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Molybdenum(V) Tetraphenylporphyrin Complex(es)

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The conditions for the preparation of solutions, in some common solvents, of single species of molybdenum(V) tetraphenylporphyrin chloride complex, O=MoTPP(Cl) (I), molybdenum(V) tetraphenylporphyrin hydroxide complex, O=MoTPP(OH) (II), their respective hydrochlorides, O=MoTPP(Cl)·HCl (III), and O=MoTPP(OH)·HCl (IV), ethoxide complex, O=MoTPP(OEt) (V) and the μ-oxo-dimer, $O=MoTPP)_2O$ (VI) have been established. In contrast to the previous results, reproducible visible spectra, characteristic of metalloporphyrins were observed. Two sets of esr spectra, corresponding respectively to the interaction of d¹-electron of ^{96}Mo isotope with the nuclear moment of 4 nitrogen atoms of the porphyrin ring system and the interaction of d¹-electron of the ^{95}Mo and ^{97}Mo isotopes with the 5/2 nuclear moment of the same isotopes of molybdenum, were recorded for these solutions. The visible spectral results and the esr absorptions were found to be mutually consistent.

Introduction

The importance of metalloporphyrins of transition metals has already been stressed correctly [1, 2]. The oxidation–reduction properties of metalloporphyrins play a major role in their biochemical and biological function. The importance of these model compounds can be discerned from published work [1–6]. The importance of oxomolybdenum(V) compounds in a number of biochemical reactions [7] and in the development of theories of bonding in their coordination compounds [8] is also noteworthy.

Many workers [9–19] have reported synthetic, spectral and crystallographic studies on oxomolybdenum(V) porphyrin complexes. Because of the highly reactive nature of these products, the visible and esr spectra are not unambiguous. The assignment of spectral absorbances has therefore been tentative and rationalizations are based on conjecture.

Fleischer and Srivastava [9, 10] reported on the preparation and characterization of O=MoTPP(OH), O=MoTPP(OOH), O=MoTPP(Cl) and $[O=MoTPP(OH)]_2$. Both reports record more than one Soret band (400–500 nm region) and more than two absorptions in the 500–700 nm visible region indicating more than one species present in the solution. The spectra [10] of the first two compounds in pyridine and of the third in a mixture of chloroform and methanol are equally ambiguous. Newton [20] and Newton and Davis [2] characterized the visible spectral band as more complicated than expected and likened it to the 'manganese(III) type' spectra studied by Boucher [21]. Traces of the spectra were not published. However recorded visible spectra in Newton's Dissertation [20] showed that absorption lines were broad and overlapping and were merely supporting reported results [2, 9, 10].

The esr spectra of these compounds were first reported [9, 10] with a g-value of 1.964 ± 0.003 and hyperfine coupling constant A_{Mo} = 49.0 ± 1.0 G in chloroform or benzene solution. Newton and Davis [2], on the other hand reported an esr spectrum consisting of 9 evenly spaced, 2.5 G apart lines with a total signal width of 28 G and a g-value of 1.9742.

It is noteworthy that esr spectra reported by these workers [2, 9, 10, 20], for the same (supposed) compounds were so different; in one report [10] the hyperfine splittings are due to the interaction of d^1-electron with a nuclear spin moment of 5/2 for the isotopes ^{95}Mo and ^{97}Mo without any mention of an absorption due to the d^1-electron of the more abundant isotope ^{96}Mo with zero nuclear spin moment, while in the other reports [2, 20] the splitting is due to a hyperfine coupling of d^1-electron of ^{96}Mo isotope and the nuclear spin moment of four equivalent nitrogen atoms of the porphyrin ring. For the same product this is rather difficult to rationalize.

The present study is concerned with these ambiguities and is based on visible and esr spectra of

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TABLE I. Visible Absorbances of Molybdenum Complexes in Solutions.

