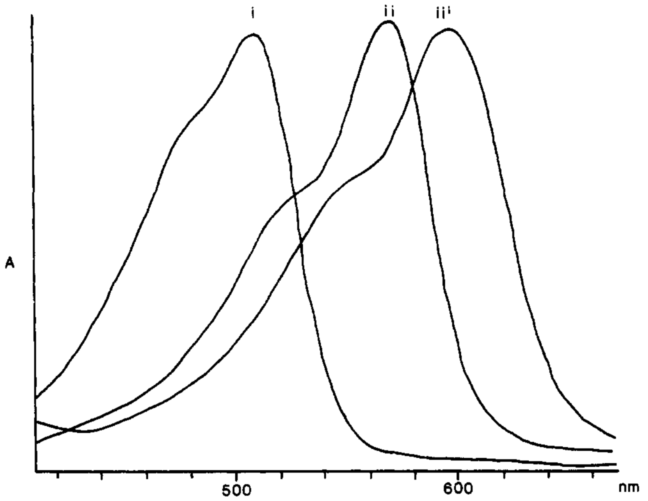


Figure 1. Visible spectra of the tetrakis(5-*tert*-butyl-2-chalcopyrimidinato)tungsten(IV) complexes in $CHCl_3$: (i) $W(bhpm)_4$; (ii) $W(bmpm)_4$; (iii) $W(bspm)_4$.

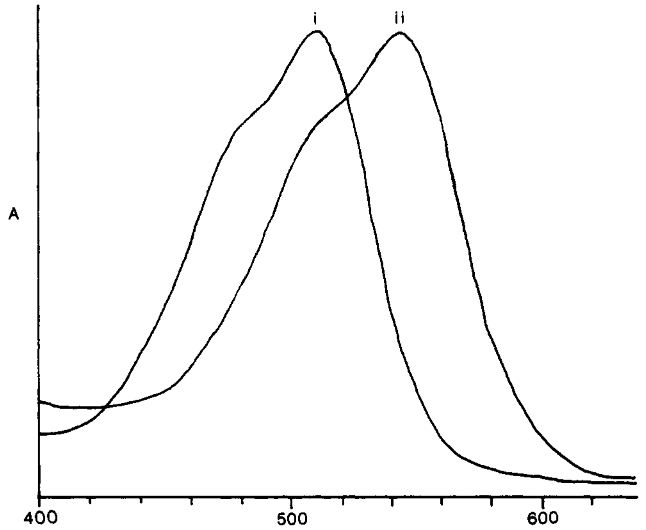


Figure 2. Visible spectra of the tetrakis(5-*tert*-butyl-2-chalcopyrimidinato)molybdenum(IV) complexes in $CHCl_3$: (i) $Mo(bmpm)_4$; (ii) $Mo(bspm)_4$.

intense ($\epsilon > 10^4$) set of overlapping bands, which fall within a region of 3000 cm^{-1}—see Table V. The contour of these bands is similar for all six of the aforementioned complexes. The spectrum of each of these complexes exhibits a shoulder that is plainly visible on the high-energy side of the stronger band.

Replacement of the oxygen donor atom with sulfur and the sulfur donor atom with selenium in the three tetrakis tungsten(IV) pyrimidinato complexes leads to a shift in the maxima of these bands to lower energy in each case—see Figure 1. Substitution of oxygen with sulfur in the tungsten(IV) pyrimidinato complex produces a larger shift, 2100 cm^{-1}, than substitution of the sulfur with selenium, which leads to a shift of 900 cm^{-1}. The same trend is observed for the pair of tetrakis molybdenum(IV) pyrimidinato complexes—see Figure 2. The $Mo(bmpm)_4$ complex has a maxima at 19 700 cm^{-1}, while the $Mo(bspm)_4$ complex has a maxima at 18 500 cm^{-1}, a difference of 1200 cm^{-1}. Relative to the maxima of the tetrakis tungsten(IV) pyrimidinato complexes, the corresponding tetrakis molybdenum(IV) pyrimidinato complexes exhibit a maxima at higher energy. The $W(bmpm)_4$ and $Mo(bmpm)_4$ complexes possess maxima different by 2100 cm^{-1}, while the $W(bspm)_4$ and $Mo(bspm)_4$ complexes possess maxima different by 1700 cm^{-1}.

