Synthesis and Characterization of Some Five-Coordinated Tetraazaporphyrin and Phthalocyanine Manganese(III) Complexes

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Soluble pentacoordinated manganese(III) complexes with substituted tetraazaporphyrins (TAPs) containing m-trifluoromethylphenyl, p-tert-butylphenyl groups and phthalocyanines (Pcs) containing m-trifluoromethylphenyl, m-trifluoromethylphenoxy and 3,5-di-tert-butylphenoxy groups have been synthesized either by direct metallation of macrocycles (TAPMn, 1a, and PcMns, 3a and 4a) or by template cyclotetramerization of the corresponding fumaronitrile (TAPMn, 2a) and phthalonitrile (PcMn, 5a) and characterized in details.

Keywords: Phthalocyanines, tetraazaporphyrins, manganese complexes, synthesis, spectroscopic properties.

Introduction

At present, the practical uses of porphyrins (P), tetraazaporphyrins (TAP), phthalocyanines (Pc) and their metal complexes are intensively developing.[1,2] The steady interest in TAPMn and PcMn compounds has grown up after it was found that the manganese complexes are active catalysts in oxidation processes as the iron derivatives are.[3] Therefore, when applying PMns and PcMns as catalysts, it is reasonable to expect some selectivity in oxidation of hydrocarbons, which can be achieved and controlled by optimization of the reaction conditions.[4]

Processes of hydrogen peroxide decomposition catalyzed by PMn and PcMn are also important. Along with the widespread heme catalase, which is known to decompose hydrogen peroxide in living cells, non-heme catalase containing manganese ions have been found in a number of bacteria.[5,6]

MnIII porphyrins and phthalocyanines have also been utilized as building blocks for molecular magnets.[7,8]

Manganese tetraazaporphyrins and phthalocyanines are reported in a number of publications, where their X-ray data,[9,10] EPR spectra,[11-14] electrochemical[15,16] and catalytic[13,17-19] properties are described. The progress in the study and use of the properties of manganese complexes is significantly defined by their solubility in various solvents.

Octaaryltetraazaporphyrins (Ar)TAPMn(OAc), where Ar = m-trifluoromethylphenyl (m-CF3Ph) (1a) and p-tert-butylphenyl (p-tBuPh) (2a), and new manganese(III) octaaryl- and octaaryloxyphthalocyanines (Ar)PCMN(OAc), where Ar = m-trifluoromethylphenyl (m-CF3Ph) (3a), m-trifluoromethylphenoxy (m-CF3PhO) (4a) and 3,5-di-tert-butylphenoxy (3,5-di-tBuPhO) (5a) were studied.

Experimental

Bis(p-tert-butylphenyl)fumaronitrile and 4,5-bis(3,5-di-tert-butylphenoxy)-phthalonitrile were prepared according to literature.[20-22] Octakis(m-trifluoromethylphenyl)tetraazaporphyrin (m-CF3Ph)TAPH2 (1), octakis(m-trifluoromethylphenyl)
The present paper describes the synthesis and characterization of complexes of tetraazaporphyrin and phthalocyanine with manganese(III) acetate. The complexes were synthesized using the following reactions:

1. Reaction of Mn(OAc)2 with 4H2O in DMF at room temperature and treated further as described for 1a. Yield: 0.61 g (0.27 mmol, 46%). UV-vis (CHCl3) λmax (lg ε): 393 (4.52), 513 (4.16), 735 (4.82). IR (KBr) νmax cm⁻¹: 3293 s, 2928 s, 2986 w, 1725 w, 1608 w, 1586 s, 1508 w, 1459 s, 1421 s, 1407 s, 1384 w, 1363 m, 1373 w, 1296 s, 1246 w, 1199 w, 1119 w, 1084 m, 1042 w, 1002 w, 961 w, 903 w, 864 w, 745 w, 707 m. Found: C 77.37, H 8.65, N 4.74 %. C146H179N8O10Mn requires C 77.56, H 7.98, N 4.95. MS (MALDI-TOF) m/z: 2199.52 [(3,5-di-tert-butylphenoxy)phthalocyaninato)manganese(III) acetate (pBuO)4PCl2Mn(OAc)].

