to yellow. Evaporation to dryness and extraction into hexane gave only $MeCpMn(CO)_2(t\text{-}Bu_2PH)$ (15%). An intractable residue, presumably containing unidentified Ir species, was left after the hexane extraction.

X-ray Experimental Section

General Procedures. Data were collected on an Enraf-Nonius CAD-4 diffractometer by using graphite-monochromated Mo Kα radiation. Data were collected by the $\theta/2\theta$ scan technique at 23 ± 2 °C. Details of the standard data collection methods were similar to those outlined in ref 12. All calculations were performed on a PDP 11/44 computer using the Enraf-Nonius software package SDP PLUS.[13]

Crystals of **1** and **2** were grown from hexane solution at −20 °C and mounted in thin-walled glass capillaries under nitrogen. Unit cell parameters were obtained by carefully centering 25 reflections having 2θ values between 24.0 and 26.0° for **1** and 22.0 and 24.0° for **2**. For both compounds, the monoclinic space group $P2_1/n$ (No. 1014) was uniquely determined by systematic absences ($h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$; $h00$, $h = 2n + 1$; $00l$, $l = 2n + 1$). Data were collected in the $\pm h,+k,+l$ and $+h,+k,\pm l$ quadrants for **1** and **2**, respectively. Details of crystal data parameters and other relevant information are collected in Table I. For both structures, the data were corrected for Lorentz and polarization effects and also for absorption by using an empirical ψ scan method program (program EAC). For **2**, a 7.5% decay of the standard reflections occurred, and so an anisotropic decay correction was applied. The observed structure factors of equivalent reflections were averaged. Both structures were solved by direct methods (SIMPEL) followed by successive cycles of difference Fourier maps followed by least-squares refinement. A non-Poisson contribution weighting scheme with an experimental instability factor, P, was used in the final stages of refinement ($P = 0.05$ for both **1** and **2**).[14] All non-hydrogen atoms were refined anisotropically for **1**. For **2** all non-hydrogen atoms except for C(4), C(10), C(15), and C(24) were refined anisotropically. Hydrogen atoms were not located in either structure.

For **1**, the maximum peak in the final difference Fourier map had a height of 0.67 e Å^{-3} and was located 0.89 Å from C(14). For **2**, the maximum peak in the final difference Fourier was 0.855 e Å^{-3} and was 0.90 Å from Ir. Scattering factors were taken from ref [15]. Supplementary material is available.[16]

Acknowledgment. We thank the Robert A. Welch Foundation (Grant F-816), the National Science Foundation (Grant CHE-8517759), and the Texas Advanced Technology Research Program for support. We also thank Johnson Matthey, Inc., for generous loans of $RhCl_3\cdot xH_2O$ and $IrCl_3\cdot xH_2O$. R.A.J. thanks the Alfred P. Sloan Foundation for a fellowship (1985–1987).

Supplementary Material Available: Complete listings of bond angles and thermal parameters (8 pages); tables of observed and calculated structure factors (51 pages). Ordering information is given on any current masthead page.

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(12) Jones, R. A.; Wright, T. C.; Organometallics **1983**, *2*, 1842.

(13) *SDP-PLUS*, 4th Ed.; B. A. Frenz and Associates: College Station, TX, 1981.

(14) P is used in the calculation of $\sigma(I)$ to downweight intense reflections in the least-squares refinement. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 4(F_o)^2/[\sum(F_o)^2]^2$, where $[\sum(F_o)^2]^2 = [S^2(C + R^2B) + \{P(F_o)^2\}^2]/(Lp)^2$, where S is the scan rate, C is the total integrated peak count, R is the ratio of scan time to background counting time, B is the total background count and Lp is the Lorentz–polarization factor.

(15) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4.

(16) See paragraph at end of paper regarding supplementary material.

Contribution from the Department of Chemistry,
Purdue University, West Lafayette, Indiana 47907

Preparation and Spectroscopic Characterization of the Series of Mixed-Ligand Complexes $Mo_2X_n(mhp)_{4-n}(PR_3)_n$ (X = Cl, Br; PR_3 = $PMePh_2$, PMe_2Ph, PEt_3; mhp = Anion of 2-Hydroxy-6-methylpyridine; n = 1–3)

William S. Harwood, S. Mark Kennedy, Fred E. Lytle,* Ju-sheng Qi, and Richard A. Walton*

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The mixed-ligand complexes $Mo_2X_2(mhp)_2(PR_3)_2$ (X = Cl, Br; mhp = monoanion of 2-hydroxy-6-methylpyridine; PR_3 = PEt_3, PMe_2Ph, $PMePh_2$) have been prepared through the reactions of $Mo_2X_4(PR_3)_4$ with Hmhp in toluene and ligand redistribution reactions on admixing equimolar amounts of $Mo_2X_4(PR_3)_4$ and $Mo_2(mhp)_4$ in toluene. Similar procedures can be used to prepare the chloride complexes $Mo_2Cl_3(mhp)(PR_3)_3$ and $Mo_2Cl(mhp)_3(PR_3)$. The 2,4-dimethyl-6-hydroxypyrimidine analogues $Mo_2X_2(dmhp)_2(PEt_3)_2$ (X = Cl, Br) were prepared from the reactions between $Mo_2X_4(PEt_3)_4$ and Hdmhp. The complexes $Mo_2X_2(mhp)_2(PR_3)_2$ and $Mo_2X_2(dmhp)_2(PEt_3)_2$ possess very similar ^{31}P NMR and electronic absorption spectral properties and display similar cyclic voltammograms, thereby indicating their close structural relationship to the structurally characterized derivative *cis*-$Mo_2Cl_2(mhp)_2(PEt_3)_2$. The $^{31}P\{^1H\}$ NMR spectra of $Mo_2X_3(mhp)(PR_3)_3$ show a doublet and a triplet ($J(P\text{-}P) \simeq 14$ Hz; intensity ratio doublet:triplet = 2:1), which accords with these complexes possessing a structure in which a pair of trans PR_3 ligands are mutually cis to the O atom of the mhp bridge, while the other phosphine is trans to the N atom of the bridging ligand at the other Mo atom. Electrochemical measurements on $Mo_2X_n(mhp)_{4-n}(PR_3)_n$ show the presence of a reversible oxidation ($E_{1/2}$ between +0.55 and +0.26 V vs. Ag/AgCl). The $E_{1/2}$ values shift to a more negative potential as the number of mhp ligands increases. The species $Mo_2X_2(mhp)_2(PR_3)_2$ exhibit an interesting case of bimodal luminescence. The emission spectra show bands at ca. 600 and ca. 400 nm, the intensities of which are reciprocally related. The intensity ratio $I(400\ nm)/I(600\ nm)$ increases with an increase in solvent viscosity. Models are proposed that can explain these luminescence properties.