Table VI. Cyclic Voltammetric Data for the Tetrakis(5-*tert*-butyl-2-chalcopyrimidinato)tungsten(IV) Complexes and the Tetrakis(4-*tert*-butyl-2-mercaptopyridinato)tungsten(IV) Complex

scan rate, V/s	$E_{1/2}$, V	ΔE_p, mV	i_{pa}/i_{pc}	$(E_p - E_p)/2$, mV	$i_{pc}/v^{1/2}$, $\mu A/(mV/s)^{1/2}$
			$W(bhpm)_4$		
0.05	0.28	163	1.28	83	0.184
0.10	0.30	136	1.27	85	0.183
1.00	0.31	159	1.17	112	0.215
			$W(bmpm)_4$		
0.05	0.28	105	1.02	77	4.29
0.10	0.28	112	1.17	79	3.42
1.00	0.29	135	1.01	101	3.13
			$W(bspm)_4$		
0.05	0.22	62	0.98	59	0.120
0.10	0.21	60	0.98	57	0.123
1.00	0.21	63	0.97	62	0.134
			$W(bmp)_4$		
0.05	−0.05	60	1.09	58	0.133
0.10	−0.05	65	0.98	59	0.145
1.00	−0.05	67	0.95	68	0.165

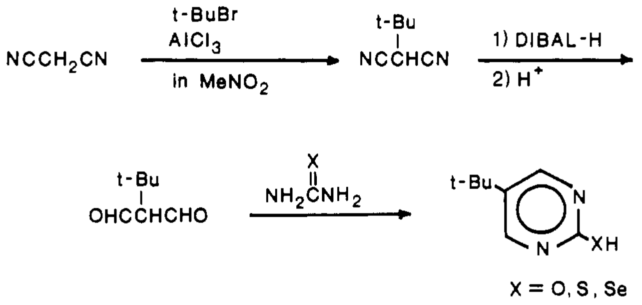
Table VII. Cyclic Voltammetric Data for the Tetrakis(5-*tert*-butyl-2-mercaptopyrimidinato)molybdenum(IV) and Tetrakis(5-*tert*-butyl-2-(hydroseleno)pyrimidinato)molybdenum(IV) Complexes

scan rate, V/s	$E_{1/2}$, V	ΔE_p, mV	i_{pa}/i_{pc}	$(E_p - E_p)/2$, mV	$i_{pc}/v^{1/2}$, $\mu A/(mV/s)^{1/2}$
			$Mo(bmpm)_4$, Anodic Wave		
0.05	0.51	67	1.02	61	0.238
0.10	0.51	68	1.01	61	0.237
1.00	0.51	77	1.02	65	0.232
			$Mo(bmpm)_4$, Cathodic Wave		
0.05	−1.09	67	0.97	58	0.196
0.10	−1.09	69	0.96	59	0.142
1.00	−1.09	84	0.95	63	0.191
			$Mo(bspm)_4$, Anodic Wave		
0.05	0.32	65	0.94	64	0.191
0.10	0.32	64	0.96	63	0.187
1.00	0.31	62	0.96	61	0.204

Where the metal center and the donor atoms are identical, but the heterocyclic ring is different, as is the case with the $W(bmp)_4$ and the $W(bmpm)_4$ complexes, the maxima of the complex possessing the pyridinato ring is observed to be at higher energy. The maxima of the $W(bmp)_4$ complex occurs at 18 900 cm^{-1}, which is 1300 cm^{-1} higher in energy than the $W(bmpm)_4$ complex.