Spectrum Number	Absorbance Maxima (in nm units)			Solvent	Remarks
1	629	588	456	$CHCl_3$	Green, obtained on reaction mixture and separated product.
2	635	595	461	$CHCl_3$	Greenish yellow to light yellow.
2a	632	590	461	$CHCl_3$	Acetone, used to release adsorbed product, present in solution, though only relatively small.
2b	633	595	461	$CHCl_3$	Pyridine used as acetone in above case
2c	625	585	456	Acetone	Released from acidic alumina
2d	623	580	453	Ethanol	Released from acidic alumina
3	680	632	500	$CHCl_3$	Brown. HCl treatment of product in Table I-1
4	682	634	504	$CHCl_3$	HCl treatment of product in Table I-2
5	626	586	453	Ethanol	Crystallized chloride complex corresponding to product Table I-1 in Ethanol
6	627	578	450	Acetone	Intense green
7	620	581	452	C_6H_6, CH_2Cl_2, DMSO, Pyridine	Intense green
8	622	582	453	Ethanol	Intense green
9	675	630	498	C_6H_6, CH_2Cl_2, pyridine $CHCl_3$	Yellowish brown
10	656	611	483	DMSO	
11	650	605	480	Ethanol	

the complex oxomolybdenum(V) tetraphenylporphyrin, O=MoTPP(X) where x is an anionic ligand.

Experimental

Benzonitrile (Aldrich Chemical) was dried over phosphorus pentoxide and distilled before use.

Tetraphenylporphine was prepared according to the literature [22].

Molybdenum(V) oxytrichloride (K and K Laboratories) was used as available.

All other reagents and solvents used were Analar or Spectrograde quality. When required these were dried over dry alumina (grade 1 or higher) and filtered through a sintered glass crucible having a bed of alumina.

A Cary-17 Spectrophotometer, Varian Instrument Division, was used to obtain the visible spectra.

A Varian E-3 Epr Spectrometer System was used to obtain the esr spectra. The g-value was calibrated against DPPH using the Spectrometer System provided with a dual epr cavity.

Preparation of Oxo-molybdenum(V) Tetraphenylporphyrin Complex [23], *O=MoTPP(X)*

Benzonitrile (35 ml) and tetraphenylporphine, $TPPH_2$ (400 mg), were brought to a near reflux in a 100 ml ground jointed flask, fitted with a condensor and an arrangement for dry nitrogen connection.

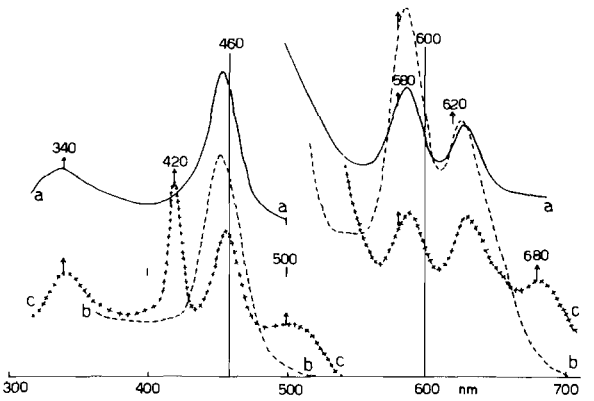


Fig. 1. Visible spectra of O=MoTPP(X) complex. a, Freshly prepared or crystallized product in $CHCl_3$; b, same in ethanol; c, same exposed to limited acid moiety in $CHCl_3$.

Molybdenum(V) oxytrichloride, 1 g, was added in small amounts at a time. The mixture was refluxed for 5.5 hours when a reaction mixture aliquot on the tip of nickel spatula dissolved in chloroform gave a typical metalloporphyrin spectrum, Fig. 1a, with no absorptions for the free porphine or its hydrochloride. The absorptions were 629, 588, 456 nm.

The reaction product was purified by removal of the solvent by distillation under reduced pressure, followed by chromatography of the solid residue over alumina (A-540 Fischer Scientific) in a 15″ high

