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# Some Chromium and Molybdenum Tetraphenylporphines

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*The synthesis and characterization of several chromium and molybdenum tetraphenylporphines are described. Chemical analysis, magnetic susceptibility measurements, electron spin resonance spectra, infrared spectra, and visible absorption spectra clearly define the chemical composition and metal oxidation states in these new metalloporphines.*

## Introduction

In 1966 the first bivalent-chromium mesoporphyrin IX dimethyl ester[1] was prepared by facile metal insertion reaction using chromium carbonyl and porphyrin in high boiling solvents viz., n-decane and decalin. This method was also employed recently in the synthesis of a chromium phthalocyanine complex.[2] Some new ruthenium, rhodium, and iridium porphyrins[3,4,5,6,7] were prepared by reacting together metal carbonyl halides and porphyrins. The titanyl mesoporphyrin dimethyl ester has been prepared by refluxing diphenyl titanim and porphyrin in mesitylene or triethylbenzene.

This paper presents the method of preparation and the characterization of some new chromium and molybdenum porphyrins. The chemistry of these new compounds with special emphasis on the lower oxidation states of the metals ($Cr^{II}$ and $Mo^{IV}$) will be discussed in a later paper.

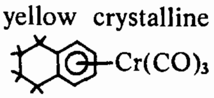
The metallopthalocyanines of chromium and molybdenum[19,20] have been synthesized. The phthalocyanines can be prepared by condensation reactions; this procedure when employed in the synthesis of metalloporphyrins, for most metals, does not yield the porphyrin but long chain polymers. Thus, in metalloporphyrin synthesis the metal insertion reaction, in general, must be employed for a successful synthesis.

## Experimental Section

Reagents and Solvents: analytical solvents viz., chloroform, methanol, benzene, petroleum ether, pyridine, and xylene were used. Decalin (Aldrich Chemical Company), $Cr(CO)_6$ (Strem Chemicals), $Mo(CO)_6$ (Alfa inorganics), piperidine (Eastman Organic, Chemicals), hydazine anhydrous (Research Organic/Chemical Co.) and aluminum oxide (Merck suitable for chromatographic adsorption) were used.

Infrared spectra were taken using the Beckman IR-10 with Nujol or hexachlorbutadiene mulls. Visible absorption spectra were taken with matched 1.00 cm cell. Esr spectra were obtained on a varian E-3 EPR spectrometer. Samples were run in clorohform or benzene solutions at room temperature. An Alpha, regulated power supply, magnet and Cahn microanalytical balance were used for the determination of the magnetic susceptibilities in the solid state by the Faraday method using $HgCo(NCS)_4$ as a standard.

*Preparations.* Tetraphenylporphine (TPP) was prepared by literature procedures.[9] *Tetraphenylporphinechromium(III)methoxide* TPP (1 mole) and $Cr(CO)_6$ (10-15 moles) were refluxed in deaerated decalin under nitrogen for 6 hours. The unreacted $Cr(CO)_6$ and the solvent were removed under reduced pressure. The residue was dissolved in 1:1 mixture of $CHCl_3$ and $CH_3OH$ and passed through a column packed with activated $Al_2O_3$ using 1:1 $CHCl_3$ and $CH_3OH$ mixture. The first-fraction obtained was concentrated to dryness and the residue was heated in a sublimitation apparatus when a yellow crystalline sublimate, the known compound[10]



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was obtained. This compound was characterised by chemical analysis, ir, nmr, and mass spectra. The second and last fraction was chromatographed through a column of activated $Al_2O_3$ and eluted with a 1:2 mixture of $CH_3OH$ and $CHCl_3$. The first fraction was discarded. The second fraction was concentrated to dryness. The residue was heated in the sublimation apparatus at 120°-150°C, but no sublimate was obtained. The solid showed two intense bands at 1898 and 1972 $cm^{-1}$ [11] in the carbonyl region of ir which were probably due to Cr(OMe)TPP . $nCr(CO)_3$ where n = 1, 2, 3, or 4. The solid was crystallized from methanol. The intensities of bands at 1898 and 1972 $cm^{-1}$ were reduced considerably. The solid was crystallized a second time from methanol at which time there were no bands at 1898 and 1972 $cm^{-1}$. This procedure got rid of the $Cr(CO)_3$ fragment that was bound to the phenyl rings. The solid was filter dried in air. *Anal.* Calcd. for $C_{47}H_{39}O_3N_4Cr$: C, 74.27; H, 5.16; N, 7.38. Found: C, 73.82; H, 4.51; N, 7.79.

