Inorg. Chem. **1980**, *19*, 3488–3491

Contribution from the Centre National de la Recherche Scientifique,
Institut de Recherches sur la Catalyse, 69626 Villeurbanne Cêdex, France

Molybdenum(V) Tetraphenylporphyrin Complexes Revisited. Preparation and Characterization of Oxohydroxo(5,10,15,20-tetraphenylporphyrinato)molybdenum(V), O═Mo(TPP)OH

HENRY J. LEDON,* MICHEL C. BONNET, YVES BRIGANDAT, and FRANÇOIS VARESCON

Received February 25, 1980

UV–visible spectra of CH_2Cl_2 solutions of several oxo(5,10,15,20-tetraphenylporphyrinato)molybdenum(V) complexes, O═Mo(TPP)X (X = Cl, OMe, OEt, O(*i*-Pr), O(*t*-Bu)) have been reexamined. The positions and intensities of the absorptions are extremely sensitive to the nature of the axial ligand X. The hydroxo complex O═Mo(TPP)OH (**2**) has been prepared by reaction of O═Mo(TPP)Cl with aqueous NaOH and characterized, both in solution and in the solid state, by IR spectroscopy, including ^{18}O and ^2H labeling experiments. Reaction of **2** with diazomethane afforded the methoxo complex O═Mo(TPP)OMe. Selective crystallization of the μ-oxo dimer $[O{=}Mo(TPP)]_2O$ was observed when a CH_2Cl_2 solution of O═Mo(TPP)OH was concentrated in the presence of aromatic solvents. Factors which may determine the hydroxo vs. μ-oxo axial ligation are discussed.

Introduction

A recent paper by Bains and Davis[1] reports the preparation and some spectroscopic data of several oxo(5,10,15,20-tetraphenylporphyrinato)molybdenum(V) complexes, O═Mo(TPP)X. Their interpretation of the UV–visible spectra of these compounds rests on the assumption that reaction of the free-base H_2TPP with $O{=}MoCl_3$, in refluxing benzonitrile, affords the chloride complex O═Mo(TPP)Cl (**1**). Unfortunately, no unambiguous physical method or even elemental analysis was provided to support this structure.[2] We have previously reported a synthesis of O═Mo(TPP)Cl (**1**) and its full characterization by X-ray crystal structure analysis.[3] For this compound, our published UV–visible spectrum is clearly at variance with the absorbances reported by Bains and Davis, and therefore, the UV–visible spectra of O═Mo(TPP)X complexes have been completely misinterpreted by these authors. We wish to present here a reinvestigation of the nature of O═Mo(TPP)X complexes in solution.

Experimental Section

Techniques and Instrumentation. All solvents were purified following standard procedures[4] and kept under argon. Just prior use, they were passed on a small column of alumina (2 × 10 cm, Merck, neutral, activity grade I) under argon. All manipulations were performed with use of Schlenk-tube techniques[5] under argon in order to avoid any atmospheric contamination.

UV–visible spectra were recorded on a Cary 19 Varian Associates spectrophotometer using two 10-mm matched quartz cells for the solutions and on an Optica CF-4 spectrophotometer, using MgO as reference, for the solid diffuse reflectance spectra.

IR spectra were obtained on a Perkin-Elmer 580 spectrophotometer, using 1% KBr pellets for the solids and two variable-path cells for CH_2Cl_2 solutions fitted with KBr windows ($1000–500\text{-cm}^{-1}$ region) or CaF_2 windows ($3000–2500\text{-cm}^{-1}$ region).

X-Band ESR spectra were recorded at room temperature on a Varian E-9 spectrometer using DPPH as internal standard.

Elemental analyses were carried out by the Service Central de Microanalyse du CNRS in Lyon.

Preparation of Complexes. O═Mo(TPP)Cl (**1**)[3] and $[O{=}Mo(TPP)]_2O$ (**3**)[6,7] were prepared following published procedures. The alkoxo complexes O═Mo(TPP)OR (**4**) were obtained by chromatography of **1** over alumina (Merck, neutral, activity grade III, eluant CH_2Cl_2–ROH (80:20)) followed by crystallization from CH_2Cl_2–ROH as previously reported.[7] They were dried overnight under high vacuum and characterized by their IR spectra.

