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]

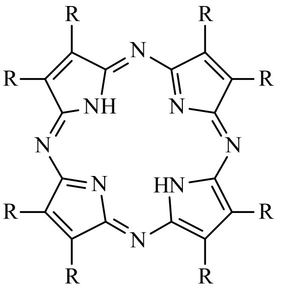
Mn^{III} porphyrins and phthalocyanines have also been utilized as building blocks for molecular magnets.[7,8]

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[3,17-19] properties are described. The progress in the study and use of the properties of manganese complexes is substantially defined by their solubility in various solvents. We report here synthesis and spectral properties of a series of new manganese(III) complexes with substituted phenyl and phenoxy groups in macrocycle soluble in organic solvents.

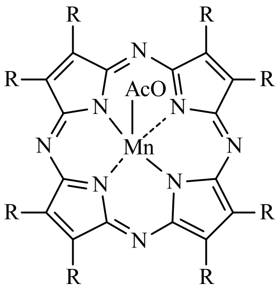
Octaaryltetraazaporphyrins $(Ar)_8TAPMn(OAc)$, where Ar = *m*-trifluoromethylphenyl (*m*-CF_3Ph) (**1a**) and *p*-*tert*-butylphenyl (*p*-^{t}BuPh) (**2a**), and new manganese(III) octaaryl- and octaaryloxyphthalocyanines $(Ar)_8PcMn(OAc)$, where Ar = *m*-trifluoromethylphenyl (*m*-CF_3Ph) (**3a**), *m*-trifluoromethylphenoxy (*m*-CF_3PhO) (**4a**) and 3,5-di-*tert*-butylphenoxy (3,5-di-^{t}BuPhO) (**5a**) were studied.

Experimental

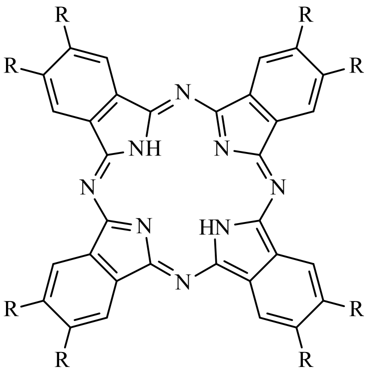
Bis(*p*-*tert*-butylphenyl)fumaronitrile and 4,5-bis(3,5-di-*tert*-butylphenoxy)-phthalonitrile were prepared according to literature.[20-22] Octakis(*m*-trifluoromethylphenyl)tetraazaporphyrin (*m*-$CF_3Ph)_8TAPH_2$ (**1**), octakis(*m*-trifluoromethylphenyl)



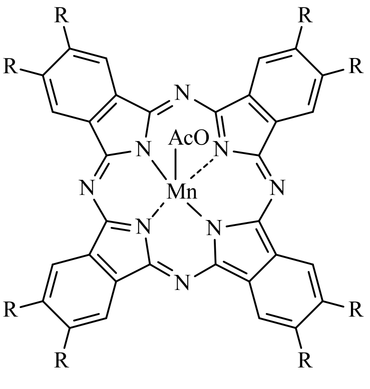
1: R = *m*-CF_3Ph
2: R = *p*-^{t}BuPh



1a: R = *m*-CF_3Ph
2a: R = *p*-^{t}BuPh



3: R = *m*-CF_3Ph
4: R = *m*-CF_3PhO



3a: R = *m*-CF_3Ph
4a: R = *m*-CF_3PhO
5a: R = 3,5-di-^{t}BuPhO

phthalocyanine (*m*-$CF_3Ph)_8PcH_2$ (**3**) and octakis(*m*-trifluoromethylphenoxy)phthalocyanine (*m*-$CF_3PhO)_8PcH_2$ (**4**) were synthesized as we have described earlier.[23, 24]

Solvents for the synthesis, chromatography, and spectroscopic characterization of compounds were pure chemicals (Aldrich, Fluka).