Introduction

There are a variety of quadruply bonded dinuclear complexes that either contain no ligand bridges or have the metal atoms bridged by four monoanionic ligands.[1] Fewer complexes have been synthesized in which there are an intermediate number of anionic bridging ligands. One early example is the bis(carboxylate)-bridged compound $Mo_2Br_2(O_2CPh)_2(P\text{-}n\text{-}Bu_3)_2$,[2] in which the carboxylate bridges are disposed in a trans arrangement with respect to one another.[3] Subsequently, a variety of other dimolybdenum(II) complexes have been characterized in which a similar trans disposition of carboxylate groups is present.[4] However, the alternative cis arrangement of carboxylate ligands

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(1) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982; and references therein.

(2) San Filippo, J., Jr.; Sniadoch, H. J. *Inorg. Chem.* **1976**, *15*, 2209.

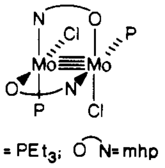
(3) Potenza, J. A.; Johnson, R. J.; San Filippo, J., Jr. *Inorg. Chem.* **1976**, *15*, 2215.

(4) (a) Hursthouse, M. B.; Abdul Malik, K. M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *B35*, 2709. (b) Mainz, V. V.; Andersen, R. A. *Inorg. Chem.* **1980**, *19*, 2165. (c) Green, M. L. H.; Parkin, G.; Bashkin, J.; Fail, J.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1982**, 2519. (d) Girolami, G. S.; Mainz, V. V.; Andersen, R. A. *J. Am. Chem. Soc.* **1982**, *104*, 2041.

0020-1669/87/1326-1784$01.50/0

is seen in the case of the quadruply bonded dirhenium(III) complexes $Re_2Cl_4(O_2CR)_2{\cdot}2L$ (R = CH_3, C_2H_5; L = H_2O, py, 4-Mepy, Me_2SO, DMF).[1,5]

Prompted by these previous findings, we decided to examine the synthesis and spectroscopic and electrochemical properties of a series of dimolybdenum(II) complexes that contain one, two, or three ligand bridges between the metal centers and have focused our study on complexes that contain the anion of 2-hydroxy-6-methylpyridine (Hmhp). Our hope had been to isolate species intermediate between the two extremes of $Mo_2X_4(PR_3)_4$[6,7] and $Mo_2(mhp)_4$.[8] Shortly after our study began, Fanwick reported the synthesis and the structure of *cis*-$Mo_2Cl_2(mhp)_2(PEt_3)_2$,[9] in which the mhp bridges are shown to be in a cis arrangement (see I). The Mo–Mo bond distance of 2.103 (1) Å determined for this compound is intermediate between the values determined for $Mo_2Cl_4(PMe_3)_4$[10] and $Mo_2(mhp)_4$[8] of 2.130 (1) and 2.065 (1) Å, respectively. He reported that this compound was always obtained with small amounts of impurities, which he suggested were $Mo_2Cl_3(mhp)(PEt_3)_3$ and $Mo_2Cl(mhp)_3(PEt_3)$. We report here two alternative syntheses that afford the red $Mo_2X_2(mhp)_2(PR_3)_2$ complexes in good yield. These involve (1) direct substitution of $Mo_2X_4(PR_3)_4$ with Hmhp in toluene and (2) ligand redistribution reactions from admixing equimolar amounts of $Mo_2X_4(PR_3)_4$ and $Mo_2(mhp)_4$ in toluene. These methods can also be modified to obtain samples of $Mo_2Cl(mhp)_3(PR_3)$ and $Mo_2Cl_3(mhp)(PR_3)_3$ of sufficient purity for spectroscopic and electrochemical identification. In the course of characterizing these complexes, we have discovered an interesting case of bimodal luminescence for the species $Mo_2X_2(mhp)_2(PR_3)_2$, and we describe herein the details of our studies on these complexes.



P = PEt_3; O N = mhp

I

Experimental Section

Starting Materials. Molybdenum hexacarbonyl was purchased from Strem; 2-hydroxy-6-methylpyridine (Hmhp) and 2,4-dimethyl-6-hydroxypyrimidine (Hdmhp) were purchased from the Aldrich Chemical Co. and were used without further purification. Tertiary phosphine ligands were obtained from Strem and stored under an atmosphere of dry nitrogen. The following compounds were prepared by standard literature procedures: $K_4Mo_2Cl_8$,[11] $(NH_4)_4Mo_2Br_8$,[12] and $Mo_2X_4(PR_3)_4$ (X = Cl, Br; PR_3 = $PMePh_2$, PMe_2Ph, PEt_3).[6,7]

Reaction Procedures. All reactions were performed under an atmosphere of dry nitrogen, and reagent grade solvents were deoxygenated before use. In those cases where microanalytical data are not reported, identification of products is based on their spectroscopic and electrochemical properties.