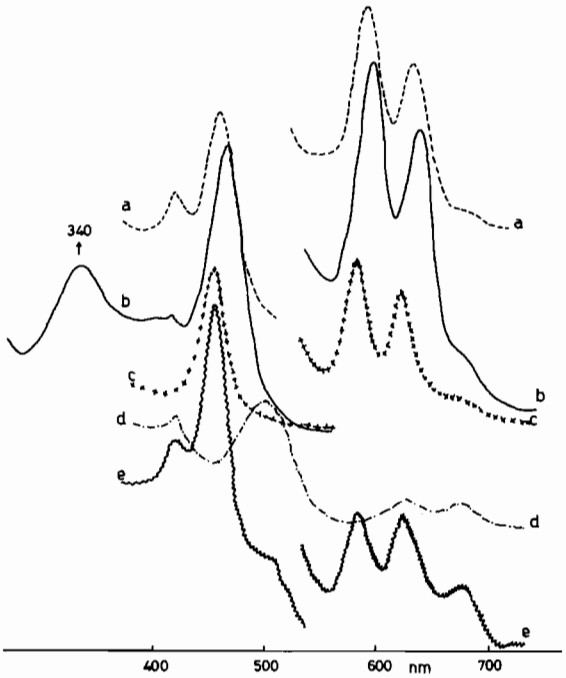


Fig. 2. Visible spectra of O=MoTPP(X) complexes. a, Freshly prepared product in CH_2Cl_2; b, chloride complex in $CHCl_3$; c, hydroxide complex in acetone; d, hydrochloride of hydroxide complex in $CHCl_3$; e, hydroxide complex exposed to limited acid moiety in CH_2Cl_2.

column using chloroform as the eluant. The first fraction contained a small amount of $TPPH_2$ as indicated by its visible spectrum.

Results and Discussion

Visible Spectra

The stable and easily reproducible species of molybdenum(V) tetraphenylporphyrin complex O=MoTPP(X) that was prepared, crystallized, and characterized is represented in Fig. 1a and Fig. 2a by a typical metalloporphyrin spectrum with a single intense soret absorption in the 400–500 nm region, and two α and β absorptions in the 500–700 nm region. The absorption peaks for this spectrum are recorded in Table I-1. The absorption at 340 nm is not characteristic of the metalloporphyrins and therefore will not be discussed.

This spectrum with the same absorptions was obtained under various circumstances and conditions. It was recorded when a run was made on a chloroform solution obtained by dissolving a small aliquot drawn from the hot reaction mixture on the tip of a spatula. The same spectrum was realized on a chloroform solution of the main green portion of the chromatographed product. It was obtained by dissolving a crystalline product of the chromatographed green portion. On standing the solution of this product changes in color and spectrum which could be restored by shaking the chloroform solution with a small amount of neutral alumina (Fisher Scientific) of high grade (*i.e.* with higher content of water). Even though color and spectrum of the solutions changed rapidly, the solutions made in solvents that were freshly distilled and treated with neutral and basic aluminia were stable over indefinite periods of time in closed vessels, that were rendered acid free.

On exposure to open environment of the laboratory over a relatively longer period, repeated treatment with solvents from reagent bottles, the green solutions of this product in chloroform, dichloromethane, benzene, acetone, etc. changed to brown color. More dramatically the exposure of its green solution in any of the above solvents to a vapor of hydrochloric acid gas from the acid bottle turned it instantly to a brown solution; the green color could be restored once again by shaking the solution with requisite amount of alumina. This green solution gave the same spectrum as in Table I-1.

Chlorohydrocarbons, hydrocarbons, acetone, ether, etc. indicated no solvent effect suggesting no coordination, solvation or hydrogen bonding with these solvents. However, there are noticeable differences in their ability to elute the product over alumina, the decreasing order of R_f values is acetone $> CHCl_3 > CH_2Cl_2 > C_6H_6 >$ hydrocarbons.

On treatment of green solution of this product in chloroform with hydrogen chloride gas and passing of the resultant solution over a small bed of acidic (preferably) or neutral alumina of high grade in a fritted glass crucible, it gave a spectrum Fig. 2b, absorbing at a slightly longer wavelength. The absorbances are recorded in Table I-2. The solution had a greenish yellow color and could also be reproduced by adsorbing the brown solution obtained by treating the green solution with excess of hydrochloric acid gas, on dry acidic alumina, eluting with chloroform any impurities, followed by adding a small amount of acetone to release the adsorbed complex and washing it down with chloroform.

The green solutions corresponding to absorbances, Table I-1, on treatment with hydrochloric acid gas or long exposure to open environment of the laboratory (effected more efficiently by repeated solution and solvent evaporation) gave a spectrum shown in Fig. 2d while absorbances are recorded in Table I-3. In the same manner greenish yellow solution corresponding to absorbances in Table I-2 generated a spectrum similar to Fig. 2d but the absorbances were correspondingly displaced to a longer wavelength: absorbances were as in Table I-4.