The following equipment was used for characterization: Shimadzu UV-365 (UV-vis spectra); Bruker Tensor 27 (FT-IR spectra); Euro EA 3000 (elemental analysis); Bruker Autoflex MS (MALDI-TOF).

(Octakis(m-trifluoromethylphenyl)tetraazaporphyrinato)manganese(III) acetate (m-$CF_3Ph)_8$TAPMn(OAc), ***1a***. $Mn(OAc)_2 \cdot 4H_2O$ (53.2 mg, 0.21 mmol) and (*m*-$CF_3Ph)_8TAPH_2$ (**1**) (51.4 mg, 0.035 mmol) were reacted 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 CH_2Cl_2 and chromatographed (silica gel/CH_2Cl_2). Yield: 26.0 mg (0.017 mmol, 47%), yellow-green powder. UV-vis (CH_2Cl_2) λ_{max} nm (lgε): 406 (4.57), 461 (4.32), 654 (4.71). IR (KBr) ν_{max} cm^{-1}: 1719 w, 1620 w, 1481 w, 1420 w, 1384 w, 1330 vs, 1312 s, 1279 w, 1169 s, 1128 s, 1098 m, 1076 s, 1016 m, 920 m, 810 m, 762 m, 722 m, 699 s. Found: C 54.33, H 2.40, N 6.95 %. $C_{74}H_{35}N_8F_{24}O_2Mn$ requires C 56.29, H 2.23, N 7.10 %. MS (MALDI-TOF) *m/z*: 1519.95 [(*m*-$CF_3Ph)_8TAPMn]^+$ (calcd. for $C_{72}H_{32}N_8F_{24}Mn$ 1519.0).

(Octakis(p-tert-butylphenyl)tetraazaporphyrinato)manganese(III) acetate (p-$^tBuPh)_8$TAPMn(OAc), ***2a***. A mixture of bis(*p*-*tert*-butylphenyl)fumaronitrile (1 g, 2.91 mmol) and $Mn(OAc)_2 \cdot 4H_2O$ (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 was monitored by TLC, until no traces of starting material were detected. The reaction mixture was cooled, poured into 50 ml of methanol and the precipitate was centrifugated. For purification, the product was dissolved in chloroform and an equal amount of methanol was added to the solution. Chloroform was partially removed from the obtained solution using a rotary evaporator, and the formed precipitate was filtered off, chromatographed (silica gel/$CHCl_3$-1%CH_3OH) and dried under vacuum (60°C, 24 h). Yield: 0.52 g (0.35 mmol, 48%). UV-vis (CH_2Cl_2) λ_{max} nm (lgε): 413 (4.42), 493 (4.38), 674 (4.58). IR (KBr) ν_{max} cm^{-1}: 2962 s, 2905 m, 2868 m, 1717 w, 1609 m, 1477 m, 1463 m, 1384 m, 1364 m, 1299 w, 1269 m, 1197 w, 1147 w, 1109 m, 997 s, 891 s, 850 w, 839 m, 811 s, 751 s, 635 w, 599 w, 585 w, 563 m. Found: C 78.82, H 7.47, N 7.31 %. $C_{98}H_{107}N_8O_2Mn$ requires C 79.32, H 7.27, N 7.55 %. MS (MALDI-TOF) *m/z*: 1423.78 [(*p*-$^tBuPh)_8TAPMn]^+$ (calcd. for $C_{96}H_{104}N_8Mn$ 1423.0).