Physical Measurements. Electronic absorption spectra were recorded for solutions of the complexes in dichloromethane in the range 350–900 nm by using an IBM Instruments 9420 UV-vis spectrophotometer. The luminescence spectra of the dimolybdenum compounds were obtained by using the PAR nitrogen laser system described elsewhere.[13] Methanol, propanol, and butanol from Burdick & Jackson as well as ethylene glycol and glycerin from Baker Chemicals and USI 200-proof ethanol were used as solvents. ^1H NMR spectra, which were recorded at 200 MHz by using a Varian XL-200 spectrometer, are referenced to the residual protons of the incompletely deuteriated solvents. $^{31}P\{^1H\}$ NMR spectra were recorded by using a Varian XL-200 spectrometer operated at 80.98 MHz with an internal deuterium lock and with aqueous 85% H_3PO_4 as an external standard. Positive chemical shifts were measured downfield from H_3PO_4.

Elemental microanalyses were performed by Dr. H. D. Lee and Y. P. Wu of the Purdue University Microanalytical Laboratory.

A. Synthesis of $Mo_2X_2(mhp)_2(PR_3)_2$. (i) $Mo_2Cl_2(mhp)_2(PMePh_2)_2$. A solution consisting of 0.69 g (0.61 mmol) of $Mo_2Cl_4(PMePh_2)_4$ and 0.13 g (1.21 mmol) of Hmhp in 21 mL of toluene was refluxed for 6 h and then kept warm (50–70 °C) for 12 h while being stirred. The red precipitate was collected by filtration, washed with 3 × 10 mL of methanol, and then vacuum-dried; yield 0.42 g (80%). Anal. Calcd for $C_{38}H_{38}Cl_2Mo_2N_2O_2P_2$: C, 51.90; H, 4.36; Cl, 8.06. Found: C, 52.05; H, 4.54; Cl, 8.53.

(ii) $Mo_2Br_2(mhp)_2(PMePh_2)_2{\cdot}0.25CH_2Cl_2$. A solution that contained an equimolar mixture of $Mo_2Br_4(PMePh_2)_4$ (0.93 g, 0.71 mmol) and $Mo_2(mhp)_4$ (0.44 g, 0.71 mmol) in 20 mL of toluene was refluxed for 6 h and stirred while still warm for 12 h. The red reaction mixture was cooled to room temperature, evaporated under a stream of dry nitrogen to a volume of ~5 mL, and then filtered. The red powder was washed with 3 × 10 mL of methanol and then vacuum-dried; yield 0.88 g (64%). This product was purified for microanalysis by column chromatography (silica gel; CH_2Cl_2 as eluent). The eluate was collected and evaporated to dryness and the resulting red powder recrystallized from CH_2Cl_2/methanol. Anal. Calcd for $C_{38.25}H_{38.5}Br_2Cl_{0.5}Mo_2N_2O_2P_2$: C, 46.42; H, 3.92; total halogen, 17.94. Found: C, 46.06; H, 3.76; total halogen, 17.44. The presence of lattice dichloromethane was confirmed by ^1H NMR spectroscopy in $CDCl_3$ (δ +5.30; CH_2Cl_2).

(iii) $Mo_2Cl_2(mhp)_2(PMe_2Ph)_2$. This compound was prepared by procedure A(ii); yield 71%. Anal. Calcd for $C_{28}H_{34}Cl_2Mo_2N_2O_2P_2$: C, 44.52; H, 4.54; Cl, 9.39. Found: C, 44.17; H, 4.84; Cl, 10.19. The slightly high value for the halogen analysis is consistent with the presence of a trace of lattice CH_2Cl_2.

(iv) $Mo_2Br_2(mhp)_2(PMe_2Ph)_2$. This compound was synthesized by procedure A(ii). The compound was purified by column chromatography (as in procedure A(ii)) and the red band collected and evaporated to dryness; yield 14%. An orange band was also collected (see procedure C(ii)). Anal. Calcd for $C_{28}H_{34}Br_2Mo_2N_2O_2P_2$: C, 39.84; H, 4.06; Br, 18.93. Found: C, 40.23; H, 4.42; Br, 19.22.

(v) $Mo_2Cl_2(mhp)_2(PEt_3)_2$. This compound was synthesized from the reaction between $Mo_2Cl_4(PEt_3)_4$ and $Mo_2(mhp)_4$ by the method outlined in procedure A(i); yield 56%. The spectroscopic properties of this compound were identical with those reported by Fanwick.[8]

(vi) $Mo_2Br_2(mhp)_2(PEt_3)_2$. This compound was synthesized by the method outlined in procedure A(i); yield 53%. Anal. Calcd for $C_{24}H_{42}Br_2Mo_2N_2O_2P_2$: C, 35.84; H, 5.26; Br, 19.87. Found: C, 36.09; H, 5.45; Br, 20.08.

B. Synthesis of $Mo_2X_3(mhp)(PR_3)_3$. (i) $Mo_2Cl_3(mhp)(PMePh_2)_3$. A mixture containing 0.66 g (1.04 mmol) of $K_4Mo_2Cl_8$ and 0.58 mL (3.15 mmol) of $PMePh_2$ was stirred at room temperature in 20 mL of methanol for 3 h. A solution of 0.14 g (1.07 mmol) of Na(mhp) in 10 mL of methanol was then syringed into the flask and the resulting slurry refluxed for 3 h. The dark blue precipitate was collected by filtration, washed with methanol, and then vacuum-dried; yield 0.71 g (68%). A sample for microanalysis was purified by column chromatography (silica gel; methanol/CH_2Cl_2 (1:1) as eluent). Anal. Calcd for $C_{45}H_{45}Cl_3Mo_2NOP_3$: C, 53.67; H, 4.51; Cl, 10.56. Found: C, 54.03; H, 4.80; Cl, 12.71. The high halogen value is consistent with a trace of lattice CH_2Cl_2 present in the sample, and this was confirmed from a ^1H NMR spectrum (200 MHz) recorded in acetone-d_6.

(ii) $Mo_2Br_3(mhp)(PMePh_2)_3$. This compound was synthesized by a ligand redistribution reaction upon refluxing a solution of 0.32 g (0.25 mmol) of $Mo_2Br_4(PMePh_2)_4$ and 0.24 g (0.25 mmol) of $Mo_2Br_2(mhp)_2(PMePh_2)_2$ in 20 mL of toluene for 4 h. The suspension was stirred while still warm for an additional 12 h and then cooled to room temperature and the volume reduced to ~5 mL by evaporating the solvent under a stream of dry nitrogen. The product was collected by filtration and washed with 3 × 5 mL of methanol; yield 0.21 g (76%).