On treatment of the green solution with hydrochloric acid gas or even exposure to the open air in the laboratory caused demetallation as indicated by absorbances at 419–20 nm and 444–46 nm cor-

responding to the parent tetraphenylporphine, $TPPH_2$ and its hydrochloride. On passing the brown solutions over neutral alumina the 420 nm absorption still persists in the green solution. $TPPH_2$ could, however be eluted with chloroform, when dry (low grade) neutral alumina adsorbed the complex and characterized by its spectrum or that of its hydrochloride.

The solutes represented by absorbances recorded in Table I-2 and Table I-4 appear to correspond to the chloride complex, O=MoTPP(Cl) I and its hydrochloride III, whereas those corresponding to Table I-1 and Table I-3 may have some of the hydrolysed product, O=MoTPP(OH) II and its hydrochloride IV explaining small shifts in the absorptions to lower wavelength.

The solid product corresponding to the chloride complex Table I-1 in ethanol gives a spectrum identical in form to that for the chloride complex, but absorbs at a smaller wavelength, *cf.* Fig. 1b (superimposed for comparison) and Table I-5. This may indicate that chloride complex is stable to reaction with alcohol to form its ethoxide and the small shift may be attributed to solvent effect or an equilibrium between the chloride and ethoxide complex as below.

$$O{=}MoTPP\ Cl + C_2H_5OH \rightleftharpoons O{=}MoTPP(OC_2H_5) + HCl \qquad (1)$$

The chloride complex solution if passed over an 8–10 inch column of anhydrous basic alumina, eluted with chloroform to remove any impurities or decomposition products such as $TPPH_2$, followed by extraction with acetone gave a spectrum, Fig. 2c (*cf.* Fig. Ia) that absorbed at a smaller wavelength, Table I-6. If the procedure above was repeated with neutral alumina, the result above could be reproduced.

This product when carefully handled in acid-free solvents and protected from laboratory environment gave spectra with ±1 nm in chloroform, dichloromethane, benzene, DMSO, pyridine, acetone, *etc.*, the absorptions being recorded Table I-7. This product most likely is a monomeric hydroxide complex O=MoTPP(OH) (II).

These absorptions were also reproduced by treating the chloride complex, Table I-1, I-2 and the hydrochloride complex Table, I-3, I-4 with sodium hydroxide solution or by eluting over basic alumina.

This hydroxide complex in absolute ethanol absorbed, Table I-8, at a slightly longer wavelength as compared to the hydroxide complex in other solvents, but at a smaller wavelength than chloride complex in ethanol Table I-5. The form of the spectrum is identical to the chloride or hydroxide complex. This then represents its ethoxide, $O{=}MoTPP(OC_2H_5)$ or the following equilibrium.

$$O{=}MoTPP(OH) + C_2H_5OH \rightleftharpoons O{=}MoTPP(OC_2H_5) + H_2O \qquad (2)$$

Like the chloride complex the hydroxide complex does not indicate any significant concentration or solvent effect over a 100-fold change in concentration in hydrocarbon solvents and acetone.

As compared to the color of chloride complex in solutions the color of the hydroxide complex is intense green. It does not form crystals with the same ease as the chloride; it rather forms flakes which may or may not be crystalline.

When hydroxide complex, O=MoTPP(OH), in solution in various solvents was exposed to hydrochloric acid gas (this could simply and usually be done by taking a dropperful or pipetful of the gas from concentrated acid acid bottle and pouring it over the swirled solution or by bubbling it through it) it turned into yellowish brown solution. The absorbances in different solvents were within ±1 nm range in the 500–700 nm region and ±3 nm in the 400–500 nm region. A typical spectrum is similar to that shown in Fig. 2d and the absorptions are recorded in Table I-9.

The absorptions of the hydroxide hydrochloride complex, O=MoTPP(OH)·HCl (IV) were same in form, but absorbed at about 6 nm shorter wavelength as compared to those of the chloride hydrochloride complex III (*cf.* Table I-4). Acetone solutions, however, absorbed at another 1–2 nm shorter in wavelength.

Any excess application of hydrochloric acid gas did not alter the positions of absorbances. Treatment of complex II with hydrochloric acid gas as that of the chloride complex I effected some demetallation. That demetallation has taken place is confirmed by an absorbance at 420 nm.

