Organometallic Chemistry

Study of complex formation between lead(II) acetate and *meso*-tetraphenylporphin

O. V. Molodkina, T. N. Lomova, and E. G. Mozhzhukhina*

Institute of Chemistry of Non-Aqueous Solutions, Russian Academy of Sciences,
1 ul. Akademicheskaya, 153018 Ivanovo, Russian Federation.
Fax: +7 (093 2) 37 8509. E-mail: tnl@ihnr.polytech.ivanovo.su

The reaction of $Pb(OAc)_2$ with *meso*-tetraphenylporphin in boiling pyridine or *N,N*-dimethylformamide gave complexes of Pb^{II} with tetraphenylchlorin or Pb^{IV} with tetraphenylporphin. The scheme of redox reactions occurring during the complex formation involving Pb^{2+} as the reducing agent was suggested.

Key words: *meso*-tetraphenylporphin, *meso*-tetraphenylchlorin, complex formation, lead, synthesis.

The reaction of tetraphenylporphyrin (H_2TPP) with $Pb(OAc)_2$ in boiling pyridine has been described previously.[1] A crystalline dark-blue-green substance, to which the PbTPP · Py structure has been ascribed, was the reaction product isolated first from the reaction mixture and then from a solution in benzene. However, its electronic absorption spectrum (EAS) consisting of six bands with different intensities indicates that this solid contains a colored admixture, whose composition and procedure for removal were not studied.

In this work, we present the results of studies of the nature of processes that occur in the reaction of H_2TPP with $Pb(OAc)_2$ and the composition of the final products aimed at obtaining the individual metalloporphyrin.

Experimental

$Pb(OAc)_2$ (analytical grade) and H_2TPP (available from the Armenian Division of the Institute of Chemical Reagents and Special-Purity Substances) purified by a standard procedure using column chromatography were taken in a certain variable ratio (Table 1) and added to anhydrous pyridine (10 mL, the content of water was not greater than 0.03%, reagent grade). The homogeneous solution was boiled under reflux until EAS of the reaction mixture no longer changed

Table 1. Yield of products of the reaction of $Pb(OAc)_2$ with H_2TPP

Solvent	$Pb(OAc)_2$: H_2TPP /mol mol^{-1}	Yield (%)		
		PbTPC	$(AcO)_2$PbTPP · Py	H_2TPP
Pyridine	2 : 1	97.5	2.5	—
Pyridine	5 : 1	97.0	3.0	—
Pyridine	20 : 1	95.4	4.6	—
Pyridine	30 : 1	96.0	4.0	—
AcOH	20 : 1	—	0	100
DMF	11 : 1	92.2	2.8[a]	5
Pyridine	20 : 1[b]	92.9[b]	7.1[b]	—
Pyridine	20 : 1[c]	100[c]	0[c]	—

[a] Yield of $(AcO)_2$PbTPP · DMF. [b] Under dark conditions. [c] In an N_2 atmosphere.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 10, pp. 2052—2055, October, 1998.

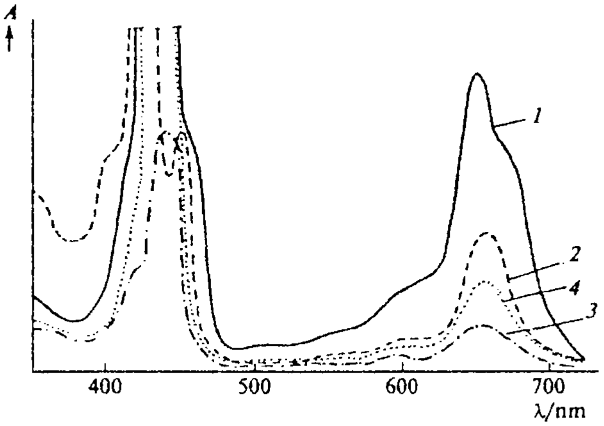


Fig. 1. Electronic absorption spectra of the H_2TPP—$Pb(OAc)_2$—AcOH reaction mixture in chloroform (*1—3*) and H_2TPP in 100% AcOH (*4*). τ/s = 900 (*1*), 1800 (*2*), and 5400 (*3*).