*Tetraphenylporphinechromium(III)ethoxide,* Cr(OEt)TPP . 2EtOH. (II) TPP (1 mole) and $Cr(CO)_6$ (10-15 moles) were refluxed in decalin under nitrogen for 6 hours. The solution was diluted with $CHCl_3$ and a few ml of concentrated hydrochloric acid was added. The solution was shaken and dried overnight over Linde Molecular Sieves (Type 4A). The dried solution was purified by passing it through a column packed with activated $Al_2O_3$ and eluted with $CHCl_3$. The first-fraction was discarded. The second fraction was concentrated on a hot plate after adding absolute alcohol. The cold solution gave crystals which were filtered and dried in air. *Anal.* Calcd. for $C_{52}H_{51}O_3N_4Cr$: C, 73.58; H, 6.01; N, 6.60. Found: C, 73.11; H, 6.01; N, 6.70.

*Tetraphenylporphinechromium(III)hydroxide,* Cr(OH)TPP . $2H_2O$(III). TPP (1 mole) and $Cr(CO)_6$ (10-15 moles) were refluxed in decalin under nitrogen for 6-7 hours and the mixture was left aside. After a month, the mixture was passed through a column packed with activated $Al_2O_3$ and eluted with $CHCl_3$. The first fraction was discarded. The second fraction was concentrated and again passed through a column packed with activated $Al_2O_3$ and eluted with $CHCl_3$. The second and last-fraction was concentrated and the petroleum ether was added to it when chromium porphine was precipitated. The solid was filtered and dried in vacuum at 100°. *Anal.* Calcd. for $C_{44}H_{33}O_3N_4Cr$: C, 73.60; H, 4.60; N, 7.80. Found: C, 73.69; H, 5.66; N, 5.60.

*Tetraphenylporphinemolybdylhydroxide,* O=Mo(OH)TPP(IV). TPP (1 mole) and $Mo(CO)_6$ (10-15 moles) were refluxed in deairated decalin under nitrogen for 6 hours. The decalin solution was passed through a column packed with activated $Al_2O_3$ and eluted with a column packed with activated $Al_2O_3$ and eluted with $CHCl_3$. The first-fraction contained chlorin. The second and last-fraction was concentrated and again passed through a column packed with activated $Al_2O_3$ using $CHCl_3$ as eluting agent. The first-fraction was discarded. The second and last-fraction was concentrated after adding xylene and kept aside. The crystals obtained were filtered, washed with xylene and dried in vacuum at 100°C. *Anal.* Calcd. for $C_{44}H_{29}O_2N_4Mo$: C, 71.26; H, 3.91; N, 7.56. Found: C, 71.30; H, 3.78; N, 7.36.

*Tetraphenylporphinemolybdylchloridehydrochloride,* O=Mo(Cl)TPP • HCl (VI). Mo(OH)TPP was dissolved in $CHCl_3$ and concentrated hydrochloric acid (few ml) was added and the solution was well shaken. The final solution was concentrated to dryness under reduced pressure. The residue was dissolved in $CHCl_3$ and xylene was added. The solution was kept for crystallization and the crystals obtained were filtered and dried in vacuum at 100°C. *Anal.* Calcd. for $C_{44}H_{29}OCl_2N_4Mo$: C, 66.33; H, 3.64; N, 7.04; Cl, 8.92. Found: C, 66.94; H, 3.62; N, 6.74; Cl, 8.40.

*Tetraphenylporphinemolybdylhydroperoxide.* O=Mo(OOH)TPP (V). O=Mo(Cl)TPP • HCl was dissolved in benzene and it was passed through a column packed with activated $Al_2O_3$ and teluted with a 1:1 mixture of benzene and $CHCl_3$. The first-fraction was discarded. The second and last-fraction was concentrated. The crystals obtained were filtered and dried in air. *Anal.* Calcd. for $C_{44}H_{29}O_3N_4Mo$: C, 69.75; H, 3.83; N, 7.40. Found: C, 69.81; H, 3.94; N, 6.99.

*Tetraphenylporphinemolybdylhydroxide dimer,* $[O=Mo(OH)TPP]_2$ . (VII). This compound was prepared by dissolving O=Mo(OH)TPP in pyridine. The solution was heated on a hot plate for one hour. The solution was then concentrated under reduced pressure after adding xylene and kept for crystallization. The solid obtained was filtered and dried in air. *Anal.* Calcd. for $C_{44}H_{22}O_2N_4Mo$: C, 71.26; H, 3.91; N, 7.56. Found: C, 71.36; H, 4.20; N, 7.33.

*Tetraphenylporphinemolybdyl . 2pyridine.* O=MoTPP . $py_2$ (VIII). O=Mo(OH)TPP was dissolved in excess pyridine and hydrazine was added to it in sufficient excess. Deoxygenated nitrogen gas was bubbled in the mixture for 14 hours. The final solution was concentrated to dryness under reduced pressure until the solid was obtained. This compound has properties similar to a molybdenum phthalocyanine that has been prepared.[19] *Anal.* Calcd. for $C_{54}H_{38}ON_6Mo$: C, 73.47; H, 4.31; N, 9.52. Found: C, 73.29; H, 4.56; N, 9.68.