It is worth observing here that in case of hydrocarbon solvents when the solutions of the chloride or hydroxide complex are exposed to insufficient hydrochloric acid gas absorptions for both the parent complex and its hydrochloride are observed as shown in Figs. 1c and 2e and the absorbances for the spectra are recorded below (in nm units):

680 629 588 500 456; For chloride complex; *cf.* Fig. Ic

675 620 578 494 451; For hydroxide complex; *cf.* Fig. 2e.

The relative concentration of complex I and its hydrochloride and complex II and its hydrochloride can vary depending upon exposure to acid moiety. However, in case of basic solvents with available electron-donor atoms, absorptions in the Soret region are intermediate and broad probably due to the hydrochloric acid exchange between the complex and the solvent. The hydroxide complex in DMSO and ethanol, on treatment with hydrochloric acid gas did

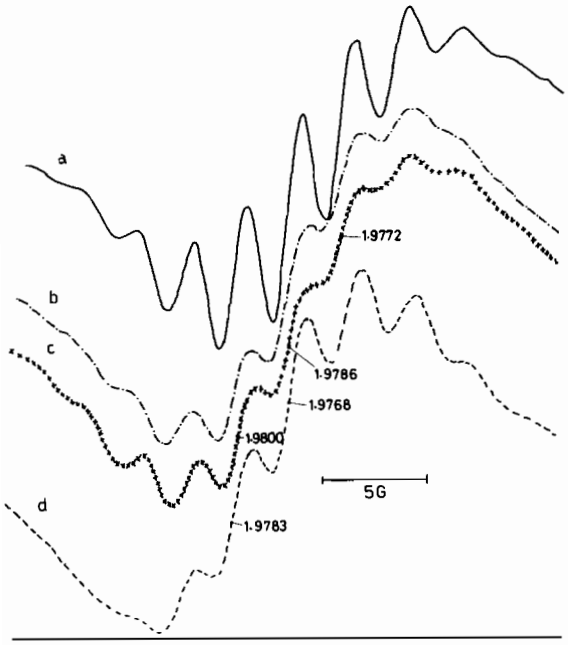


Fig. 3. Esr spectra of O=MoTPP(X) complexes. a, Chloride complex in chloroform, MA = 1; b, same exposed to acid moiety in chloroform, MA = 4; c, same in absolute ethanol, Ma = 5; d, same in DMSO, MA = 4.

not absorb at the same wavelengths as it did in other solvents. Some of the typical absorptions are recorded in Table I-10 and I-11.

The hydrochloride of the hydroxide complex was chromatographed over dry neutral or basic alumina with large amount of chloroform to get rid of the impurities followed by extraction with a solution of acetone and chloroform. The mixed solvent was evaporated off. The spectrum of a chloroform solution of this product had absorptions at 653, 609, 490 nm. A similar spectrum was recorded in dichloromethane for a solid product obtained on extracting the alumina adsorbed complex with acetone.

The solution in chloroform for which a spectrum is recorded above indicated a negligible dilution effect in the 500–750 nm region, but in the 400–500 nm region the effect was significant as the data below will indicate:

Relative Conc.	Absorbances (nm)		
1.0	653	609	490
0.5	653	608	486
0.1	652	610	484
0.05	652	610	481
0.01	–	–	480

The 480–490 nm absorption above is broader than the Soret absorption at 450–460 nm for the chloride I, and the hydroxide II, monomer complexes, but is narrower than the 500 nm absorption for the hydro-

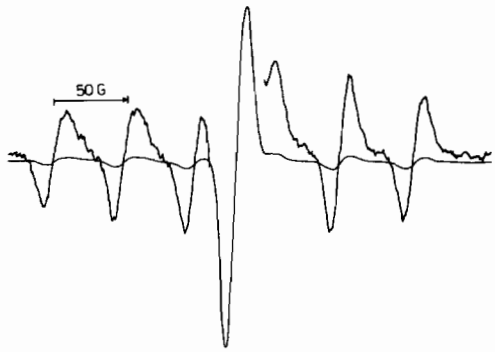


Fig. 4. Esr spectrum of O=MoTPP(X) complex. Chloride complex in chloroform Ma = 10.

chloride complexes III and IV of these two monomers. This product is most likely the dimer $(O{=}MoTPP)_2O$, as discussed later.

On treating the solution above with hydrochloric acid gas, the spectrum of the resultant brown solution corresponded with the one for the hydrochloride of the hydroxide complex IV with absorptions at 674, 625, 496 nm.