Cyclic Voltammetric Studies. The results of the cyclic voltammetric studies on the five isolable tetrakis 5-*tert*-butyl-2-chalcopyrimidinato complexes along with the $W(bmp)_4$ complex are summarized in Tables VI and VII. For the series of three tetrakis eight-coordinate tungsten(IV) pyrimidinato complexes a one-electron oxidation wave is observed over a very narrow range. The $E_{1/2}$ values decrease from 0.30 to 0.28 to 0.21 V vs SSCE on going from the (hydroxy- to the (mercapto- to the ((hydroseleno)pyrimidinato)tungsten(IV) complex. On the basis of the ΔE_p and i_{pa}/i_{pc} values, the oxidation processes for the $W(bhpm)_4$ and $W(bmpm)_4$ complexes are appropriately described as quasi-reversible, while the same process for the $W(bspm)_4$ complex

Scheme I



is labeled reversible. No reversible or quasi-reversible cathodic waves are observed for these complexes. However, one and, in some cases, two irreversible cathodic waves are observed for each of these complexes in the range −1.55 to −1.95 V vs SSCE. Like the tungsten(IV) pyrimidinato complexes, the W(bmp)$_4$ complex exhibits a one-electron oxidation wave and no reversible or quasi-reversible reduction wave. The $E_{1/2}$ value for the anodic wave is −0.05 V vs SSCE for this complex. Substitution of the pyrimidinato ring with the pyridinato ring results in a complex that is easier to oxidize, on the basis of the comparison of $E_{1/2}$ values for the W(bmp)$_4$ complex versus the W(bmpm)$_4$ complex. The one-electron oxidation process is also much closer to being reversible for the W(bmp)$_4$ complex.

Like the tungsten(IV) complexes, the tetrakis molybdenum(IV) pyrimidinato complexes, Mo(bmpm)$_4$ and Mo(bspm)$_4$, both exhibit a one-electron oxidation wave. However, unlike the tungsten(IV) complexes, the Mo(bmpm)$_4$ complex also exhibits a reversible cathodic wave. The Mo(bspm)$_4$ complex, however, does not. Relative to the corresponding tungsten(IV) pyrimidinato complexes, the molybdenum(IV) complexes are more difficult to oxidize. The $E_{1/2}$ values for Mo(bmpm)$_4$ and Mo(bspm)$_4$ are 0.51 and 0.32 V vs SSCE compared to 0.28 and 0.21 V for the W(bmpm)$_4$ and W(bspm)$_4$ complexes. The same trend in $E_{1/2}$ values observed for the tungsten(IV) pyrimidinato complexes is also observed for the pair of molybdenum(IV) pyrimidinato complexes, Mo(bmpm)$_4$ and Mo(bspm)$_4$; the $E_{1/2}$ value for the Mo(bspm)$_4$ is less than the $E_{1/2}$ value for Mo(bmpm)$_4$, in this case by 0.19 V.

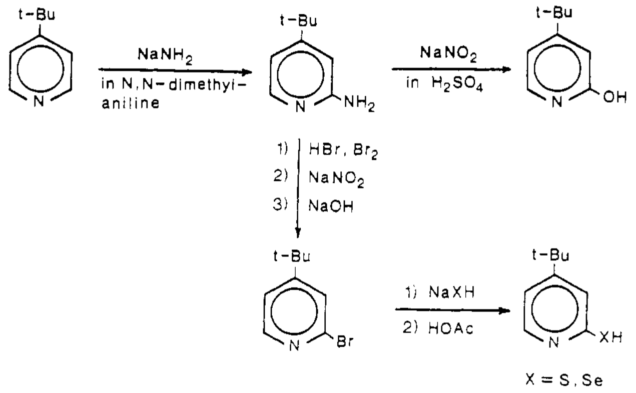
Discussion

Selection and Preparation of the 5-*tert*-Butyl-2-chalcopyrimidines and the 4-*tert*-Butyl-2-chalcopyridines. We choose to utilize the *tert*-butyl-substituted 2-chalcopyrimidines and 2-chalcopyridines for several reasons. The addition of the *tert*-butyl group to the pyrimidine or pyridine ring greatly enhances the solubility of the resulting complexes in organic solvents, thus making their purification a much easier task. The presence of the *tert*-butyl group also provides a convenient NMR handle by which to probe the stereochemistry of these complexes in solution. Finally, the presence of the *tert*-butyl group on the pyrimidine or pyridine ring simplifies the splitting pattern of the ring hydrogens.