(~1 h). Pyridine was removed *in vacuo*, and the solid residue was dissolved in chloroform and washed many times with water to remove the excess of $Pb(OAc)_2$. The solution was placed on a column with Al_2O_3 L 40/250 (neutral, Chemapol, Czech Republic) and chromatographed with a 1 : 1 chloroform—benzene mixture to elute a bright-green zone. The second pink zone, which remained strongly absorbed at the top of the column, was eluted with *N,N*-dimethylformamide.

The reactions of $Pb(OAc)_2$ with H_2TPP under dark and anaerobic conditions using DMF and AcOH as the solvents were carried out with different molar ratios of the reagents (see Table 1). The reaction products were isolated according to the procedure described above. The reaction of $Pb(OAc)_2$ with 7,8-dihydrotetraphenylporphin (*meso*-tetraphenylchlorin) (H_2TPC) in a 20 : 1 molar ratio was carried out in Py. H_2TPC was synthesized by the method described previously.[2] The course of the reaction in AcOH was monitored by following the bands of protonated H_2TPC at 435 and 655 nm (Fig. 1).

Thin layer chromatography (TLC) of compounds isolated from the green (compound **1**) and pink (compound **2**) zones was performed on Silufol plates in a chloroform—benzene (1 : 1) system.

Electronic absorption spectra were recorded on Specord M 400 and SF-26 spectrophotometers; IR spectra were obtained on a Specord 75 IR instrument; and ^1H NMR spectra were recorded on Tesla BS-497 (HMDS as the internal standard, working frequency 100 MHz) and Bruker WM-360 (TMS as the internal standard, working frequency 360 MHz) instruments. Lead was quantitated by atomic-adsorption spectroscopy on an AASIN spectrometer. Bands in the IR spectra of the complexes were analytically assigned on the basis of our own and published data (see Ref. 3).

Compound 1. Electronic absorption spectrum ($CHCl_3$), λ_{max}/nm (logε): 652 (3.37), 609 (3.52), 551 (3.25), 516 (3.4), 466 (4.33), 419 (4.5), 355 (3.76). IR (KBr), ν/cm^{-1}: vibrations of pyrrole rings, 796 (γ(C—H)), 1000 (ν(C—C), δ(C—H), ν(C—N)), 1440 (ν(C=N)), 1525 (in-the-plane vibrations of pyrrole rings); vibrations of benzene rings, 704 and 752 (γ(C—H)), 1072 and 1176 (δ(C—H)); 1470, 1576, and 1592 (ν(C=C)), 2860, 2920, and 3080 (ν(C—H); vibrations of the Pb—$N_{porphyrin}$ bonds, 416. ^1H NMR ($CDCl_3$), δ: 7.73 (m, 12 H, *m*-, *p*-C_6H_5); 8.16 (m, 8 H, *o*-C_6H_5); 8.77 (d, 4 H, C_4H_4N); 8.89 (t, 6 H, C_4H_2N). Found (%): Pb, 24.74. $C_{44}H_{30}N_4Pb$. Calculated (%): Pb, 25.20.

Compound 2. Electronic absorption spectrum ($CHCl_3$), λ_{max}/nm: 584, 444, 345 sh, and 310 nm with a decrease in the absorption intensity in the series IV > III > II > I. IR (KBr), ν/cm^{-1}: vibrations of pyrrole rings, 798 (γ(C—H)), 976 (ν(C—C), δ(C—H), ν(C—N)), 1340 (ν(C—N)), 1440 (ν(C=N)), 1523 (vibrations of pyrrole rings in the plane); vibration of benzene rings, 704 and 778 (γ(C—H)); 1072, 1159 (δ(C—H)); 2860, 2920 (ν(C—H)); vibrations of the pyridine bonds 700, 1460, 1560; vibrations of the bonds Pb—$N_{pyridine}$, 405; Pb—$N_{porphyrin}$, 450; $O{=}C{=}O$, 1655 and 1734. Found (%): Pb, 20.15. $C_{48}H_{34}N_4O_4Pb \cdot Py$. Calculated (%): Pb, 20.37.