O═Mo(TPP)OMe (4a):[21] yield 90%; IR 2799 w (ν_{C-H}), 1116 m (ν_{C-O}), 905 vs ($\nu_{Mo=O}$), and 475 cm^{-1} w (ν_{Mo-O}) in excellent agreement with the spectrum reported for the related octaethylporphyrin complex O═Mo(OEP)OMe.[10] Anal. Calcd for $C_{45}H_{31}N_4O_2Mo{\cdot}0.08CH_2Cl_2$: C, 71.01; H, 4.12; N, 7.35; Mo, 12.58; Cl, 0.75. Found: C, 71.24; H, 4.36; N, 7.11; Mo, 12.5; Cl, 0.75.

O═Mo(TPP)OEt (4b): yield 89%; IR 2958, 2930, 2855, 2835 vw (ν_{C-H}), 1127 m (ν_{C-O}), 901 vs ($\nu_{Mo=O}$), and 520 cm^{-1} w (ν_{Mo-O}). Anal. Calcd for $C_{46}H_{33}N_4O_2Mo{\cdot}0.18CH_2Cl_2$: C, 70.66; H, 4.28; N, 7.14; Mo, 12.22; Cl, 1.63. Found: C, 70.14; H, 4.27; N, 6.81; Mo, 11.9; Cl, 1.63.

O═Mo(TPP)O(*i*-Pr) (4c): yield 93%; IR 2958 w, 2910, 2855 vw (ν_{C-H}), 1145 m (ν_{C-O}), and 904 cm^{-1} vs ($\nu_{Mo=O}$).

O═Mo(TPP)O(*t*-Bu) (4d): yield 92%; IR 2958 m (ν_{C-H}), 1198 m (ν_{C-O}), 902 vs ($\nu_{Mo=O}$), and 518 cm^{-1} w (ν_{Mo-O}).

No satisfactory elemental analyses were obtained for **4c** and **4d**, even after prolonged drying under high vacuum. A reasonable agreement between the calculated and found values could only be achieved by including both CH_2Cl_2 and the alcohol as solvation molecules.

O═Mo(TPP) (2). A brown solution of O═Mo(TPP)Cl (50 mg) in CH_2Cl_2 (100 mL) was vigorously stirred with an aqueous solution of sodium hydroxide (1 N; 10 mL) for 3 h. The organic layer was separated and filtered on a small column of alumina (Merck, neutral, activity grade III). Elution with purified CH_2Cl_2 and evaporation of the solvent under a slow stream of argon afforded a green solid which was dried overnight under vacuum. Anal. Calcd: C, 71.26; N, 7.55; H, 3.94. Found: C, 71.50; N, 7.44; H, 3.95; Cl, not detectable.

However, when benzene was added to a solution of O═Mo(TPP)OH in CH_2Cl_2 and the mixture concentrated under reduced pressure, dark blue crystals of the μ-oxo complex $[O{=}Mo(TPP)]_2O$ were obtained. Anal. Calcd: C, 72.13; N, 7.65; H, 3.85. Found: C, 72.74; N, 7.66; H, 3.96; Cl, not detectable.

Results and Discussion

O═Mo(TPP)Cl (1). The UV–visible spectrum of O═Mo(TPP)Cl (**1**) in purified ethanol-free CH_2Cl_2 is shown in Figure 1. The X-ray crystal structure analysis has revealed a very long Mo–Cl bond (2.494 (3) Å) which has probably a partial ionic character. In CH_2Cl_2 solution, the chloride ligand is still coordinated to the molybdenum atom as the UV–visible spectrum suffers no significant modification when up to 1% (v/v) of pyridine or dioxane is added, and the IR spectrum (saturated solution) exhibits a strong absorption at 934 cm^{-1} which compares well with the Mo═O stretch found

---

[1] Bains, M. S.; Davis, D. G. *Inorg. Chim. Acta* **1979**, *37*, 53.

[2] A similar procedure, using mesitylene instead of benzonitrile, was reported for the preparation of oxo(5,10,15,20-tetra-*p*-tolylporphyrinato)molybdenum(V), O═Mo(TTP)Cl·HCl, albeit only a poor elemental analysis was provided. Cf.: Diebold, Th.; Chevrier, B.; Weiss, R. *Inorg. Chem.* **1979**, *18*, 1193.