To our knowledge none of the 5-*tert*-butyl-2-chalcopyrimidines or the 4-*tert*-butyl-2-chalcopyridines utilized in this study have been previously synthesized. The same synthetic approach is employed to prepare all three of the pyrimidine ligands (Scheme I). The 5-*tert*-butyl-2-hydroxypyrimidine is white in color, while the corresponding 2-mercapto and 2-hydroseleno ligands are yellow and orange in color, respectively.

Scheme II summarizes the synthetic procedures used to prepare the 4-*tert*-butyl-2-chalcopyridines. While both 4-*tert*-butyl-2-hydroxypyridine and 4-*tert*-butyl-2-mercaptopyridine are air-stable, the corresponding 2-(hydroseleno)pyridine is not. It appears to be readily oxidized in air, presumably to the diselenide.

Scheme II



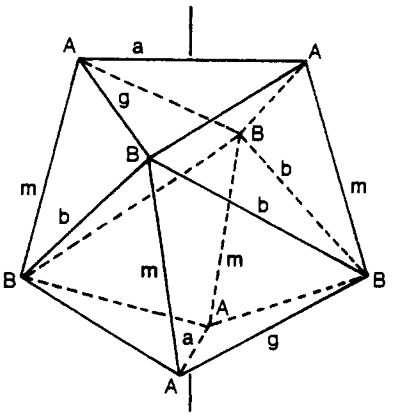


Figure 3. D_{2d} dodecahedron. The two sets of nonequivalent sites are labeled A and B. The four different edges are labeled a (2), b (4), g (8), and m (4).

2-(Hydroseleno)pyridine and 2-(Hydroseleno)pyrimidine. While the preparation and characterization of 2-(hydroseleno)pyridine[17] occurred decades ago, the preparation of 2-(hydroseleno)pyrimidine has only recently been reported.[18,19] In both reports, the preparation of 2-(hydroseleno)pyrimidine was achieved via the cyclization of a 1,1,3,3-tetraalkoxypropane with selenourea. Their yields of 38% and 25% are similar to the 30% yield we obtained for 5-*tert*-butyl-2-(hydroseleno)pyrimidine. Rye and co-workers[18] also report the mass spectrum and fragmentation pattern of 2-(hydroseleno)pyrimidine, while Shunmugan et al.[19] report its IR and Raman spectrum along with peak assignments.

As was mentioned earlier, we are unaware of any reports involving the use of 2-(hydroseleno)pyridine or 2-(hydroseleno)pyrimidine as a ligand to form a transition-metal complex. On the other hand, 2,4-bis(hydroseleno)pyrimidine has been used as a bridging ligand to form binuclear bis(η^5-methylcyclopentadienyl)titanium(III) complexes.[20]

Stabilization of Eight-Coordinate Complexes. It is well documented that the nature of the metal atom and the ligands both play a role in determining whether an eight-coordinate complex will be stabilized. Discrete eight-coordinate complexes are most frequently observed in the d-block or transition metals, when the metal atom (1) is large in size (comes from the second- or third-row series), (2) possesses a high formal positive charge (+3, +4, +5, or +6), and (3) possesses a set of d orbitals that are empty or nearly empty (d^0, d^1, or d^2 configurations).

Although the metal atoms found in eight-coordinate complexes seem to fall in the category of hard acids, the ligand donor atoms found in these same complexes span a wider range, all the way from hard bases to soft bases. With the demonstration that the 2-(hydroseleno)pyrimidinato ligand can stabilize eight-coordinate complexes, the different donor atoms found in early-transition-

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(17) Mautner, H. G.; Chu, S. H.; Lee, C. M. *J. Org. Chem.* **1962**, *27*, 3671.

(18) Rye, R. T. B.; Tee, O. S.; Kazdan, E. M. *Can. J. Chem.* **1984**, *62*, 2340.

(19) Shunmugam, R.; Sathyanarayana, D. W. *Bull. Soc. Chim. Belg.* **1984**, *93*, 121.

