

## **A new protonated form of porphyrins in solutions**

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### *Experimental*

Absorption spectra were recorded on Agilent 8453 UV-VIS, Specord M-400; IR, <sup>1</sup>H NMR and mass spectra were measured on VERTEX 80v, Bruker Avance-500 (TMS as a standard) and MALDI-TOF (Bruker Autoflex) spectrometers, respectively; elemental analysis was performed on a Flash EA 1112 Series CHNS-O Analyzer.

*(Diacetato)(5,10,15,20-tetraphenylporphinato)(pyridine)lead(IV)*, (AcO)<sub>2</sub>PbTPP·Py.<sup>17</sup> H<sub>2</sub>TPP and Pb(OAc)<sub>2</sub> in the molar ratio 1:20 were situated in pyridine and refluxed under heating at dark during 60 min up to complete conversion (TLC, Silufol, CHCl<sub>3</sub>–benzene 1:1). Then, the solvent was distilled off *in vacuo*, the residue was dissolved in minimum CHCl<sub>3</sub>, washed with water and purified twice on an Al<sub>2</sub>O<sub>3</sub>-packed column (Al<sub>2</sub>O<sub>3</sub> L 40/250, Chemapol) with CHCl<sub>3</sub> as eluent. Pink zone was washed off the column by DMF. Yield, 7.1%. UV-VIS (CHCl<sub>3</sub>, λ<sub>max</sub>/nm): 584, 444, 345 (sh), 310 with intensity decreasing IV > III > II > I. IR (KBr, ν/cm<sup>-1</sup>): phenyl ring vibrations, 704, 778 (γ<sub>C-H</sub>), 1072, 1159 (δ<sub>C-H</sub>), 2860, 2920 (ν<sub>C-H</sub>); pyrrole ring vibrations, 798 (γ<sub>C-H</sub>), 976 (ν<sub>C-C</sub>, δ<sub>C-H</sub>, ν<sub>C-N</sub>), 1340 (ν<sub>C-N</sub>), 1440 (ν<sub>C=N</sub>), 1523 (skeletal vibrations in pyrrole ring), 2853, 2973 (ν<sub>C-H</sub>), 405 (Pb–N<sub>Py</sub>), 450 (Pb–N), 1655, 1734 (O–C–O). Found (%): Pb, 20.15. Calc. for C<sub>46</sub>H<sub>31</sub>N<sub>4</sub>O<sub>2</sub>Pb (%): Pb, 20.37.

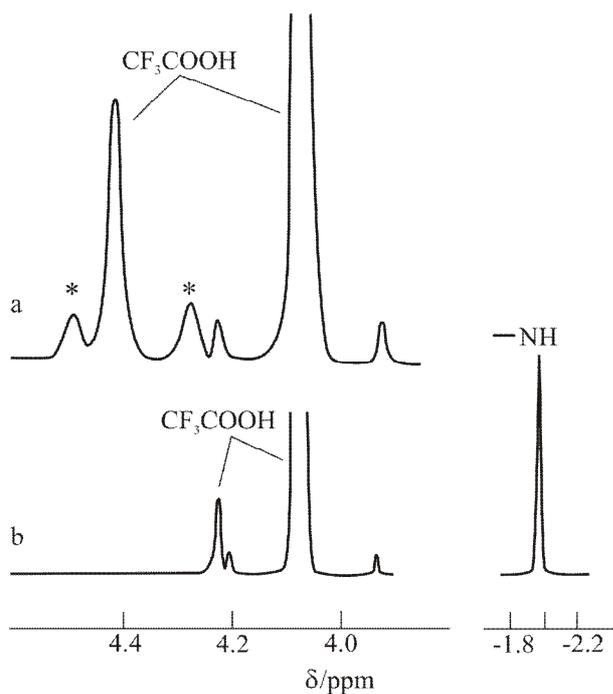
*Hydroxooxo(5,10,15,20-tetraphenylporphinato)tungsten(V)*, O=W(OH)TPP.<sup>17</sup> H<sub>2</sub>TPP (0.1 g, 0.16 mmol) and WCl<sub>6</sub> (0.2 g, 0.53 mmol) were boiled in phenol until H<sub>2</sub>TPP bands disappeared from the UV-VIS spectrum of the reaction mixture. Then, the solvent was distilled off *in vacuo*, the residue was dissolved in minimum CHCl<sub>3</sub> and purified twice on an Al<sub>2</sub>O<sub>3</sub>-packed column (Al<sub>2</sub>O<sub>3</sub> L 40/250, Chemapol) with chloroform as eluent. Yield, 60%. UV-VIS (CHCl<sub>3</sub>, λ<sub>max</sub>/nm (log ε)]: 621 (2.85), 585 (3.11), 449 (4.25). IR (KBr, ν/cm<sup>-1</sup>): benzene ring vibrations, 708, 758 (γ<sub>C-H</sub>), 1075, 1180 (δ<sub>C-H</sub>), 1485, 1610 (ν<sub>C=C</sub>); pyrrole ring vibrations, 805 (γ<sub>C-H</sub>), 1020 (C<sup>3</sup>–C<sup>4</sup>, ν<sub>C-N</sub>, δ<sub>C-H</sub>), 1335 (ν<sub>C-N</sub>), 1445 (ν<sub>C=N</sub>), 1540 (skeletal vibrations in pyrrole ring), 447 (W–N), 630 (W–O), 940 (W=O).