[3] Ledon, H.; Mentzen, B. *Inorg. Chim. Acta* **1978**, *31*, L393.

[4] Riddick, J. A.; Bunger, W. B. "Organic Solvents", 3rd ed.; Wiley-Interscience: New York, 1970; Vol. II.

[5] Shriver, D. F. "The Manipulation of Air-Sensitive Compounds"; McGraw-Hill: New York, 1969.

[6] Johnson, J. F.; Scheidt, W. R. *J. Am. Chem. Soc.* **1977**, *99*, 294; *Inorg. Chem.* **1978**, *17*, 1280.

[7] Ledon, H. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1978**, *287*, 59.

0020-1669/80/1319-3488$01.00/0

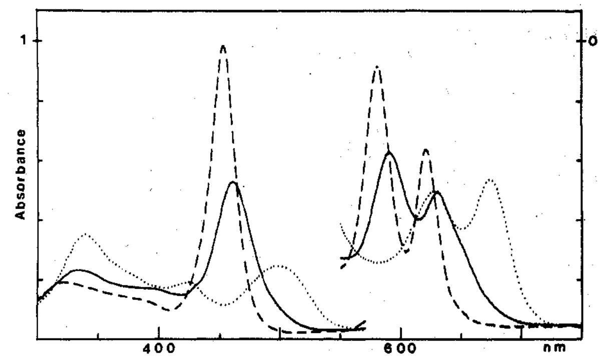


Figure 1. UV–visible spectra of O=Mo(TPP)X complexes in CH_2Cl_2 solution: ···, O=Mo(TPP)Cl (**1**); —, O=Mo(TPP)OH (**2**); ---, O=Mo(TPP)OEt (**4b**).

at 937 cm^{-1} in the solid state.[3] Only new UV–visible spectra are obtained when stronger bases like triethylamine are added. Small shifts of the absorbances of **1** are observed in the presence of protic compounds, alcohols or aqueous HCl, and may reflect the formation of hydrogen bonds or modifications of possible intermolecular interactions.[8]

O=Mo(TPP)OH (2) and [O=Mo(TPP)]$_2$O (3). The preparation of the hydroxo complex O=Mo(TPP)OH was reported by Fleischer[9] ten years ago, but this structure has been questioned by Buchler[10,11] who suggested that in fact this product was more likely the μ-oxo dimer [O=Mo(TPP)]$_2$O (**3**). This was confirmed *in the solid state* by an X-ray crystal structure determination.[6] **3** can be easily characterized by its IR spectrum[6,7,9] which exhibits strong absorptions in the 650–550-cm^{-1} region (Figure 2b) attributed to the Mo–O–Mo vibrations and a weak Mo=O stretch at 905 cm^{-1}. Dissolution of this complex in anhydrous benzene gives a UV–visible spectrum which compares well with values reported by Fleischer for "O=Mo(TTP)OH".[9] A very similar UV–visible spectrum was obtained, in the solid state, by diffuse reflectance spectroscopy. This leads us to assume that the μ-oxo dimer structure O=Mo(TPP)—O—(TPP)Mo=O is, at least, mainly kept in solution.[12] However, when a CH_2Cl_2 solution of **3** was shaken with water, a new UV–visible spectrum was obtained that we attributed to the product of hydrolysis of the μ-oxo dimer (eq 1).

$$^{1}/_{2}\mathrm{O{=}Mo(TPP){-}O{-}(TPP)Mo{=}O} + \mathrm{H_2O} \rightarrow \mathrm{O{=}Mo(TPP)OH} \quad (1)$$

These results prompt us to carefully reexamine previous work concerning the preparation and identification of **2** and **3**.