(iii) $Mo_2Cl_3(mhp)(PMe_2Ph)_3$. This compound was prepared by a method similar to procedure B(ii); yield 88%.

(iv) $Mo_2Cl_3(mhp)(PEt_3)_3$. A mixture comprising 0.60 g (0.74 mmol) of $Mo_2Cl_4(PEt_3)_4$ and 0.81 g (0.74 mmol) of Hmhp in 20 mL of toluene was refluxed for 4 h. The volume of the mixture was then reduced to ~5 mL and the blue product collected by filtration, washed with 3 × 5 mL of methanol, and vacuum-dried; yield 0.55 g (92%).

C. Synthesis of $Mo_2X(mhp)_3(PR_3)$. (i) $Mo_2Cl(mhp)_3(PMePh_2)$. A suspension consisting of 0.71 g (0.80 mmol) of $Mo_2Cl_2(mhp)_2(PMePh_2)_2$ and 0.088 g (0.80 mmol) of Hmhp in 20 mL of toluene was refluxed for

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(5) Chakravarty, A. R.; Cotton, F. A.; Cutler, A. R.; Walton, R. A. *Inorg. Chem.* **1986**, *25*, 3619.

(6) San Filippo, J., Jr.; Sniadoch, H. J.; Grayson, R. L. *Inorg. Chem.* **1974**, *13*, 2121.

(7) Glicksman, H. D.; Hamer, A. D.; Smith, T. J.; Walton, R. A. *Inorg. Chem.* **1976**, *15*, 2205.

(8) Cotton, F. A.; Fanwick, P. E.; Niswander, R. H.; Sekutowski, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4725.

(9) Fanwick, P. E. *Inorg. Chem.* **1985**, *24*, 258.

(10) Cotton, F. A.; Extine, M. W.; Felthouse, T. R.; Kolthammer, B. W. S.; Lay, D. G. *J. Am. Chem. Soc.* **1981**, *103*, 4040.

(11) Brencic, J. V.; Cotton, F. A. *Inorg. Chem.* **1970**, *9*, 351.

(12) Brencic, J. V.; Leban, I.; Segedin, P. *Z. Anorg. Allg. Chem.* **1976**, *427*, 85.

(13) Coburn, J. T.; Lytle, F. E.; Huber, D. M. *Anal. Chem.* **1985**, *57*, 258.

Table I. Spectroscopic and Electrochemical Properties of the Dimolybdenum(II) Complexes $Mo_2X_n(mhp)_{4-n}(PR_3)_n$

				electrochemistry[c]	
complex	color	$^{31}P\{^1H\}$ NMR δ[a]	UV-vis λ_{max}, nm[b]	$E_{p,a}$, V	$E_{1/2}$, V
$Mo_2Cl_4(PMePh_2)_4$	blue	6.4 (s)	600	1.69	0.62 (120)
$Mo_2Cl_3(mhp)(PMePh_2)_3$	blue-purple	10.4 (d), 8.95 (t)[d]	578 (1380), 430 (sh), 366 (sh)	1.53	0.48 (120)
$Mo_2Cl_2(mhp)_2(PMePh_2)_2$	red	10.5 (s)[e]	550 (1960), 414 (sh)	1.44	0.41 (110)
$Mo_2Cl(mhp)_3(PMePh_2)$	orange	12.5 (s)	530 (1600), 410 (sh)	1.37	0.31 (120)
$Mo_2Br_4(PMePh_2)_4$	blue	*f*	618 (1920)	~1.50	0.66 (100)
$Mo_2Br_3(mhp)(PMePh_2)_3$	blue	10.2 (d), 3.4 (t)	580 (960), ~335 (sh)	1.65	0.55 (120)
$Mo_2Br_2(mhp)_2(PMePh_2)_2$	red	8.5 (s)	555 (2200), 410 (sh), 363 (sh)	1.48	0.48 (120)
$Mo_2Br(mhp)_3(PMePh_2)$	orange	*f*	519 (890), 409 (3250), 377 (sh)	1.36	0.30 (120)
$Mo_2Cl_4(PMe_2Ph)_4$	blue	−0.3 (s)	594 (870)	1.50	0.56 (120)
$Mo_2Cl_3(mhp)(PMe_2Ph)_3$	blue-purple	*f*	574 (1960), 418 (sh), 366 (sh), 327 (6900)	*j*	0.48 (130)
$Mo_2Cl_2(mhp)_2(PMe_2Ph)_2$	red	*f*	551 (1900), 416 (sh)	1.39	0.40 (160)
$Mo_2Br_4(PMe_2Ph)_4$	bright green	−2.35 (s)	607 (800)	1.47	0.74 (160)
$Mo_2Br_2(mhp)_2(PMe_2Ph)_2$	red	0.0 (s)	552 (2400), 407 (sh), 351 (sh)	1.39	0.43 (120)
$Mo_2Br(mhp)_3(PMe_2Ph)$	orange	1.7 (s)	520 (1800), 410 (8200), 380 (sh)	1.30	0.30 (120)
$Mo_2Cl_4(PEt_3)_4$	blue	8.3 (s)	583	1.43	0.40 (120)
$Mo_2Cl_3(mhp)(PEt_3)_3$	blue-purple	11.6 (t), 10.1 (d)	569 (1530), 418 (720), 365 (1720), 320 (6260)	1.50	0.35 (140)
$Mo_2Cl_2(mhp)_2(PEt_3)_2$	red	14.2 (s)[g]	542 (1400), 410 (3200), 390 (3100), ~350 (3500)	1.42	0.31 (120)
$Mo_2Cl(mhp)_3(PEt_3)$	orange	15.8 (s)[g]	528 (800), 413 (3900)	1.35	0.26 (160)
$Mo_2Br_4(PEt_3)_4$	blue	*f*	610	1.44	0.54 (130)
$Mo_2Br_2(mhp)_2(PEt_3)_2$	red	11.1 (s)	548 (1800), 415 (sh), 354 (sh)	1.45	0.39 (120)
$Mo_2Br(mhp)_3(PEt_3)$	peach	12.8 (s)	*h*	*h*	
$Mo_2Cl_2(dmhp)_2(PEt_3)_2$	red	15.6 (s)	550 (1500), 406 (sh), 343 (4400)	1.23	0.51 (120)
$Mo_2Br_2(dmhp)_2(PEt_3)_2$	red	12.1 (s)	552 (2100), 408 (sh), 350 (5200)	~1.30	0.70[k]
$Mo_2(mhp)_4$	yellow-orange	*f*	490 (2100), 405 (12 000), 285 (30 000)[i]	1.31	0.18 (150)