(20) Corbin, D. R.; Francesconi, L. C.; Hendrickson, D. N.; Stucky, G. D. *Inorg. Chem.* **1979**, *18*, 3069.

metal eight-coordinate complexes now number 12: F, Cl, Br, I; O, S, Se; N, P, As; C, H.[21,22]

All of the title complexes should possess the same geometry and stereochemistry. Both the tetrakis(2-mercaptopyrimidinato)tungsten(IV) complex[1] and the tetrakis(2-mercaptopyrimidinato)molybdenum(IV) complex[2] possess dodecahedral geometry with each of the four bidentate ligands spanning an *m* edge and with the nitrogen and sulfur donor atoms occupying the dodecahedral B and A sites, respectively—see Figure 3. We anticipate, because of the similarity in the structure of all of the ligands, that the newly prepared eight-coordinate tungsten(IV) and molybdenum(IV) complexes discussed here also exist as the dodecahedral D_{2d} (*mmmm*) stereoisomer with the nitrogen donor atoms occupying the B sites and with the oxygen, sulfur, or selenium donor atoms occupying the A sites.

Eight-coordinate complexes possessing asymmetric bidentate ligands have been the subject of both theoretical studies[23] and structural studies.[21] For asymmetric bidentate ligands with short bites, dodecahedral geometry appears to be preferred over square-antiprismatic geometry. Whether the donor atoms occupy the dodecahedral A sites or B sites and which edge is spanned depends on a variety of factors including the d-electron configuration of the metal, the nature of the donor atoms, and steric considerations.[21,23,24] Only one other eight-coordinate complex possessing a d^2-electron configuration and asymmetric bidentate ligands has been structurally characterized besides the two 2-mercaptopyrimidinato complexes, i.e. the tetrakis(5-bromo-8-quinolinato)tungsten(IV) complex.[25] In all three cases the asymmetric bidentate ligands spanned the *m* edges, the π-donor atoms (O, S) occupied the A sites, and the π-acceptor atoms (N) occupied the B sites in accord with Orgel's prediction made in 1960.[26]

Electronic Spectra. By virtue of their intensities ($\epsilon > 10^4$), the low-energy (16800–19700 cm^{-1}) bands observed for the (2-chalcopyrimidinato)molybdenum(IV) and -tungsten(IV) complexes are assigned as charge-transfer bands rather than as d–d transitions. The transitions appear to be metal-to-ligand ($\pi^* \leftarrow$ d) type transitions on the basis of the shift to lower energy on going from Mo(bmpm)$_4$ to W(bmpm)$_4$ and from Mo(bspm)$_4$ to W(bspm)$_4$. In each case, the W(IV) complexes are the more readily oxidizable of the pair of complexes. Metal-to-ligand charge-transfer transitions have been assigned to other d^2, Mo(IV) and W(IV) eight-coordinate complexes including Mo(pic)$_4$,[27] W(pic)$_4$,[28] and W(dcq)$_4$.[29]

Electrochemical Results. Completely chelated eight-coordinate complexes of tungsten(IV) and molybdenum(IV) constitute a small, but well-documented, class of compounds. These low-spin d^2 complexes are typically diamagnetic[28] and substitution inert. One measure of their inertness has been the ability to prepare and isolate isomers.[30,31] One common feature of these compounds is their ability to undergo a one-electron oxidation in a reversible or quasi-reversible fashion. Other oxidation states are also attainable in certain instances.

This class of compounds has been subject of several recent cyclic voltammetric (CV) studies. Schultz and co-workers[32] have conducted a CV study of several tetrakis eight-coordinate complexes containing the MoS$_8$ coordination shell. The bidentate ligands utilized included the mononegative dithiocarbamate and dithioxanthate and the dinegative ethylenedithiolate ligands. Starting with the Mo(V) eight-coordinate complexes, a reversible one-electron oxidation to Mo(VI) was observed for all but one of the complexes and a one-electron reduction to Mo(IV) was observed for all the complexes.