Treatment of a CH_2Cl_2 solution of O=Mo(TPP)Cl (**1**) with aqueous 1 N NaOH afforded an olive green solution which

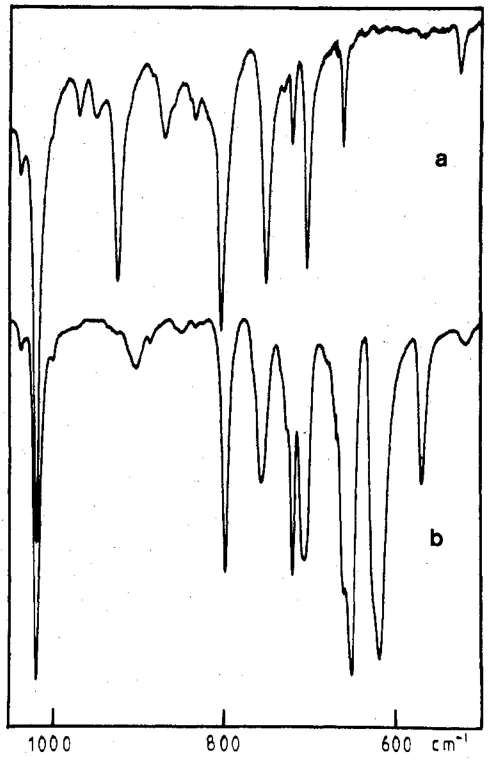


Figure 2. IR spectra of (a) O=Mo(TPP)OH (**2**) and (b) [O=Mo(TPP)]$_2$O (**3**) in a KBr pellet.

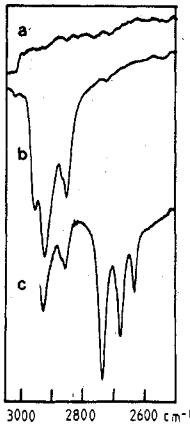


Figure 3. IR spectra of (a) [O=Mo(TPP)]$_2$O (**3**) (KBr pellet), (b) O=Mo(TPP)OH (**2**) (KBr pellet), and (c) O=Mo(TPP)OH (**2**) (CH_2Cl_2 solution in the presence of ^{2}H-enriched water).

was filtered on a small column of alumina. The IR spectrum of this solution (ca. 2 × 10^{-2} mol l^{-1}) revealed no strong absorption in the 650–550-cm^{-1} region, indicating that no μ-oxo dimer **3** was present (estimated <10%). The IR spectrum of the solid obtained by evaporation of this solution under argon is presented in Figure 2a. It is clearly different from that of the μ-oxo dimer **3** depicted in Figure 2b. The medium absorption at 923 cm^{-1} was attributed to the Mo=O stretch. This was confirmed by ^{16}O-labeling experiments.[13] A total of 10 mg of this solid was dissolved in CH_2Cl_2 (5 mL) and stirred for 6 h with 30 μL of 99% ^{18}O-enriched water. The IR spectrum of the solid obtained after removal of the solvent under vacuum exhibited a new band at 885 cm^{-1} (medium) whereas the absorption at 923 cm^{-1} has disappeared. Quite different patterns are also observed between **3** and this com-

---

[8] Matsuda, Y.; Kubota, F.; Murakami, Y. *Chem. Lett.* **1977**, 1281. Ohta, N.; Scheuermann, W.; Nakamoto, K.; Matsuda, Y.; Yamada, S.; Murakami, Y. *Inorg. Chem.* **1979**, *18*, 457.

[9] Srivastava, T. S.; Fleischer, E. B. *J. Am. Chem. Soc.* **1970**, *92*, 5518. Fleischer, E. B.; Srivastava, T. S. *Inorg. Chim. Acta* **1971**, *5*, 151.

[10] Buchler, J. W.; Eickelmann, G.; Puppe, L.; Rohbock, K.; Schneehage, H. H.; Weck, D. *Justus Liebigs Ann. Chem.* **1971**, *745*, 135. Buchler, J. W.; Rohbock, K. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 1073. Buchler, J. W.; Puppe, L.; Rohbock, K.; Schneehage, H. H. *Ann. N. Y. Acad. Sci.* **1973**, *206*, 116; *Chem. Ber.* **1973**, *106*, 2710. Buchler, J. W. In "Porphyrins and Metalloporphyrins"; Smith, K. M.,. Ed.; Elsevier: Amsterdam, 1975; p 157. Buchler, J. W. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. I, p 389.