## Results and Discussion

The properties and spectra of three new chromium porphyrins will be treated first, followed by the properties and spectra of the molybdenum porphyrins.

*Chromium Porphyrins.* The magnetic susceptibilities of Cr(OMe)TPP . 2MeOH (I) and Cr(OEt)TPP . 2EtOH (II) were measured by the Faraday Method

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and found to be:

$\mu_{eff}$ of I = 3.63 B.M. (294°K); 3.60 B.M. (79°K)

$\mu_{eff}$ II = 3.60 B.M. (294°K); 3.59 B.M. (79°K)

(B. M. stands for the Bohr Magneton).

**Table I.** Visible Absorption of Chromium Tetraphenylporphine*

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Cr(OMe)TPP . 2MeOH in CHCl$_3$ | | | | | | | | |
| Band | 3957 | 4357 | 5242 | 5579 | 5955 | 6267 Å | | |
| ε | 27 | 329 | 6.05 | 14.7 | 10.8 | 4.1 | | |
| Cr(OMe)TPP . 2MeOH in CHCl$_3$ (solution was shaken with one drop of Conc HCl) | | | | | | | | |
| Band | 3628 | 3873 (sh) | 3964 | 4488 | 5129 | 5256 | 5638 | 6017 Å |
| ε | 31 | 38 | 50 | 303 | 5.7 | 6.5 | 14. | 12. |
| Cr(OMe)TPP . 2MeOH in CHCl$_3$ (solution was shaken with one drop of hydrazine hydrate) | | | | | | | | |
| Band | 3654 | 4012 | 4545 | 5251 | 5653 | 6033 | 6275 Å | |
| ε | 43 | 54 | 216 | 6.2 | 13.4 | 14.1 | 4.4 | |
| Cr(OMe)TPP . 2MeOH in pyridine | | | | | | | | |
| Band | 3737 | 4095 | 4436 | 4454 | 5275 | 5697 | 6048 Å | |
| ε | 36 | 48 | 129 | 148 | 6.1 | 13. | 15. | |
| Cr(OMe)TPP . 2MeO in piperidine | | | | | | | | |
| Band | 3950 | 4422 | 4528 | 5185 | 5680 | 6054 | 6760 Å | |
| ε | 33 | 92 | 65 | 7.45 | 10.2 | 11.9 | 9.35 | |
| Cr(OEt)TPP . 2EtOH in CHCl$_3$ | | | | | | | | |
| Band | 3966 | 4363 | 5228 | 5575 | 5957 | 6265 Å | | |
| ε | 21.5 | 245 | 5.7 | 12 | 9.0 | 9.0 | | |
| Cr(OH)TPP . 2H$_2$O in CHCl$_3$ | | | | | | | | |
| Band | 3976 | 4499 | 5142 | 5221 | 5527 | 5909 | 6645 Å | |

* ε in $M^{-1}$ cm$^{-1}$ ×10$^3$.

The above chromium compounds appear to be monomeric species. The chromium ion is in the tripositive oxidation state in both compounds (for the Cr$^{III}$d$^3$ configuration $\mu_{eff}$ = 3.80 B.M.).

The N–H stretch (3324 cm$^{-1}$) and deformations (980, 725 cm$^{-1}$)[12,13] present in free TPP were not present in the ir spectra of Cr(OMe)TPP . 2MeOH, Cr(OEt)TPP . 3EtOH or Cr(OH)TPP . 2H$_2$O. Other ir absorptions are similar to those assigned for usual TPP or metallotetraphenylporphines.[14]

A summary of the visible absorptions of the chromium(III) of the chromium(III) and molybyl porphines is given in Table I.

The Cr(OMe)TPP . 2MeOH (I) interacts with pyridine, piperidine and hydrazine forming new species. Hydrochloric acid also interacts with I to form the metalloporphyrin chloride.

*Molybdenum Porphyrins.* The magnetic susceptibilities of O=Mo(OH)TPP (IV), O=Mo(OOH)TPP (V) and O=Mo(Cl)TPP . HCl (VI), measured by the Faraday Method, were found to be:

IV. $\mu_{eff}$ = 1.75 B.M. (294°K); 1.70 B.M. (79°K)

V. $\mu_{eff}$ = 1.76 B.M. (294°K); 1.72 B.M. (79°K)

VI. $\mu_{eff}$ = 1.74 B.M. (294°K); 1.68 B.M. (79°K)

The magnetic moments of the above compounds clearly support the fact that the molybdenum in these compounds has a formal oxidation number of five (d$^1$ configuration).