[a] Measured in CH_2Cl_2 unless otherwise stated; positive values are downfield of 85% H_3PO_4. Abbreviations are as follows: s = singlet, d = doublet, t = triplet. [b] Measured in CH_2Cl_2. Values in parentheses are molar absorptivities when measured. For complexes of the type $Mo_2X_4(PR_3)_4$ only the lowest energy band ($\delta \rightarrow \delta^*$) is reported. [c] Measured in 0.1 M TBAH-CH_2Cl_2 solutions at a Pt-bead electrode and referenced to Ag/AgCl. Numbers in parentheses are the values of ΔE_p ($=E_{p,a} - E_{p,c}$) in mV. [d] Spectrum measured in $CDCl_3$ has $\delta = +9.2$ (t) and $\delta = +10.5$ (d). [e] Spectrum measured in $CDCl_3$ has $\delta = +11.1$ (s). [f] Not measured. [g] Spectrum recorded in acetone-d_6. [h] Samples contaminated by $Mo_2Br_2(mhp)_2(PEt_3)_2$. [i] Data taken from ref 17. [j] Contamination by $Mo_2Cl_2(mhp)_2(PMe_2Ph)_2$ precluded an accurate measurement of the $E_{p,a}$ value at ~+1.5 V. [k] $E_{p,a}$ value.

8 h. The suspension was cooled to room temperature and the solvent evaporated to small volume (<5 mL) under a stream of dry gaseous nitrogen. The orange-red product was collected by filtration, washed with methanol, and vacuum-dried; yield 0.47 g (78%).

(ii) $Mo_2Br(mhp)_3(PMe_2Ph)$. This compound was obtained in very low yield from the purification of $Mo_2Br_2(mhp)_2(PMe_2Ph)_2$ as outlined in procedure A(iv). Elution of the orange band using CH_2Cl_2, followed by evaporation of the solvent, gave an orange solid; yield 4%. Anal. Calcd for $C_{26}H_{29}BrMo_2N_3O_3P$: C, 42.53; H, 3.98. Found: C, 41.87; H, 4.41.

(iii) $Mo_2Cl(mhp)_3(PEt_3)$. This compound was synthesized by using a method similar to procedure C(i); yield 57%.

(iv) $Mo_2Br(mhp)_3(PEt_3)$. This compound was synthesized by using a method similar to procedure C(i); yield 96%.

D. Synthesis of $Mo_2X_2(dmhp)_2(PEt_3)_2$. (i) $Mo_2Cl_2(dmhp)_2(PEt_3)_2$. A solution consisting of 0.75 g (0.93 mmol) of $Mo_2Cl_4(PEt_3)_4$ and 0.23 g (1.86 mmol) of Hdmhp in 20 mL of toluene was refluxed for 4 h and then stirred for an additional 12 h. The suspension was evaporated to low volume (<5 mL) under a stream of dry nitrogen gas and filtered, and the solid was washed with methanol. The compound was purified by column chromatography (silica gel; methanol as eluent). The collected eluate was evaporated to dryness and the red powder vacuum-dried; yield 0.14 g (20%). Anal. Calcd for $C_{24}H_{44}Cl_2Mo_2N_4O_2P_2$: C, 38.67; H, 5.95; Cl, 9.51. Found: C, 38.43; H, 5.88; Cl, 9.44.

(ii) $Mo_2Br_2(dmhp)_2(PEt_3)_2$. This compound was synthesized by the method outlined in procedure D(i) using $Mo_2Br_4(PEt_3)_4$; yield 37%. Anal. Calcd for $C_{24}H_{44}Br_2Mo_2N_4O_2P_2$: C, 34.55; H, 5.32; Br, 19.16. Found: C, 34.69; H, 5.41; Br, 19.31.

Results and Discussion

The compounds of stoichiometry $Mo_2X_2(mhp)_2(PR_3)_2$ (X = Cl, Br; PR_3 = $PMePh_2$, PMe_2Ph, PEt_3) are easily synthesized either by the direct reaction between $Mo_2X_4(PR_3)_4$ and Hmhp or by a ligand redistribution reaction between $Mo_2X_4(PR_3)_4$ and $Mo_2(mhp)_4$ in toluene. In the case of the derivative $Mo_2Cl_2(mhp)_2(PEt_3)_2$, the spectroscopic properties of our sample and those obtained by Fanwick,[9] who used a different synthetic procedure (namely the reaction between $Mo_2(mhp)_4$, Me_3SiCl, and PEt_3), are identical. Since the general spectroscopic properties of all the $Mo_2X_2(mhp)_2(PR_3)_2$ complexes are so similar (vide infra), we feel these bis-mhp complexes possess a similar structure, viz., a cisoid arrangement of the mhp ligands (see I).