Table VIII. Electrochemical and Spectroscopic Values for Figure 4

	$E_{1/2}$, V vs SSCE	MLCT, eV
Mo(bmpm)$_4$	0.51	2.44
Mo(bspm)$_4$	0.32	2.29
W(bhpm)$_4$	0.30	2.45
W(bmpm)$_4$	0.28	2.19
W(bspm)$_4$	0.21	2.08
W(bmp)$_4$	−0.05	2.35

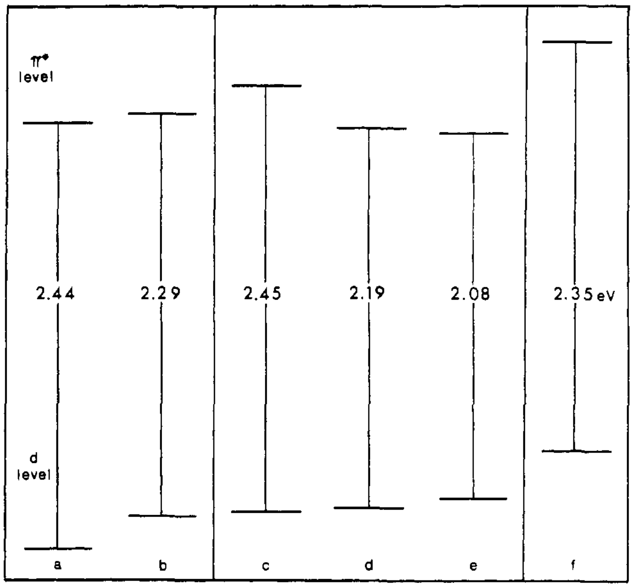

Figure 4. HOMO and LUMO levels for (a) Mo(bmpm)$_4$, (b) Mo(bspm)$_4$, (c) W(bhpm)$_4$, (d) W(bmpm)$_4$, (e) W(bspm)$_4$, and (f) W(bmp)$_4$.

In another recent CV study, Nowak and Archer[33] examined the series of mixed-ligand eight-coordinate tungsten(IV) complexes WL$_n$L$'_{4-n}$, where L = 5,7-dichloroquinolinolato and L$'$ = 5-methylpicolinato, and found a smooth change in $E_{1/2}$ values from 0.404 V for W(mpic)$_4$ to 0.27 V for W(dcq)$_4$ in THF vs SSCE. In addition, the authors found a correlation between the $E_{1/2}$ values observed for this series and the low-energy MLCT bands exhibited by the complexes. The linear increase in the $E_{1/2}$ values as dcq$^-$ ligands were replaced by mpic$^-$ ligands was found to parallel the increase in the energy of the lowest energy CT transition.

A comparison of the $E_{1/2}$ values and the low-energy MLCT bands for the molybdenum and tungsten pyrimidinato complexes studied in this report exhibit some of the same trends noted by Nowak and Archer for their mixed-ligand eight-coordinate complexes. For the tungsten pyrimidinato complexes the increase in $E_{1/2}$ as the Se donor atom is replaced by S and S is replaced by O is, like the aforementioned complexes, paralled by an increase in the energy of the low-energy MLCT band—see Table VIII. The same pattern also occurs for the pair of molybdenum pyrimidinato complexes (Table VIII).

Figure 4 is based on the assumptions of Nowak and Archer,[33] that is, that the $E_{1/2}$ values can be considered qualitatively to be a measure of the HOMO energy level and that the CT transition can be considered qualitatively to be a measure of the energy difference between the HOMO and the LUMO levels. For the complexes in question, we assume the LUMO corresponds to the pyrimidinato or pyridinato π^* level.

With reference to Figure 4 several observations can be made. For the three-member tungsten pyrimidinato series, there is only

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(21) Drew, M. G. V. *Coord. Chem. Rev.* **1977**, *24*, 179.
(22) Lippard, S. J. *Prog. Inorg. Chem.* **1967**, *8*, 109.
(23) Kepert, D. L. *Prog. Inorg. Chem.* **1978**, *24*, 179.
(24) Burdett, J. K.; Hoffman, R.; Fay, R. C. *Inorg. Chem.* **1978**, *17*, 2553.
(25) Bonds, W. D.; Archer, R. D.; Hamilton, W. C. *Inorg. Chem.* **1971**, *10*, 1764.
(26) Orgel, L. E. *J. Inorg. Nucl. Chem.* **1960**, *14*, 136.
(27) Donahue, C. J.; Archer, R. D. *Inorg. Chem.* **1978**, *17*, 1677.
(28) Donahue, C. J.; Archer, R. D. *Inorg. Chem.* **1977**, *16*, 2903.
(29) Bonds, W. D.; Archer, R. D. *Inorg. Chem.* **1971**, *10*, 2057.
(30) Donahue, C. J.; Clark-Motia, D.; Harvey, M. E. *Inorg. Chem.* **1985**, *24*, 801.
(31) Donahue, C. J.; Archer, R. D. *J. Am. Chem. Soc.* **1977**, *99*, 6613.
(32) Smith, D. A.; McDonald, J. W.; Finklea, H. O.; Ott, V. R.; Schultz, F. A. *Inorg. Chem.* **1982**, *21*, 3825.
(33) Nowak, R. J.; Archer, R. D. *Inorg. Chem.* **1986**, *25*, 3323.