[11] To account for the reported IR spectrum of "O=Mo(TPP)OH", Buchler suggested that **3** could be contaminated by some amount of the complex O=Mo(TPP)OEt, the ethoxo ligand arising from the ethanol present as stabilizer in chloroform. We have demonstrated that the complex claimed by Fleischer as O=Mo(TPP)OOH was in fact such a similar mixture see ref 7.

[12] In solution, a partial dissociation of the μ-oxo dimer **3** has been suggested. See: Hayes, R. G.; Scheidt, W. R. *Inorg. Chem.* **1978**, *17*, 1082.

[13] Sharpless, K. B.; Townsend, J. M.; Williams, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 295. Ledon, H.; Bonnet, M.; Lallemand, J.-Y. *J. Chem. Soc., Chem. Commun.* **1979**, 702.

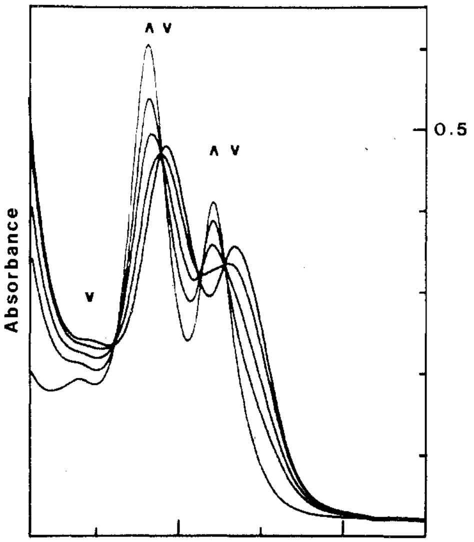


Figure 4. Effect of the presence of traces of ethyl alcohol upon the visible spectrum of O=Mo(TPP)OH (**2**) in CH_2Cl_2 solution (ca. 4 × 10^{-5} M, 3 mL). Arrowheads indicate the spectral changes observed when respectively 0.5, 2.5, and 10 μL of EtOH were addd to the solution.

pound in the 3000–2500-cm^{-1} region of the IR spectrum (Figure 3). The presence of medium-intensity bands (Figure 3b) at 2950, 2923, and 2852 cm^{-1} was attributed to MoO–H stretching vibrations. This was confirmed by ^1H–^2H exchange in CH_2Cl_2 solution. In the presence of ca. 50% ^2H-enriched water, a new set of bands appeared at 2731, 2677, and 2631 cm^{-1} whereas two of the former absorptions were at 2926 and 2855 cm^{-1}, the last one being masked by the solvent (Figure 3c). The large red shift from the expected value for a MoO–H vibration, i.e., 3600–3400 cm^{-1},[14,15] may reflect either a bridging of the hydroxo groups or the presence of strong hydrogen bonds.[16] This should be associated with a high acidity of the hydroxide ligand. In fact, titration of a CH_2Cl_2 solution of **2** with a diethyl ether solution of CH_2N_2 afforded quantitatively the methoxo complex (eq 2). When this reaction

$$\mathrm{O{=}Mo(TPP)OH + CH_2N_2 \rightarrow O{=}Mo(TPP)OCH_3} \qquad (2)$$

was monitored by UV–visible spectroscopy, isobestic points were obtained at 631, 608, 597, 556, 470, and 432 nm.

Thus O=Mo(TPP)OH (**2**) exists either in solution or in the solid state and can be conveniently characterized by its IR spectrum. Its UV–visible spectrum in CH_2Cl_2 solution, presented in Figure 1b, is identical with that obtained after hydrolysis of **3**. However, when a CH_2Cl_2 solution of **2** was concentrated in the presence of benzene, the solid μ-oxo dimer **3** was obtained. It seems reasonable to assume that the equilibrium between **2** and **3** is displaced by azeotropic elimination of water during concentration, leading to selective crystallization of the μ-oxo dimer **3**, which is also favored by its extremely low solubility in aromatic solvents. In agreement with Buchler,[10] these results fully confirm that the solid compound obtained by Fleischer[9] after crystallization in a $CHCl_3$–xylene mixture was mainly the μ-oxo dimer **3**. The presence of an equilibrium between **2** and **3** may be related to the close intramolecular porphyrin interplanar spacing ca. 3.85 Å revealed by the X-ray crystal structure of **3**.[6] Closer approach of the two porphyrin moieties is prevented by the steric hindrance of the phenyl substituents. Very short nonbonded contacts between phenyl hydrogen atoms of a core and β-pyrrole carbon atoms of the other are found, ranging upwards from 2.8 Å. These repulsive interactions may favor the dissociation of the μ-oxo complex in solution.[17] The influence of such steric factors upon hydroxo vs. μ-oxo axial coordination has been recently exemplified in the case of a highly hindered iron(III) porphyrin for which only the hydroxo complex has been characterized.[18]