2. Reaction of Mn(OAc)2 with 4H2O in 2-dimethylaminoethan-1-ol (6 ml) under reflux in the presence of formamide, followed by addition of Mn(OAc)2 (41.0 mg, 0.17 mmol) and 4H2O (0.85 g, 3.48 mmol) in 2-dimethylaminoethanol (7 ml) was heated gradually with stirring to 150°C and the temperature was maintained for 10 h. Completion of the reaction mixture was monitored by TLC, until no traces of starting material were detected. The reaction mixture was cooled, poured into 50 ml of water and the formed precipitate was centrifugated, dried, dissolved in CH2Cl2 and its UV-vis spectrum was found to be similar as in the case of the other solvents (chloroform and chromatographed (silica gel/CHCl3-1%CH3OH) and dried under vacuum (60°C, 24 h). Yield: 0.52 g (0.35 mmol, 48%). UV-vis (CHCl3) λmax nm (lg ε): 413 (4.42), 493 (4.38), 674 (4.58). IR (KBr) νmax cm⁻¹: 2962 s, 2905 w, 2868 m, 1717 w, 1609 m, 1463 m, 1384 m, 1364 m, 1299 w, 1269 w, 1197 w, 1147 w, 1109 w, 997 s, 891 s, 850 w, 839 m, 811 s, 751 s, 635 w, 599 w, 585 w, 563 s. Found: C 78.82, H 7.27, N 7.55 %. MS (MALDI-TOF) m/z: 1243.78 [(p-BuO)4PCl2Mn]+ (calcd. for C144H176N8O8Mn 1423.10).

3. Reaction of Mn(OAc)2 with 4H2O (60.3 mg, 0.25 mmol) and (m-CF3PhO)4PCl2Mn(OAc) (4.16), 735 (4.82). IR (KBr) νmax cm⁻¹: 3293 s, 2928 s, 2986 w, 1725 w, 1608 w, 1586 s, 1508 w, 1459 s, 1421 s, 1407 s, 1384 w, 1363 m, 1373 w, 1296 s, 1246 w, 1199 w, 1119 w, 1084 m, 1042 w, 1002 w, 961 w, 903 w, 864 w, 745 w, 707 m. Found: C 77.37, H 8.65, N 4.74 %. C146H179N8O10Mn requires C 77.56, H 7.98, N 4.95. MS (MALDI-TOF) m/z: 2199.52 [(3,5-di-tert-butylphenoxy)phthalocyaninato)manganese(III) acetate (m-CF3PhO)4PCl2Mn(OAc)].

4. Reaction of Mn(OAc)2 with 4H2O (61.9 mg, 0.034 mmol) were heated (100°C) in DMF (10 ml) at room temperature for 5 min with following addition of AcOH (3 drops). After 1 h the reaction mixture was poured into water and the formed precipitate was centrifugated, dried, dissolved in CH2Cl2 and filtered. The obtained precipitate was dissolved in methanol, precipitated by dropwise addition of water, and filtered. The obtained precipitate was dissolved in chloroform and chromatographed (silica gel/CH2Cl2-1%CH3OH) and dried under vacuum (60°C, 24 h). Yield: 0.61 g (0.27 mmol, 46%). UV-vis (CHCl3) λmax (lg ε): 393 (4.52), 513 (4.16), 735 (4.82). IR (KBr) νmax cm⁻¹: 3293 s, 2928 s, 2986 w, 1725 w, 1608 w, 1586 s, 1508 w, 1459 s, 1421 s, 1407 s, 1384 w, 1363 m, 1373 w, 1296 s, 1246 w, 1199 w, 1119 w, 1084 m, 1042 w, 1002 w, 961 w, 903 w, 864 w, 745 w, 707 m. Found: C 77.37, H 8.65, N 4.74 %. C146H179N8O10Mn 2199.52. MS (MALDI-TOF) m/z: 2199.52 [(3,5-di-tert-butylphenoxy)phthalocyaninato)manganese(III) acetate (m-CF3PhO)4PCl2Mn(OAc)].

Results and Discussion

Synthesis

The UV-vis spectra of (m-CF3PhO)4PCl2Mn(OAc) exhibit two typical bands in the visible region with the absorption maxima at 594 and 655 nm (Figure 1). When Mn(OAc)2 is added to the solution of 1 in DMF at room temperature, the spectrum of metal-free 1 changes, resulting in two bands with absorption maxima at 561 and 644 nm and lower intensity (Figure 1). It remains unchanged for a some time. After addition of AcOH to the reaction mixture, the two-band spectrum immediately changes to a one-band spectrum with the maximum at 646 nm (Figure 1). After isolation of the resulting product in a solid state, it was dissolved in CH2Cl2 and its UV-vis spectrum was found to be similar to that of Ph2TAPMn(III)(Cl) described earlier (Table 1). The isolated TAPMn(OAc) (1a) gives a one-band spectrum in the visible region in pyridine or DMF respectively, as well as in the case of the other solvents (chloroform, dichloromethane). No second band at ~ 560 nm was observed. The
same spectral changes with two bands at final spectrum were also observed in the reaction of octaphenyltetraazaporphyrin Ph1TAP1 and octa(p-bromophenyl)tetraazaporphyrin (p-BrPh)2TAP1 respectively with Mn(OAc)2, in pyridine at room temperature,[25] as in the case when reaction of I with Mn(OAc)2 is proceeding in pyridine.