Electron Spin Resonance Spectra

The solutions of crystalline or purified chromatographed molybdenum tetraphenylporphyrin complex O=MoTPP(X) in different solvents gave a complex esr spectrum with two sets of parameters as shown in Figs. 3 and 4.

A set of intense, narrow, nine absorptions with relative intensities in the ratio of 1, 4, 10, 16, 19, 16, 10, 4, 1, were observed, and are shown in Fig. 3a. The spectrum parameters are included in Table II.

The parameters in Line 1 & 2, Table II, indicate that complex species in these solutions are single. However, as the product becomes more than one species on exposure to limited acid moiety, the apparent LW becomes broad as in Line 4 Table II, Fig. 2b, but on treatment of the solution with excess hydrochloric acid, the LW becomes slightly narrow indicating a single species with the parameter included in Line 5, Table II.

Line 6, Table II, has the result for the hydroxide complex; its g-value is comparable to the one for the chloride complex but LW is narrower (*cf.* Fig. 3a) as indicated by a better resolution and probably indicates the absence of even a minor impurity.

Slightly air exposed solution, having picked up some acid from the atmosphere results in slight broadening of the LW and indicating a lower resolution of the lines. In these cases a small amount of ethanol will improve the resolution and give a narrower LW. However, in other cases addition of small amount of ethanol into CH_2Cl_2 solution broadened the LW indicating that the original solution was a mixture of the chloride and hydroxide complexes

TABLE II. Esr Parameters of Molybdenum Complexes.

Line No.	Complex	Solvent	g-value	A_N	A_{Mo}	LW	Remarks
1	O=MoTPP(Cl)	$CHCl_3$	1.9665	2.50		1.25	g-value calibrated against DPPH
2	O=MoTPP(Cl)	$CHCl_3$	1.9800	2.50		1.25	g-value calculated from parameters
3	O=MoTPP(Cl)	CH_2Cl_2	1.9770	2.50		1.45	Modulation study; Min. LW 1.25 G; peak to peak total at MA 8, 10.75 G. Limited air exposure.
4	O=MoTPP(Cl)	$CHCl_3$	1.9767	2.50		1.65–1.85	LW varies from line to line and depending on the extent of exposure to air.
5	O=MoTPPCl·HCl	$CHCl_3$	1.9764	2.5		1.6	When solution is treated with HCl most likely a single species exists.
6	O=MoTPP(OH)	$CHCl_3$	1.9799	2.5		1.25	LW is same for all lines
7	O=MoTPP(Cl)	C_2H_5OH	1.9800				LW varying from 1.5 to 2.4 G depending upon resolution
			1.9786	2.3			
			1.9772				
8	O=MoTPP(Cl)	DMSO	1.9783	2.5			LW varying from 1.5 to 2.4 G depending upon resolution
			1.9768				
9	Various Above	Various Above	1.9781 ± 0.0013		48.5 ± 0.5	12.0 ± 0.5	Parameters are not affected by conditions of solvent and solution.

which both have same g-value and LW, but addition of alcohol differentiates them, the overlap of lines resulting in broadening of lines to 1.8–1.9 G; however peak to peak separation is lowered insignificantly. The same chloride product in pure ethanol, Fig. 3c, resulted in a spectrum with 11 absorption lines instead of the 9 expected and the g-value of the center line is 1.9786. Careful scrutiny lends support to the observation that two nonets are overlapped with a separation equivalent to two times the A_N value, the g-values of the 5th and 7th absorption lines on either side of the central line are 1.9800 and 1.9772. A slight difference in the A_N values of the two absorption systems can explain why lowfield half of the 11 line spectrum is better resolved than the other half. On the other hand esr spectrum in DMSO solution gives a ten line absorption spectrum, Fig. 3d confirming that the two species absorb only at a one A_N separation from each other. The data are included in lines 7 and 8, Table II. It is observed that ethanol solution spectrum shows its highfield half less well resolved in contrast to the case of DMSO solution. In these two spectra the LW for lines on the well resolved side is 1.5 G and increases steadily to beyond the A_N value.

Considering the general properties of the nonet, it is noted that peak to peak line width of each individual hyperfine absorption varies from 1.25 to 1.75 G depending upon the solvent or the complex. The peak to peak line width for the entire set is 10-11 G, before broadening starts at higher modulation amplitude. The superhyperfine splitting parameter A_N is very close to 2.5 G and is not subject to much change. The intensity ratio of these lines is characteristic of the hyperfine splitting due to the interaction of four equivalent nitrogen-14 atoms (with nuclear spin moments of 1) of the porphyrin ring, with d′-electron of the molybdenum-96 (with nuclear spin moment of zero).