a small difference in the energy of the HOMO as the chalcogen atom is varied from O to S to Se. The LUMO also decreases in energy on going from O to S to Se; however, the energy change is larger. The energy change pattern in the HOMO and LUMO levels for tungsten pyrimidinato complexes is identical with that observed for the $W(dcq)_4(mpic)_{4-n}$ complexes.[33] This, however, is not the case with regard to the two-member molybdenum pyrimidinato series. Here both the HOMO and LUMO increase in energy on going from $Mo(bmpm)_4$ to $Mo(bspm)_4$.

It is also interesting to compare the energy values for $E_{1/2}$ and the MLCT band for the $W(bmpm)_4$ vs the $W(bmp)_4$ complex. For these two complexes, the metal center and the donor atoms remain the same, while the ligand ring structure changes from pyrimidine to pyridine. For these two complexes the energy change in the $E_{1/2}$ values is in the opposite direction as the energy change in the MLCT band. The $E_{1/2}$ values drop from 0.28 to −0.05 V for $W(bmpm)_4$ compared to $W(bmp)_4$; that is, it is easier to oxidize the pyridinato complex. Conversely, a shift to higher energy occurs in the low-energy MLCT band on going from $W(bmpm)_4$ to $W(bmp)_4$. It appears that the effect of replacing the pyrimidine ring with the pyridine ring is to raise the energy of both the HOMO and the LUMO. However, the effect of this change is greater on the LUMO than the HOMO, which is consistent with the assignment of the HOMO as a metal orbital of π-symmetry and the LUMO as a π^*-ligand orbital.[33]

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Conversion of Hydroxo-Bridged Diplatinum(II) Complexes to Amido-Bridged Diplatinum(II) Complexes. X-ray Crystal Structure of *trans*-$[Pt_2(\mu\text{-}NH_2)_2(Ph_2PO)_2(PPh_2Me)_2]\cdot CH_3CH_2OH$

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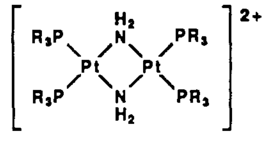
The amido-bridged diplatinum complexes *cis*- and *trans*-$[Pt_2(\mu\text{-}NH_2)_2(POPh_2)_2(PMePh_2)_2]$ (**1a,b**) as a mixture of isomers has been made by treating $[PtCl_2(dppm\text{-}P,P')]$ with sodium hydroxide in aqueous ammonia or by treatment of $[Pt_2(\mu\text{-}OH)_2(POPh_2)_2(PMePh_2)_2]$ with aqueous ammonia. The mixture **1a,b** has been characterized by ^1H, $^{31}P\{^1H\}$, and $^{15}N\{^1H\}$ NMR spectroscopy, and the X-ray crystal structure of the trans isomer **1a** has been determined (monoclinic, $C2/c$; $a = 25.576$ (10) Å, $b = 14.609$ (4) Å, $c = 26.988$ (10) Å, $\beta = 102.73$ (4)°, $R = 0.045$ for 3478 observed reflections ($I/\sigma(I) \geq 3.0$)). The $[Pt_2N_2]$ ring has a Pt–N bond of 2.114 (7) Å and a dihedral angle of 44 (1)° between the Pt coordination planes. Addition of aqueous ammonia to $[Pt_2(\mu\text{-}OH)_2(PR_3)_4]^{2+}$ complexes gives the corresponding $[Pt_2(\mu\text{-}NH_2)_2(PR_3)_4]^{2+}$ complexes.