Table 1. UV-vis spectra of substituted PcMn and TAPMn.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Solvent</th>
<th>( \lambda_{\text{max}} ) nm (lgc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>CHCl3</td>
<td>406 (4.57), 461 (4.32), 654 (4.71)</td>
</tr>
<tr>
<td>2a</td>
<td>CHCl3</td>
<td>413 (4.42), 493 (4.38), 674 (4.58)</td>
</tr>
<tr>
<td>Ph2TAPMn(Cl)2[26]</td>
<td>CHCl3</td>
<td>413 (4.40), 475(4.12), 665 (4.43)</td>
</tr>
<tr>
<td>3a</td>
<td>CHCl3</td>
<td>392 (4.52), 525 (4.11), 739 (4.82)</td>
</tr>
<tr>
<td>4a</td>
<td>CHCl3</td>
<td>389 (4.52), 515 (4.08), 724 (4.84)</td>
</tr>
<tr>
<td>5a</td>
<td>CHCl3</td>
<td>393 (4.52), 513 (4.16), 735 (4.82)</td>
</tr>
<tr>
<td>Bu4PcMn(Cl)2[16]</td>
<td>benzene</td>
<td>351 (4.72), 518 (4.23), 725 (5.06)</td>
</tr>
<tr>
<td>Bu4PcMn[16]</td>
<td>benzene</td>
<td>350, 680</td>
</tr>
<tr>
<td>Bu2PcMn[16]</td>
<td>pyridine</td>
<td>350, 480, 560, 660, 840, 880</td>
</tr>
</tbody>
</table>

Complexation of porphyrins[26] and azaporphyrins[27] with MnII salts in solution is commonly accompanied by an instantaneous oxidation of MnII to MnIII in the presence of air. Thus the compounds PMnIII(X), having characteristic electronic absorption spectra, are formed. The spectra of tetraazaporphyrinatamanganese(III) contain one intense electronic absorption spectra, are formed. The spectra of anion Pc-3a phthalocyaninatamanganese(III) acetate (3a) and octakis(p-tolyl)phthalocyaninatamanganese(III) acetate (4a) can also be achieved by direct metatllation of the corresponding macrocycles. The spectral changes during the reaction of (m-CF3Ph)2PcH1 in DMF were displayed as an example in Figure 2. The UV-vis spectra of 3 in DMF and pyridine exhibit two typical bands with absorption maxima at 682 and 713 nm. The reaction mixture spectrum however has a single absorption band at 693 nm. The intensity of this band decreases with time and finally it disappears completely (Figure 2), while a new absorption band appears at 724 nm. The spectrum of the resulting solution is similar to that of \( \text{Bu}_4\text{PcMnCl}_2[16] \) that specifies the formation of PcMn(OAc)3 (3a). The spectrum with \( \lambda_{\text{max}} = 693 \) nm corresponds probably to PcMnIII. Proceeding of the analogous complexation reaction in unaerobic conditions leads to the formation of one product PcMnIII[16] (Table 1), and the oxidation of MnII to MnIII under the air takes place during the purification. TLC of the reaction mixture 3 - Mn(OAc)2 in DMF at the beginning and at the middle of the reaction shows the presence of two compounds. DMF or pyridine can stabilize the +2 oxidation state of a central manganese atom at the moment of complex formation, but it cannot prevent the oxidation to manganese(III) phthalocyanine by air.

Figure 2. Changes of UV-vis spectra during the reaction of (m-CF3Ph)2PcH1 with Mn(OAc)2 in DMF at 298 K, C(PcH1) = 1.910−4 mol L−1, C(Mn(OAc)2) = 4.410−4 mol L−1. The time between the measurements is 5 min.

\((p-\text{BuPh})_2\text{TAPMn}^\text{III}(\text{OAc})\) (2a) and (3,5-di-\text{BuPhO})2PcMnIII(OAc) (5a) were prepared by cyclotramerization of the corresponding bis(\text{p-tert-butylphenyl}) furanominitrole and 4,5-bis(3,5-di-\text{tert-butylphenoxo}) phthalonitrile in 2-dimethylaminoethanol or hexanol-1, respectively. Direct metatllation of octakis(\text{p-tert-butylphenyl}) tetraazaporphyrin (2) by manganese(II) acetate did not result in the formation of 2a, because TAPH1 is not soluble even in boiling DMF, and its heterogeneous reaction with Mn(OAc)2 in refluxing DMF led only to the decomposition of macrocycle.

Characterization of the Compounds Prepared

Investigation of the physicochemical properties of 1a - 5a confirms their molecular composition and gives an insight on the influence of the substituents on properties of the corresponding compounds.