The esr spectra of the O=Mo(OH)TPP (IV), O=Mo(OOH)TPP (V), O = Mo(Cl)TPP . HCl (IV), O = [Mo(OH)TPP]$_2$ (VII) and O=MoTPP . 2py VIII) in

**Table II.** Visible Absorption of Molybdenum Tetraphenylporphine*

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| O=Mo(OH)TPP in C$_6$H$_6$ | | | | | | | | |
| Band | 4074 | 4449 | 5840 | 6146 | 6668 Å | | | |
| ε | 38 | 59 | 4.3 | 5.2 | 3.9 | | | |
| O=Mo(OH)TPP in pyridine | | | | | | | | |
| Band | 4022 (sh) | 4209 | 4479 | 5541 (sh) | 5516 | 6188 | 6472 Å | |
| ε | 25 | 59 | 89 | 4.1 | 6.6 | 6.2 | 3.8 | |
| O=Mo(OOH)TPP in C$_6$H$_6$ | | | | | | | | |
| Band | 4109 | 4451 | 5568 | 5844 | 6165 | 6408 (sh) | 6644 Å | |
| ε | 42 | 59 | 4.7 | 5.2 | 5.9 | 4.6 | 4.4 | |
| O=Mo(OOH)TPP in pyridine | | | | | | | | |
| Band | 4024 (sh) | 4206 | 4488 | 5479 (sh) | 5900 | 6139 | 6534 Å | |
| ε | 26.5 | 60 | 83 | 5.3 | 6.7 | 8.2 | 6.7 | |
| O=Mo(Cl)TPP . HCl in CHCl$_3$ | | | | | | | | |
| Band | 3824 (sh) | 4200 | 4476 | 5042 | 6312 | 6764 Å | | |
| ε | 42. | 32 | 27 | 44 | 8.9 | 9.5 | | |
| O=Mo(Cl)TPP . HCl in 1:1 mixture of CHCl$_3$ and CH$_3$OH | | | | | | | | |
| Band | 3712 (sh) | 4006 (sh) | 4782 | 6018 | 6470 Å | | | |
| ε | 38 | 32 | 56 | 11 | 8 | | | |
| (O=Mo(OH)TPP)$_2$ in C$_6$H$_6$ | | | | | | | | |
| Band | 4050 (sh) | 4209 | 4291 | 4554 | 4730 | 5712 | 6092 | 6512 Å |
| ε | 24 | 32 | 31 | 30 | 32 | 4.7 | 6.3 | 5.0 |
| O=MoTPP . 2py in pyridine containing hydrazine (5%) | | | | | | | | |
| Band | 3847 | 3790 (sh) | 4120 | 4341 | 4564 (sh) | 5403 | 5718 | 6497 Å |
| ε | 56 | 55 | 37 | 44 | 24 | 8.2 | 8.8 | 4.8 |

* ε is in $M^{-1}$ cm$^{-1}$ ×10$^3$.

appropriate solvents were measured and the parameters are in Table III.

**Table III.** Electron spin resonance results

| Compound | g Value | A* (Gauss) | Solvent |
|---|---|---|---|
| IV | 1.960 | 48 | benzene |
| V | 1.965 | 50 | benzene |
| VI | 1.969 | 50 | chloroform |
| VII | 1.963 | 49 | benzene |
| VIII | No signal was observed | | pyridine |

* A is the value of the hyperfine splitting due to the 5/2 spin of $^{95}$Mo and $^{97}$Mo.

The esr data[15] support the formal oxidation numbers of the molybdenum in the first four compounds as five. The last compound, VIII, does not show an esr signal and this may be due to the oxidation number of four for the molybdenum ($d^2$ configuration).[16] The hydrazine has reduced the $Mo^V$ to $Mo^{IV}$.

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**Table IV.** Infrared spectra of molybdenum porphynins

| Compound | O=M Vibrations | O–O Vibrations |
|---|---|---|
| IV | 901 (m), 648, 614 (vs) | |
| V | 901 (m), 649, 616 (vs) 941 (vs) | 1132 (s) |
| VII | 900 (m), 944 (s), 551, 619 (vs) | |
| VI | 990 (s) | |

The compound VIII, O=MoTPP, is similar in its magnetic and ir properties to the previously synthesized molybdenum phthalocyanine.[19]

The N–H stretch (3324 cm$^{-1}$) and deformations (980, 725 cm$^{-1}$)[12,13] present in free TPP were not present in the above mentioned five molybdenum porphines. Some of the absorptions found in these compounds are associated with molybdenum oxygen vibrations and they are tabulated in Table IV.

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