(Cl)InT(OCH<sub>3</sub>)<sub>4</sub>PP, (Cl)InT(Br)<sub>4</sub>PP, (Cl)TiT(OCH<sub>3</sub>)<sub>4</sub>PP, (Cl)TiT(Br)<sub>4</sub>PP, (AcO)CrTPP, CoTPP, NiTPP, CuTPP, ZnTPP, (Cl)<sub>2</sub>ZrTPP, (AcO)<sub>2</sub>ZrTPP, (Cl)<sub>2</sub>HfTPP, (OPh)ReTPP (1)

**Number 1** Unstable in strong acids media complexes.

(Cl)AlTPP<sup>\*</sup>, (Cl)<sub>2</sub>GeTPP, (Cl)<sub>2</sub>SnTPP, O=VTPP, (AcO)MnT(2-NH<sub>2</sub>)<sub>4</sub>PP, (Cl)MnT(2-NH<sub>2</sub>)<sub>4</sub>PP, (Cl)MnTAAPP, (Br)MnTAAPP, (SCN)MnTAAPP, (AcO)MnOEP<sup>\*\*</sup>, (Cl)MnOEP<sup>\*\*</sup>, (SCN)MnOEP<sup>\*\*</sup>, (Cl)<sub>3</sub>NbTPP, O=Mo(OH)TPP, (Cl)RhTPP, PdTPP<sup>\*</sup>, (Cl)<sub>3</sub>TaTPP<sup>\*\*\*</sup>, O=W(OH)TPP, (Cl)ReTPP, O=Re(OH)TPP<sup>\*\*</sup>, (Cl)IrTPP<sup>\*\*\*\*</sup>, PtTPP, (Cl)AuTPP (2)

**Number 2** Complexes existing in strong acid solution in the molecular form at 298 K. <sup>\*</sup> forms a molecular solution or H<sup>+</sup>-associate depending on the acidity of the solvent; <sup>\*\*</sup> is destroyed on coordinating center slowly; <sup>\*\*\*</sup> in 100% H<sub>2</sub>SO<sub>4</sub> only; <sup>\*\*\*\*</sup> dissociates along two Ir–N bonds up to SAT-complex with molecular ligand H<sub>2</sub>TPP.



**Figure 1S** <sup>1</sup>H NMR spectra in CF<sub>3</sub>COOH: (a) AgTPP and (b) H<sub>2</sub>TPP. The signals of associated protons are marked with an asterisk.

**Table 1S** The protonation energies ( $E_{\text{prot}}$ ) and some internuclear distances for  $\text{H}_2\text{TPP}$ ,  $(\text{Cl})\text{InTPP}$ ,  $\text{AgTPP}$  and their protonated forms calculated by quantum-chemical techniques PM3 and ZINDO.

Complex	$-E_{\text{prot}}$ , $\text{kcal mol}^{-1}$	Bond length, Å				
		M-Ct	M-X	N <sub>1</sub> -N <sub>3</sub> N <sub>2</sub> -N <sub>4</sub>	C <sub>m</sub> -H <sup>+</sup> C <sub><math>\beta</math></sub> -H <sup>+</sup> N-H <sup>+</sup>	P <sub>N<sub>4</sub></sub> <sup>a</sup>
$\text{H}_2\text{TPP}$				4.130 4.220		11.813
$\text{H}_3\text{TPP}^+$	219.63			4.156 4.237	0.992	11.880
$\text{H}_4\text{TPP}^{2+}$	152.07			4.306 4.311	0.990	12.252
$\text{H}_4\text{TPP}^{2+} \dots \text{H}_{\text{meso}}^+$	86.93			4.520 4.527	1.127	12.895
$\text{AgTPP}$		0.187		4.287 4.286		12.221
$\text{AgTPP} \dots \text{H}_{\text{meso}}^+$	320.22	0.008		4.264 4.264	1.109	12.061
$\text{AgTPP} \dots 2\text{H}_{\text{meso}}^+ (\text{cis})$	195.03	1.057		4.933 3.812	1.114 1.112	12.577
$\text{AgTPP} \dots 2\text{H}_{\text{meso}}^+ (\text{trans})$	237.80	0.031		4.249 4.249	1.111 1.110	12.019
$\text{AgTPP} \dots \text{H}_{\text{meso}}^+ \text{H}_{\beta}^{\text{+b}}$	286.08	0.091		4.277 4.291	1.109 1.099	12.140
$(\text{Cl})\text{InTPP}$		0.337	2.528	4.113 4.126		11.652
$(\text{Cl})\text{InTPP} \dots \text{H}_{\text{meso}}^+$	208.22	0.426	2.462	4.120 4.123	1.128	11.657
$(\text{Cl})\text{InTPP} \dots \text{H}_{\beta}^+$	208.80	0.384	2.441	4.107 4.130	1.111	11.650
$(\text{Cl})\text{InTPP} \dots \text{H}_{\alpha}^+$	199.57	0.549	2.449	4.098 4.023	1.130	11.522
$(\text{Cl})\text{InTPP} \dots \text{H}_{\text{meso}}^+ \text{H}_{\beta}^{\text{+c}}$	141.71	0.461	2.404	4.116 4.091	1.129 1.112	11.607
$(\text{Cl})\text{InTPP} \dots \text{H}_{\text{meso}}^+ \text{H}_{\beta}^{\text{+b}}$	140.00	0.475	2.462	4.099 4.129	1.130 1.113	11.657
$(\text{Cl})\text{InTPP} \dots \text{H}_{\text{meso}}^+ \text{H}_{\alpha}^{\text{+b}}$	129.45	0.574	2.464	4.116 4.037	1.130 1.128	11.667

<sup>a</sup> Perimeter of the coordination plane N<sub>4</sub>. <sup>b</sup> Protons of the C<sub>meso</sub> and C <sub>$\beta$</sub>  of the pyrrole fragment not connected with 'protonated' C<sub>meso</sub>. <sup>c</sup> Protons of the C<sub>meso</sub> and C <sub>$\beta$</sub>  of the neighboring pyrrole fragment.