For all the compounds 100% peak of [PcMn]3+ (or [TAPMn]3+) in mass spectra was detected and no other fragmentation signals were observed (Figure 3). The absence of [PcMn(OAc)]3+ (or [TAPMn(OAc)]3+) peak indicates the dis-
Complexes of Tetraazaporphyrin and Phthalocyanine with Manganese(III)

association of the axial ligand under the conditions of MALDI experiment in the case of compounds with both electron-donating (CF₃, Ph, CF₃Ph, and naphthyl) and electron-accepting (tBuPh, tBuPhO) groups suggesting electron buffer properties of tetraazamacrocyclic in 1a-5a. This result is in agreement with IR (see lower) and UV-vis data.

The lge values of the Q-bands of 1a-5a are in the range of 4.7–4.8 and are slightly dependent on the nature of the peripheral substituents in the case of TAP complexes and independent in Pc complexes. However, lge values of 1a and 2a are lower than those found for axially coordinated indium complexes with octakis(m-trifluoromethylphenyl)tetraazaporphyrin and octakis(p-butyphenyl)tetraazaporphyrin (with opposite electron effect of substituents). The specificity of functional groups and coordination center in Mn(III) complexes explains this regularity. Obviously, electron –l effect of m-CF₃Ph-, m-CF₃PhO- groups gradually disappears along the chain of atoms and the positive effect of the conjugation of p-tBuPh-, 3,5-di-tBuPhO- groups is not observed because the dative π-bonds Mn(3d)←N taking place in manganese(III) porphyrin complexes are absent due to strong π-acceptor properties of tetraazamacrocycle.

Two intense bands at 650–680 nm (Q-band) and 405–415 nm (B-band) in the spectra of complexes 1a and 2a correspond to π→π* transitions. Comparison of the UV-vis spectra of PcMn(OAc) 3a-5a and the corresponding complexes of tetraazaporphyrins 1a and 2a (Table 1) shows that extension of the conjugated π-system of the macrocycle leads to the bathochromic shift of the Q-band (720–740 nm) and to the hypsochromic shift of the B-band (385–395 nm). This is in good agreement with the theoretical results: annelation of benzene rings to the porphyrinaceous macrocycle results in the π-MOs destabilization, which increases in the order a₁u < a₂u < a₂g. Similar bathochromic shift of the Q-band was observed in the order of m-CF₃Ph, m-CF₃PhO- > p-tBuPhO- > 3,5-di-tBuPhO- substituted complexes of Mn(III). Thus the electronic effect of substituents on the coordination center is not observed, but the p-tert-butylphenyl groups conjugation with aromatic macrocycle takes place.

The most intense bands in the IR spectra of 1a-5a are in the region of 500 – 1700 cm⁻¹ and are caused by combined vibrations of peripheral phenyl rings and the macrocycle skeleton. They are similar to those observed for the same complexes with magnesium and indium and their frequencies are practically independent on the nature of the metal. The FT IR spectra of 2a and 5a show additional intense bands at 2963, 2905-2928, 2868 cm⁻¹ due to the stretching vibrations of the tert-butyl groups. Very intense stretching vibrations of CF₃ groups in peripheral aromatic rings, along with the mixed νC=O and deformational aryl ring modes, are dominating in the spectra of 1a, 3a and 4a. They were observed at approximately 1330, 1170, 1127 and 1071 cm⁻¹.

The presence of the axial ligand AcO⁻ was verified by IR spectroscopy. The characteristic vibrations of axial AcO⁻ group were observed at approximately 1620 and 1384 cm⁻¹, and their frequencies are practically independent of the nature of the macrocycle.

EA data for the prepared compounds are, generally, in satisfactory agreement with the calculated values. However, the relatively low conformity of the found and theoretical values for carbon in case of fluorinated TAPMn 1a and PcMns 3a and 4a can result from the influence of the high content of fluorine. Similar difficulties in combustion analysis were also observed in case of fluorine-containing phthalocyanines but not in works.

The preliminary investigation of light stability of some of the prepared compounds was carried out in chloroform or dichloromethane solutions in a quartz cuvette, directly exposed to daylight for several days. Under this conditions, no decomposition was observed for compounds 1a-5a. Because of their observed comparatively high stability in

Figure 3. MALDI-TOF spectra of compounds 1a and 3a.
solutions in the presence of air, such complexes could be used as catalysts for various oxidation processes.

Among the synthesized complexes compound 5a is the most perspective for research of liquid crystal properties as the calculation of molecular parameters and the preliminary mesomorphism forecast has shown 50% probability of thermotropic mesophase presence at this substance. Calculation and the forecast were conducted by Dr. Akopova O.B. using molecular mechanics method (MM+ force field) (HyperChem Pro 6.0) and original software product CMP ChemCard for all complexes.\[39\]

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T. N. Lomova et al.