Results and Discussion

The individual character of compounds **1** and **2** was confirmed by TLC. The electronic absorption spectrum of compound **1** in chloroform differs sharply from those of porphyrin complexes with M^{2+} (see Ref. 3). According to the number of bands and ratio of their intensities, the spectrum of the compound under study is closest to the spectrum of TPC.[4] However, it contains an additional band at 466 nm, and the intensity of the long-wave band at 652 nm is lower by approximately an order of magnitude. As is known,[3,5] the Soret band in the σ-complexes of chlorins (with Zn and In) undergoes a bathochromic shift, and the intensity of the band I increases as compared to those of the corresponding porphyrins. The EAS of compound **1** differs also from the spectra of chlorin complexes of M^{2+}, which is probably related to the specific nature of Pb^{2+}. According to the published data,[6] Pb^{II} complexes undergo charge-transfer transitions $a_1(p_z) \rightarrow e_g{}^*(\pi)$ from the p_z-orbital of the metal, which acts as the higher occupied orbital. In addition, it is assumed[7] that in PbOEP (OEP is the octaethylporphin dianion) the Pb atom goes out of the (N_4) plane. The IR spectrum of compound **1** contains no bands of stretching vibrations of C=O, Pb—O, and Pb—$N_{pyridine}$, which indicates the absence of exoligands in this compound. The ^1H NMR spectrum of compound **1** (Table 2) is similar to those of diamagnetic metalloporphyrins[3] and metallochlorins: two signals corresponding to the resonance of *m*- and *p*-protons of phenyl rings appear in the same region as in the spectra of the (Cl)InTPP, (AcO)GaTPP, and $(Cl)_2$GeTPP complexes studied previously.[8,9] However, *o*-protons of the phenyl groups located at different sides with respect to the macrocycle plane are spectrally identical, whereas due to the presence of the exoligand in (Cl)InTPP, two signals at δ 8.12 and 8.38 correspond to them. The signals for the protons of the pyrrole rings (H_β) at δ 8.77 and 8.89 in the spectrum of compound **1** instead of that at δ 9.07 for (Cl)InTPP indicate the appearance of two types of spectrally discernible β-protons. The ratio of the areas

Table 2. Chemical shifts (δ) in ^{1}H NMR spectra ($CDCl_3$, 298 K) of (Cl)InTPP, (Cl)InTPC, and PbTPC complexes

Compound	H_β	H_o	H_m	H_p
(Cl)InTPP	9.07	8.12 8.38	7.70	7.70
(Cl)InTPC	8.43 8.45	7.96 8.19	7.70	7.70
PbTPC	8.77 8.89	8.16	7.73	7.73

of the signals considered, which was determined from their integral intensity, is 1.4. The spectrum of (chloro)indium(III)tetraphenylchlorin (Cl)InTPC obtained for comparison was found to be similar (see Table 2).[8]

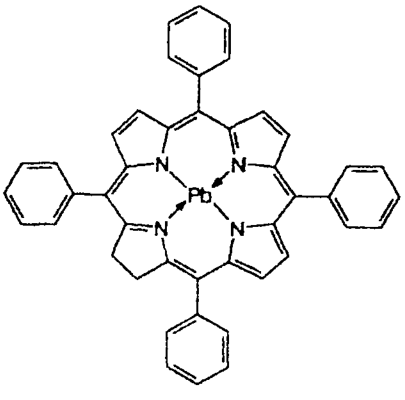
The complex identical with compound **1** in absorption spectra, solubility, and stability in solutions was obtained as the single product by complex formation of $Pb(OAc)_2$ with TPC. Both compounds are soluble and stable in ethanol, chloroform, and DMF and dissociate in an ethanol—1 m*M* AcOH mixture.

The EAS of compound **2** is classified as the spectrum of "normal type" for metallotetraphenylporphins,[10] for example, TPP complexes with Zn^{2+}, Mg^{2+}, and Cd^{2+} (see Ref. 11) as well as with lanthanides(III), titanyl, and vanadyl.[3] The presence of frequencies corresponding to vibrations of the $Pb—N_{pyridine}$, $Pb—N_{porphyrin}$, and O=C=O bonds in the IR spectrum indicates that compound **2** contains AcO and Py exoligands.