Introduction

Until recently, amido complexes of platinum(II) were rare, despite the great interest in ammine–platinum(II) chemistry associated with *cis*-platin. Previous to our report[1] of *trans*- and *cis*-$[Pt_2(\mu\text{-}NH_2)_2(POPh_2)_2(PMePh_2)_2]$ (**1a,b**) the only literature example[2] of a $Pt_2(\mu\text{-}NH_2)_2$ complex was $[Pt_2(\mu\text{-}NH_2)_2(PPh_3)_4]^{2+}$ (**2a**).

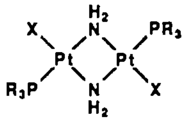


2a PR_3 = PPh_3

2b PR_3 = PPh_2Me

2c PR_3 = $PPhMe_2$

2d PR_3 = PMe_3



3a X = Me, PR_3 = PPh_3

3b X = Me, PR_3 = PEt_3

3c X = Me, PR_3 = $PMePh_2$

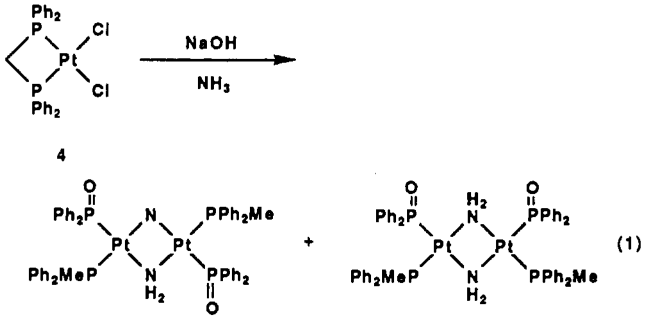
3d X = H, PR_3 = PPh_3

3e X = H, PR_3 = PEt_3

More recently,[3,4] the complexes $[Pt_2(\mu\text{-}NH_2)_2(PR_3)_4]^{2+}$ (**2b–d**) and $[Pt_2X_2(\mu\text{-}NH_2)_2(PR_3)_2]$ (**3a–e**) have been characterized. In this paper we describe the details of the synthesis of **1a** and **1b** and the easy conversion of $Pt_2(\mu\text{-}OH)_2$ species into the corresponding $Pt_2(\mu\text{-}NH_2)_2$ species.

Results and Discussion

The chelate $[PtCl_2(dppm\text{-}P,P')]$ (**4**) reacts with NaOH in liquid ammonia or simply with aqueous ammonia to give the *trans*- and *cis*-$[Pt_2(\mu\text{-}NH_2)_2(POPh_2)_2(PMePh_2)_2]$ (**1a,b**) binuclear complexes in high yield (eq 1). The assigned structures for **1a** and **1b** are



based on elemental analysis, IR and ^1H, $^{31}P\{^1H\}$, and $^{15}N\{^1H\}$ NMR spectroscopy (see Experimental Section for the data), and an X-ray crystal structure of the trans isomer **1a** (see below).

The $^{31}P\{^1H\}$ and ^1H NMR spectra indicate that the isomers **1a** and **1b** are present in an approximately 1:1 ratio. The ^1H signals for the NH_2 protons occur to high field of TMS and are broad. For the ^{15}N-labeled complexes, these signals are doublets due to ^{15}N–^1H coupling but are still broad. They do not exchange with

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(1) Alcock, N. W.; Bergamini, P.; Kemp, T. J.; Pringle, P. G. *J. Chem. Soc., Chem. Commun.* **1987**, 235.

(2) Dobinson, A. C.; Mason, R.; Robertson, G. B.; Conti, R. U. F.; Morelli, D.; Cenini, S.; Bonati, F. *J. Chem. Soc., Chem. Commun.* **1967**, 739.

(3) Park, S.; Roundhill, D. M.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 3972.

(4) O'Mahoney, C. A.; Parkin, I. P.; Williams, D. J.; Woollins, J. D. *Polyhedron* **1989**, *8*, 1979.

0020-1669/91/1330-1594$02.50/0