Another set of six lines with intensity of absorptions an order of magnitude lower, but of equal strength, corresponding to the interaction of nuclear spin moment of 5/2 of molybdenum-95 and molybdenum-97 isotopes with d′-electron of the same isotopes with a calculated g-value of 1.9781 ± 0.0013, hyperfine constant A_{Mo} of 48.0 ± 0.5 G and an average peak to peak line width of 12.0 ± 0.5 G was observed. The parameters are included in Table II, line 9 and a spectrum is represented by Fig. 4. The data for this set of absorptions indicated that the nature of the complex and solvent had no effect on the g-value and LW parameter. Therefore it may be stipulated that in the study of the nonet spectrum of molybdenum complex this absorption sextet can be used as a standard internal marker.

No superhyperfine interaction due to 4 nitrogen atoms of the porphyrin ring on sextet absorptions could be observed. This seems to be due to the

imperfect overlapping of the absorptions for individual molybdenum-95 and molybdenum-97 isotopes. The same reason may account for the slightly unequal absorption components of the sextet.

It is worthy of note that highfield half of the intense nine line spectrum is overlapping with the lowfield end of the 4th line of the sextet going from lowfield to highfield. This may result in a slightly lower resolution of the hyperfine lines on the highfield side of the nonet. This will however be the same if the nonet shifts do overlap with the lower field absorption of the sextet.

A modulation amplitude of 5 G or less does not change the line characteristics. At modulation amplitude of 8 G the line broadening almost obscures the fine structure. Between modulation amplitude of 0.63 G and 5.00 G, the splitting constant A_N for the nonet is 2.5 G for O=MoTPP(X) in CH_2Cl_2. The exposed or hydrochloric acid gas exposed sample shows line broadening; lowering of modulation amplitude and power alteration does not affect the line width.

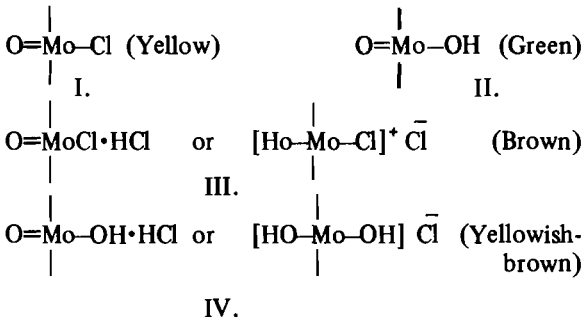
Power broadening takes place at 13 mW or higher power. Concentration has no effect on line width. In a mixture of ethanol and dichloromethane or chloroform the line width increases.

Contrary to the observations in the literature [2, 20], esr spectrum could be recorded in DMSO as the solvent, without any difficulty.

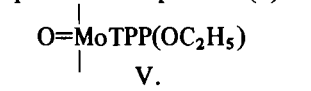
Discussion and Conclusion

In the visible absorbances of molybdenum(V) tetraphenyl porphyrin complexes recorded by Fleischer and Srivastava [10] and later supported by Newton [20] and Davis [2] the absorption bands observed were not the overlaps of the bands of complexes considered by them; stronger absorbances characteristic of the parent porphine, $TPPH_2$ itself (554, 420 nm) and its hydrochloride, $TPPH_2 \cdot 2HCl$ (665–7, 445–7 nm) were present with likely small shifts in the peaks due to overlap with bands of molybdenum complexes of interest. In the present study as outlined above the absorptions due to parent porphine and its hydrochloride were also observed but were eliminated by treatment with neutral alumina when chloroform eluted the porphine and its hydrochloride. Alternatively, acetone as the solvent carries the complex down leaving the parent porphine and its hydrochloride in the alumina matrix. In the absence of these two impurities, the spectra became simple and characteristic of the metalloporphyrins as described in detail above.