Table I. UV–Visible Spectra of O=Mo(TPP)X Complexes

complex	solvent	λ_{max}, nm ($10^{-3}\epsilon$, M^{-1} cm^{-1})
O=Mo(TPP)Cl (**1**)	CH_2Cl_2	674 (9.3), 628 (8.6), 498 (43), 417 (3.3), 343 (60)
O=Mo(TPP)OH (**2**)	CH_2Cl_2	635 (8.4), 593 (10.8), 464 (90)
O=Mo(TPP)OH (**2**)	solid	632, 590, 463
O=Mo(TPP)$_2$O (**3**)	benzene	667 (3.3), 617 (4.2, 583 (3.5), 444 (59), 410 (36)
O=Mo(TPP)$_2$O (**3**)	solid	674, 622, 590, 445
O=Mo(TPP)OMe (**4a**)	CH_2Cl_2	621 (10.8), 581 (15.7), 540 (3.8), 454 (170)
O=Mo(TPP)OEt (**4b**)	CH_2Cl_2	620 (10.9), 581 (15.9), 540 (3.5), 453 (182)
O=Mo(TPP)O(*i*-Pr) (**4c**)	CH_2Cl_2	619 (11.1), 580 (16.2), 537 (3.4), 453 (196)
O=Mo(TPP)O(*t*-Bu) (**4d**)	CH_2Cl_2	617 (12.3), 578 (17.6), 536 (3.3), 451 (224)

Table II. ESR Spectra of O=Mo(TPP)X Complexes[a]

complex	*g*	complex	*g*
O=Mo(TPP)Cl (**1**)	1.9652	O=Mo(TPP)OEt (**4b**)	1.9689
O=Mo(TPP)OH (**2**)	1.9675	O=Mo(TPP)O(*i*-Pr) (**4c**)	1.9692
O=Mo(TPP)OMe (**4a**)	1.9687	O=Mo(TPP)O(*t*-Bu) (**4d**)	1.9693

[a] The hyperfine constants A_{Mo} of the sextet and A_N for the nonet were found to fall invariably in the range $A_{Mo} = 50.0 \pm 1$ G and $A_N = 2.50 \pm 0.05$ G.

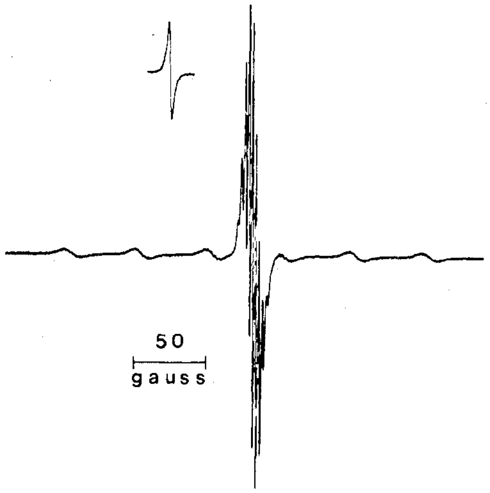


Figure 5. X-Band ESR spectrum of O=Mo(TPP)OMe (**4a**) in CH_2Cl_2 solution at room temperature.

---

(14) Very few data concerning the MoO–H IR spectra have been reported. See: Kay, A.; Mitchell, P. C. H. *J. Chem. Soc. A* **1970**, 2421. Andruchow, W., Jr.; Archer, R. D. *J. Inorg. Nucl. Chem.* **1972**, *34*, 3185. Dudek, M.; Kanas, A.; Samotus, A. *Ibid.* **1979**, *41*, 1135.

(15) IR spectra of several metalloporphyrins having a hydroxo axial ligand exhibit a sharp OH stretch in the 3640–3580-cm^{-1} region; cf. ref 10.