Fanwick[9] also mentioned that he observed the purple $Mo_2Cl_3(mhp)(PEt_3)_3$ and the orange $Mo_2Cl(mhp)_3(PEt_3)$ compounds as minor, but persistent, impurities. We report here the synthesis of several derivatives of these two types in sufficient quantities and purity for electrochemical and spectroscopic characterization. The most effective synthetic procedures involved either (i) the reaction of the appropriate $Mo_2X_4(PR_3)_4$ compound with stoichiometric proportions of Hmhp, Na(mhp), or $Mo_2X_2(mhp)_2(PR_3)_2$ or (ii) the reaction of $Mo_2X_2(mhp)_2(PR_3)_2$ with Hmhp. These complexes are much less stable than the corresponding bis-mhp derivatives. Thus, while the bis-mhp complexes can be purified by column chromatography, this is not true for the mono-mhp or tris-mhp systems. In these cases the recovered compound was contaminated with some $Mo_2X_2(mhp)_2(PR_3)_2$. All attempts at chromatography or other solution methods of separation led to the occurrence of ligand redistribution reactions and resulted in an increase in the amount of the bis-mhp species. For this reason satisfactory microanalytical data are not reported for most of the $Mo_2X_3(mhp)(PR_3)_3$ and $Mo_2X(mhp)_3(PR_3)$ compounds; their characterizations are based on electrochemical, electronic absorption, and NMR spectral measurements (vide infra). Although all possible complexes of these two types have not been isolated (see Table I), enough examples of each group have been characterized to establish their properties.

The electrochemical and spectroscopic properties of the compounds $Mo_2X_n(mhp)_{4-n}(PR_3)_n$ (n = 0–4; X = Cl, Br; PR_3 = $PMePh_2$, PMe_2Ph, PEt_3) are summarized in Table I. These quadruply bonded complexes exhibit similar electrochemistry, as measured by cyclic voltammetry in 0.1 M TBAH-CH_2Cl_2 and referenced to the Ag/AgCl electrode. Two one-electron oxidations are observed. The oxidation at more negative potential approaches reversibility,[14] while the other process is clearly irreversible.

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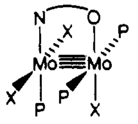
(14) For this couple, the $i_{p,c}/i_{p,a}$ ratio was close to unity and the value of $i_p/v^{1/2}$ was essentially constant for sweep rates (v) of between 50 and 400 mV/s. The potential separation between the coupled cathodic and anodic peaks, ΔE_p, ranged between 100 and 160 mV (see Table I) for v = 200 mV/s and increased slightly with an increase in sweep rate. Under similar conditions the ferrocenium/ferrocene couple was at +0.47 V vs. Ag/AgCl and had ΔE_p = 120 mV at v = 200 mV/s. Further details of our experimental setup are described elsewhere: Zietlow, T. C.; Klendworth, D. D.; Nimry, T.; Salmon, D. J.; Walton, R. A. *Inorg. Chem.* **1981**, *20*, 947.

Several trends in the electrochemistry between these compounds can be discerned, one being a shift of the $E_{1/2}$ value to a more negative potential as the number of coordinated mhp ligands increases. Thus, a smooth trend is observed for the compounds $Mo_2Cl_4(PMePh_2)_4$ ($E_{1/2}$ = +0.62 V) to $Mo_2Cl_3(mhp)(PMePh_2)_3$ ($E_{1/2}$ = +0.48 V) to $Mo_2Cl_2(mhp)_2(PMePh_2)_2$ ($E_{1/2}$ = +0.41 V) to $Mo_2Cl(mhp)_3(PMePh_2)$ ($E_{1/2}$ = +0.31 V) to $Mo_2(mhp)_4$ ($E_{1/2}$ = +0.18 V) and for the PEt_3 analogues. Another trend is the shift of the $E_{1/2}$ value to more negative potential when Cl is replaced by Br. This effect has been observed in several other dimetal systems, most recently in the quadruply bonded dimolybdenum complexes $Mo_2X_4(Ph_2PCH_2PPh_2)_2$ (X = Cl, Br, I).[15] In the same way, increasing the basicity of the tertiary phosphine shifts the $E_{1/2}$ to more negative potentials. Finally, we note that replacement of mhp with dmhp in the complexes $Mo_2X_2(LL)_2(PEt_3)_2$ (X = Cl, Br; LL = mhp, dmhp) results in a shift of the $E_{1/2}$ values to more positive potentials.

The $^{31}P\{^1H\}$ NMR spectra of the complexes with stoichiometries $Mo_2X_4(PR_3)_4$, $Mo_2X_2(mhp)_2(PR_3)_2$, and $Mo_2X(mhp)_3(PR_3)$ all exhibit a single resonance as expected (Table I). In the case of the bis-mhp complexes $Mo_2X_2(mhp)_2(PR_3)_2$, the single resonance is consistent with the structure reported by Fanwick,[9] although he did not report a ^{31}P NMR spectrum for the $Mo_2Cl_2(mhp)_2(PEt_3)_2$ compound. The mono-mhp complexes $Mo_2X_3(mhp)(PR_3)_3$ exhibit two resonances in the $^{31}P\{^1H\}$ NMR spectrum, split into a doublet and a triplet (J(P–P) = 13.6–14 Hz; ratio doublet: triplet is 2:1), which is consistent with the structure depicted in II. In general, the phosphorus resonances shift downfield (to higher frequency) as the number of coordinated mhp ligands increases (see Table I). In this way the resonances for a given complex can be distinguished from another derivative in a mixture. We also note that for a given mhp complex the resonance for the bromo derivative is located about 2–3 ppm upfield (to lower frequency) from that of the corresponding chloro derivative. The resonance found for $Mo_2Cl_2(mhp)_2(PMePh_2)_2$, for example, is located at δ +10.46, while that for $Mo_2Br_2(mhp)_2(PMePh_2)_2$ is at δ +8.50.



II

The ^1H NMR spectra of the complexes integrate in accord with the proposed stoichiometries. This is most clearly seen in the case of the PEt_3 derivatives (Table SI, supplementary material) for which the mhp resonances do not overlap with any phenyl resonances. The inequivalences of the PR_3 ligands that are seen in the $^{31}P\{^1H\}$ spectrum of $Mo_2X_3(mhp)(PR_3)_3$ are also observed in the related ^1H NMR spectrum, where the $P(CH_2–CH_3)_3$ resonances at δ ~2.28 and ~1.96 are in an intensity ratio of ca. 1:2.