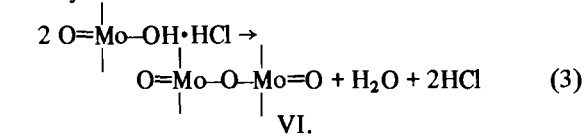
Thus the species characterized in hydrocarbon solvents are the chloride and the hydroxide complexes and their hydrochlorides with the structures proposed as follows:



Besides these four species the chloride and hydroxide complexes in absolute ethanol absorb at slightly different wavelengths supporting our contention that the hydroxide gives a monomeric ethoxide V whereas the chloride complex in ethanol has both species as in equilibria (1) and (2) above.



The product corresponding to IV above when taken in DMSO or ethanol absorbs differently. Dehydration or dehydrochlorination or both processes could take place. Dehydration would give the chloride complex and dehydrochlorination would lead to the hydroxide complex. The spectra do not agree with any of these products. Thus the most likely process is both dehydration and dehydrochlorination leading to the μ-oxo dimer product, VI as in equilibrium 3 below and giving the corresponding spectrum as already detailed.



The solid obtained from the hydroxide complex in chloroform and dichloromethane gave spectra corroborative with the above. The complex is elusive to observe as traces of acids can lead to a spectrum corresponding to product IV.

Two recent studies [16, 17] on the molybdenum(V) complexes of cyclic tetrapyrrolic ligands have recorded spectra characteristic of the metalloporphyrins, with one Soret type band and the α and β bands. The authors [16] concluded that the complex exists as a monomer species. However, in their second study [17] they suggest dimerization. The spectrum of the ethoxide complex O=MoTPP(OC_2H_5) agrees with our spectrum. Other two spectra recorded were for the octaethylporphyrin complexes which have, previously, been characterized by Buchler *et al.* [11–13], as monomeric. The spectrum [17] for the chloride complex has one feature common with our hydrochloride complex of the chloride or hydroxide in that 400–500 nm absorption is broad and absorbs at 497 nm. Instead in the

500–750 nm region there is only one absorption. This may be due to the closeness of these two absorptions or due to an overlapping band due to unknown impurities.

A more interesting observation was that their tetraphenylporphyrin complex in benzene had two Soret and 3 bands in visible proper region [17]. As indicated in our results this shows the presence of the monomer and its hydrochloride and stands explained itself.

It may be mentioned here that Buchler and coworkers [11–14] have observed and reported characteristic metalloporphyrin spectra for the octethylporphyrin (OEP) complexes of molybdenum *i.e.* O=MoOEP(OEt), O=MoOEP(OPh), O=MoOEP(OAc). From their results it appears that O=MoOEP(OMe) could not be prepared pure. Even though no attempt was made to prepare the methoxide complex by us, we could say on the basis of our experience with preparation of ethoxide complex that the previous authors' failure to do so was due to the use of the mainly chloride complex in its preparation, which according to equilibrium (1) is not favourable. Tungsten analogues [13] gave normal spectra.

Finally we may comment on the observation of Buchler *et al.* [14] that the existence of O=MoTPP-(OH) is not possible. From our results it is observed that the chloride complex is the predominant species in absolute ethanol, whereas the hydroxide complex is converted to the alkoxide complex, with an overall equilibrium being in favor of the latter species. This can only be explained on the basis of a very stable hydroxide complex, but basic enough to exist independently. The basic properties of the complex give a more stable chloride complex rather than the alkoxide complex. However, the hydroxide complex will form an alkoxide complex in absolute ethanol, in the same manner as the alkali hydroxides *vis à vis* alkali chlorides.

Our electron spin resonance spectra disagree with earlier workers [2, 20] and agree with more recent workers [16, 17] in that there are two sets of esr absorption bands. The results in Table II support that esr spectra corroborate with monomeric species [18], our parameters varying slightly with different conditions of solute and solution. In ethanol solution the eleven line spectrum represents the chloride complex I and ethoxide complex V with respective g-values of 1.9800 and 1.9772. Similarly in DMSO solution the ten line spectrum corresponds to the chloride complex I and hydroxide complex II with respective g-values of 1.9783 and 1.9768. The solvent effect and nature of the solute species accounts for the relative difference in g-values. On the basis of our experience in this research it is appropriate to support the conclusion [18] that esr spectrum for the dimer complex VI would be hard to observe in solution.

The visible and esr spectral results therefore are mutually consistent with the presence of complex species I–V in solution. More concerted effort is required to establish the dimer species VI in solid and solution state, to relate an esr spectrum with its presence. The spectrum in the visible region does however confirm the dimer species VI.

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