(16) Sartorelli, U.; Gariaschelli, L.; Ciani, G.; Bonora, G. *Inorg. Chim. Acta* **1971**, *5*, 191. Michelin, R. A.; Ros, R.; Strukul, G. *Ibid.* **1979**, *37*, L491.

(17) This effect if probably less important in the related octaethylporphyrinato complex [O=Mo(OEP)]$_2$O. This would explain that a solid monomeric hydroxo complex O=Mo(OEP)OH has never been observed (see ref 10).

(18) Cense, J.-M.; Le Quan, R. M. *Tetrahedron Lett.* **1979**, 3725. A similar effect has been observed in the case of an encumbered (5,15-di-*tert*-butylporphodimethene)iron(III) complex: Buchler, J. W. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 407. Buchler, J. W.; Lay, K. L.; Tonn, B. Abstract of the IXth the International Conference on Organometallic Chemistry, Sept 3–7, 1979, Dijon, France, No. P 52 F.

O═Mo(TPP)OR (4). Figure 4 shows the effect of addition of small amounts of ethyl alcohol upon the visible spectrum of a CH_2Cl_2 solution of the hydroxo complex **2**. Large excess results in a limiting spectrum identical with that of the ethoxo complex O═Mo(TPP)OEt (**4b**)[7] presented in Figure 1c. Therefore, equilibrium 3 exists is solution. However, in the

$$\mathrm{O{=}Mo(TPP)OH + ROH \rightleftharpoons O{=}Mo(TPP)OR + H_2O} \qquad (3)$$

presence of traces of base, it seems to be largely displaced toward the formation of the alkoxo complex. Visible spectra of several other alkoxo complexes are reported in Table I.

X-Band ESR spectra of O═Mo(TPP)X complexes in CH_2Cl_2 solution have been recorded at room temperature. As shown in Figure 5, they exhibit the typical feature previously reported.[1,8,9,19] The *g* values of the intense central set of nine lines are presented in Table II. We should point out that only small changes of this parameter are observed according to the nature of the axial X ligand.

Conclusions

Several [O═Mo(TPP)]$_n$X complexes (n = 1, X = Cl, OH, OMe, OEt, O(*i*-Pr), O(*t*-Bu); n = 2, X = O) have been characterized both in solution and in the solid state, by UV–visible, IR, and ESR spectroscopy. Extreme care must be taken for solution studies of these complexes as ligand exchanges occur extremely easily.[7,10] UV–visible spectra are very sensitive to the nature of the axial ligands whereas use of ESR spectroscopy seems to be inadequate for their identification.[20]

Our results clearly illustrate how unsecured are the structural assignments which rely only upon UV–visible data, as minor traces of impurities could dramatically change the nature of species present in the solution. On the other hand, extrapolation of structural results obtained in the solid state could easily be made safe by checking the IR or UV–visible spectra in both states.

Finally, our full characterization of O═Mo(TPP)OH puts an end to a ten year old discrepancy found in the literature about the existence of this complex.

Acknowledgment. We are indebted to J.-F. Dutel for the ESR measurements and to Dr. J.-C. Marchon for a generous gift of ^{18}O-enriched water. This paper has benefited from discussions with Dr. I. Tkatchenko, whose comments and suggestions we gratefully acknowledge. We also thank the Centre National de la Recherche Scientifique for support of this work.

Registry No. 1, 68070-21-3; **2**, 28780-74-7; **3**, 61747-27-1; **4a**, 74751-79-4; **4b**, 65404-71-9; **4c**, 68046-15-1; **4d**, 68046-16-2.

---

(19) Newton, C. M.; Davis, D. G. *J. Magn. Reson.* **1975**, *20*, 446.

(20) The same observation has been reported recently for O═Mo(TPP)X complexes (X = OEt, O_2, NCS, Cl, HCl, Br): Imamura, T.; Terui, M.; Takahashi, Y.; Namatatsu, T.; Fujimoto, M. *Chem. Lett.* **1980**, 89.