The electronic absorption spectra of the quadruply bonded complexes $Mo_2X_n(mhp)_{4-n}(PR_3)_n$ (n = 0–4) exhibit a characteristic absorption in the region 500–610 nm, which is assigned to the $\delta \rightarrow \delta^*$ transition. Previous studies have established that complexes of the type $Mo_2X_4(PR_3)_4$ have $\delta \rightarrow \delta^*$ transitions at ca. 600 nm,[1,16] while the $Mo_2(mhp)_4$ compound has its $\delta \rightarrow \delta^*$ transition at 490 nm.[17,18] The mono-, bis-, and tris-mhp complexes exhibit $\delta \rightarrow \delta^*$ transitions in a smooth trend shifting to higher energy as the number of coordinated mhp ligands is increased. Interestingly, this trend correlates in an inverse fashion with the $E_{1/2}$ values for the 1+/0 couple of the complexes (Table I). Fanwick[9] has suggested that the remainder of the spectrum is composed of four metal-to-ligand charge-transfer bands and one ligand transition. The region between 480 and 340 nm is congested, being composed of three closely spaced charge-transfer transitions. The region between 340 and 280 nm contains one intensely absorbing feature, being composed of a metal-to-phosphine transition and an mhp ligand-localized transition. All of the compounds fluoresce with their emission maxima occurring at wavelengths about 50 nm longer than those of the $\delta \rightarrow \delta^*$ absorption. Fanwick[9] has previously determined the quantum yield of the 600-nm fluorescence from $Mo_2Cl_2(mhp)_2(PEt_3)_2$ to be dependent on wavelength at room temperature, with a maximum value of 0.24 occurring with excitation directly into the $\delta \rightarrow \delta^*$ band. As expected, the excitation spectrum did not match the absorption spectrum under these conditions; but they did match at 77 K.

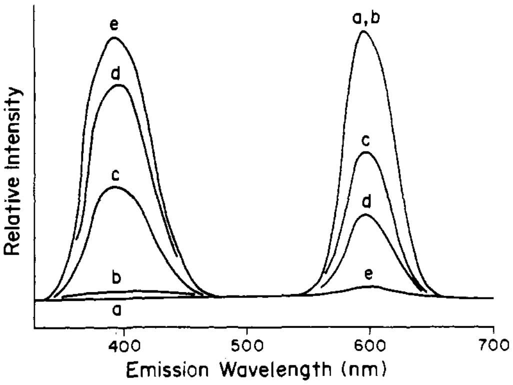


Figure 1. Emission spectra of $Mo_2Cl_2(mhp)_2(PMePh_2)_2$ excited at 337 nm in solvents of differing viscosities: (a) methanol; (b) 1-propanol; (c) 1-butanol; (d) ethylene glycol; (e) 4:1 ethanol:methanol glass at 77 K. The boxcar integrator delay and width settings are not the same as those used in Table II.

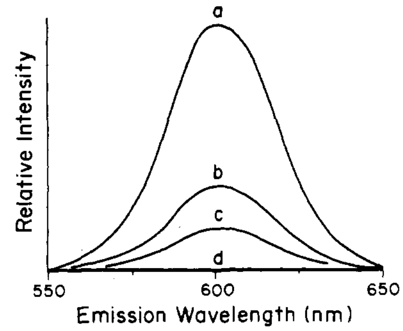


Figure 2. Emission spectra of $Mo_2Cl_2(mhp)_2(PMePh_2)_2$ excited at 514.5 nm in solvents of differing viscosities: (a) methanol; (b) 1-butanol; (c) glycerol; (d) 4:1 ethanol:methanol glass at 77 K.

While studying solvent effects on the spectral properties of the $Mo_2Cl_2(mhp)_2(PMePh_2)_2$ compound, we discovered a second emission band at 400 nm.[19] Attempts with a commercial spectrofluorometer to obtain an excitation spectrum and quantum yield for this second band were unsuccessful because of a lack of xenon lamp intensity in the near-ultraviolet region. Figure 1 shows the total emission spectra of this compound in a series of solvents having differing viscosities. Note that the intensities of the 400- and 600-nm bands are reciprocally related. The decrease in the intensity of the 600-nm band with increasing solvent viscosity can also be produced by excitation directly into the $\delta \rightarrow \delta^*$ transition. That is, very high viscosity solvents, such as low-temperature glasses, can actually eliminate emission from compounds that would emit at room temperature in the same solvents (see Figure 2). The effect of the solvent viscosity on the ratio of the 400- and 600-nm bands also depends on the phosphine ligand and the halogen. The results are summarized in Table II. As the phosphine substituent is changed from PEt_3 to PMe_2Ph to $PMePh_2$, the effect of viscosity is enhanced. Thus the PEt_3 derivative only emits weakly at 400 nm when a low-temperature glass, while the $PMePh_2$ derivative does so strongly in 1-propanol

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(15) Harwood, W. S.; Qi, J.; Walton, R. A. *Polyhedron* **1986**, *5*, 15.
(16) Hopkins, M. D.; Gray, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 2468.
(17) Manning, M. C.; Trogler, W. C. *J. Am. Chem. Soc.* **1983**, *105*, 5311.
(18) Fanwick, P. E.; Bursten, B. E.; Kaufman, G. B. *Inorg. Chem.* **1985**, *24*, 1165.
(19) An examination of the spectral properties of free phosphine and Hmhp ligands indicates that they were not responsible for this emission.