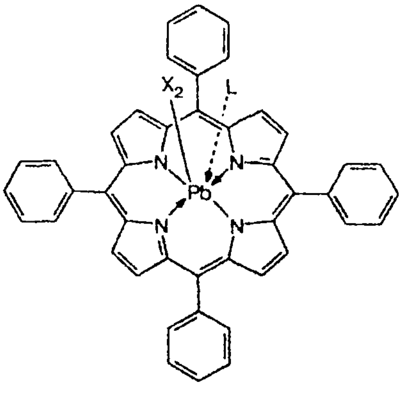
It follows from the data considered that compound **1** is a complex of H_2TPC with Pb^{II}, and compound **2** is a complex of H_2TPP with Pb^{IV}. Thus, of all expected complexes (PbTPP, $(OAc)_2PbTPP$, PbTPC, and $(AcO)_2PbTPC$) (with account of redox potentials of the Pb^{4+}/Pb^{2+} (+1.8 V [12]), $PbTPP/PbTPP^{2-}$ (−1.52 V [13]), and H_2TPP/H_2TPP^{2-} (−1.45 V [14]) pairs), it is PbTPC (compound **1**) and $(AcO)_2PbTPP$ (compound **2**) complexes in which both ions (metal cation and porphyrin dianion) exist in either reduced or oxidized state that are formed in the reaction of H_2TPP with $Pb(OAc)_2$.

These results agree well with the published data. For example, $[PbOEP]^{2+}$ containing Pb^{4+} weakly bound to the porphyrin dianion[7] is the product of two electrochemically reversible one-electron reactions of oxidation of PbOEP, and it is similar to compound **2** in lability and EAS. On the other hand, the one-electron photoreduction of water-soluble platinum(II) and palladium(II) porphyrins in aerated solutions gives only metallo(II)chlorin,[15] whose absorption spectrum is close to that of compound **1**.

The data considered suggest that a mixture of two compounds, PbTPC and $(AcO)_2PbTPP \cdot Py$, is the reaction product.



1



2

X = AcO, L = Py

Taking into account the nature of the products of the reaction of H_2TPP with $Pb(OAc)_2$ carried out under different conditions, we can suggest the following mechanism of this reaction:

$$Pb^{2+} + H_2TPP \rightarrow PbTPP + 2\,H^+, \tag{1}$$

$$2\,PbTPP + Pb^{2+} \rightarrow 2\,PbTPP^- + Pb^{4+}, \tag{2}$$

$$PbTPP^- + PbTPP^- \rightarrow PbTPP + PbTPP^{2-}, \tag{3}$$

$$PbTPP^{2-} + H^+ \rightarrow PbTPP^-, \tag{4}$$

$$PbTPP^{2-} + 2\,H^+ \rightarrow PbTPC\ (\mathbf{1}), \tag{5}$$

In the presence of oxygen:

$$PbTPP^- \rightarrow [PbTPP]^{2+}, \tag{6}$$

$$[PbTPP]^{2+} + 2\,AcO^- + Py \longrightarrow (AcO)_2PbTPP \cdot Py\ (\mathbf{2}). \tag{7}$$