(21) Following the recommendation of a reviewer, the X-ray crystal structure determination of O═Mo(TPP)OMe has been undertaken. At the present level of refinement the complex clearly exhibits a trans oxo–methoxo axial ligation of the molybdenum atom, which is slightly displaced out of the mean plane of the porphyrin, toward the oxo ligand: Mentzen, B. F.; Ledon, H. J., manuscript in preparation.

Contribution from the Department of Chemistry, Drexel University, Philadelphia, Pennsylvania 19104,
and Amoco Chemicals Corporation, Naperville, Illinois 60540

Purine Complexes with Divalent 3d Metal Perchlorates[1a]

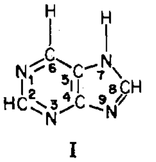
A. N. SPECA,[1b] C. M. MIKULSKI,[1c] F. J. IACONIANNI,[1d] L. L. PYTLEWSKI,[1d] and N. M. KARAYANNIS*[1c]

Received August 31, 1979

A series of $M(puH)_2(ClO_4)_2{\cdot}3H_2O$ (M = Mn, Fe, Co, Ni, Cu, Zn) complexes with neutral purine (puH), presumably protonated at N(7), was prepared by interaction of ligand and metal salt in ethanol–triethyl orthoformate. The new complexes are hexacoordinated with two puH and three aqua ligands per metal ion and exclusively ionic perchlorate. Their magnetic moments are normal at room temperature, but magnetic data over the 300–80 K range are suggestive of magnetic exchange in bi- or polynuclear puH-bridged structures. Two possible structural types, involving both one unidentate terminal and one bidentate bridging puH ligand per metal ion, are discussed, viz., a linear oligomer with single-bridged ⩾M⩽puH⩾M⩽puH– sequences and a double-bridged dimer of the $[(H_2O)_3(puH)M(PuH)_2M(puH)(OH_2)_3](ClO_4)_4$ type. The former structural type seems more likely. Unidentate puH is assumed to coordinate through the N(9) nitrogen, while with bidentate bridging puH the bonding should be either through the N(1),N(9) or through the N(3),N(9) nitrogens.

Introduction

Although metal complexes with biologically important substituted purines (i.e., adenine, guanine, hypoxanthine, xanthine, theophylline, 6-mercaptopurine, 8-azapurines, and their alkyl derivatives, nucleosides, and nucleotides) have been the subject of numerous studies,[2,3] there is a relative paucity of information regarding the corresponding complexes with unsubstituted purine (puH (I)). Only a few well-defined metal complexes with puH or the monodeprotonated anionic pu^- species have been isolated and characterized. These include Na(pu),[4] Tl(pu),[5] $Hg(puH)X_2$ (X = Cl, Br),[6] $[Cu(puH)Cl_2]{\cdot}HCl$, $[Cu(puH)(OH_2)_2]SO_4{\cdot}3H_2O$,[7] $[Cu(pu)_2$-



I

---

*To whom correspondence should be addressed at Amoco Chemicals Corporation.

(1) (a) Speca, A. N.; Mikulski, C. M.; Iaconianni, F. J.; Pytlewski, L. L.; Karayannis, N. M. "Abstracts of Papers", the Joint American Chemical Society/Chemical Society of Japan Chemistry Congress, Honolulu, HI, April, 1979; American Chemical Society: Washington, DC, 1979; INOR 33. (b) USI Chemicals Co., Research Division, Cincinnati, OH 45237. (c) Department of Chemistry and Physics, Beaver College, Glenside, PA 19038. (d) Drexel University. (e) Amoco Chemicals Corp.

(2) Hodgson, D. J. *Prog. Inorg. Chem.* **1977**, *23*, 211.

(3) Marzilli, L. G. *Prog. Inorg. Chem.* **1977**, *23*, 255.

(4) Lautié, A.; Novak, A. *C. R. Hebd. Seances Acad. Sci., Ser. B* **1971**, *273*, 908.

(5) Taylor, E. C.; Maki, Y.; McKillop, A. *J. Org. Chem.* **1969**, *34*, 1170.

(6) Lautié, A.; Novak, A. *J. Chim. Phys. Phys.-Chim. Biol.* **1971**, *68*, 1492.

(7) Weiss, R.; Venner, H. *Hoppe-Seyler's Z. Physiol. Chem.* **1963**, *333*, 169; **1965**, *340*, 138; **1966**, *345*, 122.