Table II. Solvent Viscosity Effects on Emission Mode Ratios for $Mo_2X_2(bridge)_2(PR_3)_2$ Complexes

complex			I(400 nm)/I(600 nm) by solvents[a]		
X	bridge	PR_3	n-PrOH[b]	n-BuOH[b]	77 K[c]
Cl	mhp	PEt_3	0[d]	0[d]	0.097
Cl	mhp	PMe_2Ph	0.11	0.56	1.0
Cl	mhp	$PMePh_2$	0.44	2.0	7.5
Cl	dmhp	PEt_3	0[d]	0[d]	0.054
Br	mhp	PEt_3	0[d]	0[d]	0[d]
Br	mhp	PMe_2Ph	0.073	0.19	0.24
Br	mhp	$PMePh_2$	0.084	0.27	0.76
Br	dmhp	PEt_3	0[d]	0[d]	0[d]

[a] A 600-nm emission was observed in all experiments. No 400-nm emission was observed in methanol at room temperature. The boxcar delay and window width were adjusted to allow intercomparison of trends as a function of solvent or compound. [b] Measurements at room temperature. [c] 4:1 ethanol:methanol glass. [d] No 400-nm emission was observed.

at room temperature. The effect of solvent viscosity is reduced by replacing the chlorine ligands with bromine. As an example, $Mo_2Br_2(mhp)_2(PMePh_2)_2$ has 10 times less 400-nm radiation in a low-temperature glass than does its chlorine counterpart. It appears that the larger size of the bromine atoms makes the entire compound more cylindrical, thereby reducing the effect of the bulky phosphine ligands.

The model used to explain the bimodal luminescence involves the large structural changes expected between those states having an intact δ bond and the nonbonding $\delta \rightarrow \delta^*$ excited state. The ground state and the ligand-localized excited state should have an eclipsed configuration, while the $\delta \rightarrow \delta^*$ state should have a staggered configuration that is restrained by the bridging ligands. When the molecule is excited into the ligand-localized excited state, it must internally convert to the metal–metal bond manifold before 600-nm emission can occur. For facile internal conversion, the geometry must change from eclipsed to staggered within the lifetime of the ligand-localized excited state. The apparent role of the bulky phosphines and the mhp ligands is the retardation of the twisting about the metal–metal bond, which allows emission to compete effectively with internal conversion. This same effect can be achieved through the use of a highly viscous solvent. An alternative model involves the suggestion that the $\delta \rightarrow \delta^*$ excited singlet state has a large deal of ionic character and distorts to the localized configuration, M^+M^-.[20] This drastic change in electron density would require that the nonbridging ligands undergo a geometric distortion. Such structural changes should have a similar effect on viscosity, as does the eclipsed/staggered postulate made above.

On the basis of either of the proposed models, the viscosity should have an effect on the decay of the two emission bands. One would expect that the lifetime of the ligand-localized transition would get longer as the structural changes necessary for radiationless internal conversion are retarded by viscosity. Indeed, the lifetime does increase with viscosity, going from 2.3 ns in methanol to approximately 6.7 ns in ethylene glycol. For identical reasons, one would expect that the lifetime of the $\delta \rightarrow \delta^*$ transition would get shorter as the structure is held in a configuration similar to that of the ground state. As well, this expectation is realized with a lifetime of 20 ns in methanol and 3 ns in ethylene glycol.

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Supplementary Material Available: Table SI, giving ^1H NMR spectral data for $Mo_2X_n(mhp)_{4-n}(PEt_3)_n$ and $Mo_2X_2(dmhp)_2(PEt_3)_2$ (1 page). Ordering information is given on any current masthead page.

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(20) Hopkins, M. D.; Gray, H. B.; Miskowski, V. M. *Polyhedron*, in press.

Contribution from the Laboratoire de Chimie et de Biochimie Pharmacologiques et Toxicologiques,
UA 400, Université René Descartes, 45 rue des Saints-Pères, 75270 Paris Cedex 06, France

Preparation and Properties of Iron(II), Cobalt(III), and Zinc(II) *N*-Alkylporphyrin Complexes Involving Five-Membered Metal—O—C=C—N Metallacycles

Jean-Paul Battioni, Isabelle Artaud, Daniel Dupre, Philippe Leduc, and Daniel Mansuy*

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The preparation and properties of new *N*-alkylporphyrin complexes involving five-membered metal—O—C=C—N metallacycles are described. Iron(II) complexes exhibiting such a structure were prepared by chemical or electrochemical reduction of previously reported chloro N—C=C—O—Fe^{III} porphyrin complexes obtained by reaction of the iodonium ylide $C_6H_5I{=}X$ (X = CC(O)$CH_2C(CH_3)_2CH_2C$(O)) with Fe^{III}(porphyrin)(ClO_4) (porphyrin = TPP or TpClPP). These pentacoordinated Fe(II) complexes were rapidly oxidized by dioxygen and exhibited a high affinity for ligands such as CO or pyridine. The hexacoordinated CO complexes are the first examples of diamagnetic Fe(II) *N*-alkylporphyrin complexes. Acid demetalation of the pentacoordinated ferrous TPP derivative led to the corresponding free *N*-alkylporphyrin, which was isolated and further transformed into the corresponding Zn(II) complex. Elemental analyses and mass, ^1H NMR, and ^{13}C NMR spectra of the latter showed that it was also a metallacyclic *N*-alkylporphyrin complex involving a N—C=C—O—Zn(II) metallacycle. Finally, the reaction of the iodonium ylide $C_6H_5I{=}X$ with bromo Co^{III}(TPP) led to a similar bromo N—C=C—O—Co^{III}(TPP) complex, which is also the first example of a metallacyclic *N*-alkylporphyrin complex with a Co(III) ion. These results illustrate the generality of the access to this new class of metallacyclic *N*-alkylporphyrin complexes.

N-Alkylporphyrins have been identified as products from the metabolism of drugs by animal liver cytochromes P-450.[1,2] In the particular case of the oxidative metabolism of alk-1-enes, *N*-(2-hydroxyalkyl)protoporphyrin IX compounds have been isolated after acidic extraction from livers of animals treated by alkenes.[3] Taking into account previously known data on the structure and reactivity of the oxygen-active species and on the

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(1) Ortiz de Montellano, P. R. *Ann. Rep. Med. Chem.* **1984**, *19*, 201–211.
(2) Ortiz de Montellano, P. R.; Correia, M. A. *Annu. Rev. Pharmacol. Toxicol.* **1983**, *23*, 481–503.
(3) Ortiz de Montellano, P. R.; Kunze, K. L.; Beilan, H. S.; Wheeler, C. *Biochemistry* **1982**, *23*, 1331–1339.

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