PbTPP formed due to the complex formation (Eq. (1)) is reduced to the π-radical anion $PbTPP^-$ (Eq. (2)) with an excess of Pb^{2+} in the basic medium (Py). Due to the disproprotionation of $PbTPP^-$ (Eq. (3)) followed by the protonation of the dianion (Eqs. (4) and (5)) by the acid released in reaction (1), both final products, *viz.*, the Pb^{II} complex (reaction (5), compound **1**) and Pb^{IV} complex (reactions (6) and (7), compound **2**), are formed in the presence of O_2. The complex formation under anaerobic conditions (see Table 1) results in the single product, *viz.*, lead(II)tetraphenylchlorin. The unstable anion of metallophlorin formed initially by Eq. (4) is likely isomerized under these conditions to metallochlorin after protonation to porphodimethene, as occurs when ZnTPP, H_2P, and ZnEP are chemically reduced (EP is etioporphyrin).[5] The effect of photons on the complex formation (see Table 1), *viz.*, an increase in the relative yield of PbTPP, also confirms the mechanism presented above: the phlorin anion is deprotonated under the action of light and temperature,[5] *i.e.*, it is stabilized in respect of both its transformation into porphodimethene and then to chlorin and of its further oxidation to $[PbTPP]^{2+}$. This stabilization results in a more efficient transformation of the $PbTPP^{2-}$ dianion directly into PbTPC (Eq. (5)). The reaction of $Pb(OAc)_2$ with H_2TPP in acidic rather than in basic medium makes transformation (5) predominant: one complex compound PbTPC is formed (see Fig. 1, curve *2*), which then dissociates to H_4TPP^{2+} because of its lability (see Fig. 1, curves *3* and *4*).

Two complex compounds, *viz.*, PbTPC and $(OAc)_2PbTPP \cdot DMF$, are formed when the synthesis is performed in DMF, *i.e.*, the replacement of one aprotic solvent by another (Py by DMF) does not change the result (see Table 1).

Thus, the data considered agree well with the mechanism of chemical, photochemical, or mixed reduction of porphyrins and metalloporphyrins described in the literature.[2,5,15] No formation of bacteriochlorin and isobacteriochlorin, such as that occurring in the reduction of H_2TPP and $Sn^{IV}OEP$,[2] was observed in the complex formation of H_2TPP with Pb^{2+}. The direct complex formation of H_2TPP with Pb^{4+} that is generated due to reaction (2) also does not occur, because it requires much more drastic conditions[3] than those for the complex formation with Pb^{2+}.

References

1. P. Rothemund and A. R. Menotti, *J. Am. Chem. Soc.*, 1948, **70**, 1808.
2. W. Flitsch, *Advances in Heterocyclic Chemistry*, Academic Press, San Diego, *etc.*, 1988, **43**, 73.
3. T. N. Lomova and B. D. Berezin, *Koord. Khim.*, 1993, **19**, 157 [*Russ. J. Coord. Chem.*, 1993, **19** (Engl. Transl.)].
4. J. W. Whitlock, Jr., M. Y. O. Hanauer, and B. K. Bower, *J. Am. Chem. Soc.*, 1969, **91**, 7485.
5. *The Porphyrins*, Ed. D. Dolphin, Academic Press, New York, 1978, **2**.
6. A. M. Schaffer and M. Gouterman, *Theor. Chim. Acta*, 1970, **18**, 1.
7. J. A. Ferguson, T. J. Meyer, and D. G. Whitten, *Inorg. Chem.*, 1972, **11**, 2767.
8. Author's Certificate USSR 1616124, 1990.
9. T. N. Lomova, E. G. Mozhzhukhina, and B. D. Berezin, *Zh. Neorg. Khim.*, 1993, **38**, 1552 [*Russ. J. Inorg. Chem.*, 1993, **38** (Engl. Transl.)].
10. T. N. Lomova and B. D. Berezin, *VII Mezhdunarodnaya konferentsiya po khimii porfirinov i ikh analogov* [*VII International Conference on Chemistry of Porphyrins and Their Analogs*], Abstracts, St. Petersburg, 1993, 7 (in Russian).
11. R. A. Lones, *Aust. J. Chem.*, 1963, **16**, 93.
12. Yu. Yu. Lur'e, *Spravochnik po analiticheskoi khimii* [*Handbook on Analytical Chemistry*], Khimiya, Moscow, 1967, 390 (in Russian).
13. *The Porphyrins*, Ed. D. Dolphin, Academic Press, New York, 1978, **5**.
14. G. Peychal-Heiling and G. Wilson, *Anal. Chem.*, 1971, **43**, 550.
15. I. A. Blinova and V. V. Vasil'ev, *I Mezhdunarodnaya konferentsiya po biokoordinatsionnoi khimii* [*I International Conference on Biocoordination Chemistry*], Abstracts, Ivanovo, 1994, 111 (in Russian).

Received September 11, 1997;
in revised form April 7, 1998