(Octakis(m-trifluoromethylphenyl)phthalocyaninato)manganese(III) acetate (m-$CF_3Ph)_8$PcMn(OAc), ***3a***. $Mn(OAc)_2 \cdot 4H_2O$ (41.0 mg, 0.17 mmol) and (*m*-$CF_3Ph)_8PcH_2$ (**3**) (44.0 mg, 0.026 mmol) were reacted in DMF (10 ml) at room temperature for 1 h. The reaction mixture was treated further as described for **2a**. Yield: 25.2 mg (0.014 mmol, 54%), deep-green powder. UV-vis (CH_2Cl_2) λ_{max} nm (lgε): 392 (4.52), 525 (4.11), 739 (4.82). IR (KBr) ν_{max} cm^{-1}: 1721 w, 1624 m, 1508 w, 1422 w, 1385 w, 1333 s, 1256 w, 1217 w, 1169 s, 1128 s, 1101 s, 1077 m, 1042 w, 963 w, 899 w, 825 w, 805 m, 767 w, 749 w, 714 m, 658 s. Found: C 58.66, H 2.42, N 5.86 %. $C_{90}H_{45}N_8F_{24}O_2Mn$ requires C 60.69, H 2.55, N 6.29. MS (MALDI-TOF) *m/z*: 1721.25 [(*m*-$CF_3Ph)_8PcMn]^+$ (calcd. for $C_{88}H_{42}N_8F_{24}Mn$ 1721.0).

(Octakis(m-trifluoromethylphenoxy)phthalocyaninato)manganese(III) acetate (m-$CF_3PhO)_8$PcMn(OAc), ***4a***. $Mn(OAc)_2 \cdot 4H_2O$ (60.3 mg, 0.25 mmol) and (*m*-$CF_3PhO)_8PcH_2$ (**4**) (61.9 mg, 0.034 mmol) were heated (100°C) in DMF (10 ml) and stirred for 48 h. The reaction mixture was cooled to room temperature and treated further as described for **2a**. Yield: 38.2 mg (0.02 mmol, 58%), green powder. UV-vis (CH_2Cl_2) λ_{max} nm (lgε): 389 (4.52), 515 (4.08), 724 (4.84). IR (KBr) ν_{max} cm^{-1}: 1720 w, 1617 m, 1594 m, 1492 m, 1450 s, 1409 m, 1385, 1328 vs, 1283 s, 1208 w, 1174 s, 1128 s, 1086 m, 1065 m, 1039 w, 922 m, 794 w, 748 w, 697 m. Found: C 54.63, H 2.64, N 5.90 %. $C_{90}H_{45}N_8F_{24}O_{10}Mn$ requires C 56.62, H 2.38, N 5.87. MS (MALDI-TOF) *m/z*: 1849.21 [(*m*-$CF_3PhO)_8PcMn]^+$ (calcd. for $C_{88}H_{42}N_8F_{24}O_8Mn$ 1849.0).

(Octakis(3,5-di-tert-butylphenoxy)phthalocyaninato)manganese(III) acetate (3,5-di-$^tBuPhO)_8$PcMn(OAc), ***5a***, was obtained by the reaction of 4,5-bis(3,5-di-*tert*-butylphenoxy)phthalonitrile (1.25 g, 2.33 mmol) and $Mn(AcO)_2 \cdot 4H_2O$ (0.25 g, 1.02 mmol) in hexanol-1 (6 ml) under reflux in the presence of DBU (6 drops) at 160°C. The reaction mixture was poured into 60 ml of methanol, precipitated by dropwise addition of water, and filtered. The obtained precipitate was dissolved in chloroform and chromatographed (silica gel/$CHCl_3$-1%CH_3OH). Yield: 0.61 g (0.27 mmol, 46%). UV-vis (CH_2Cl_2) λ_{max} nm (lgε): 393 (4.52), 513 (4.16), 735 (4.82). IR (KBr) ν_{max} cm^{-1}: 2963 s, 2928 m, 2868 w, 1725 w, 1608 m, 1586 s, 1508 w, 1459 s, 1421 s, 1407 s, 1384 w, 1363 m, 1337 w, 1296 s, 1246 w, 1199 s, 1119 w, 1084 m, 1042 w, 1002 w, 961 s, 903 w, 864 w, 745 w, 707 m. Found: C 77.37, H 8.65, N 4.74 %. $C_{146}H_{179}N_8O_{10}Mn$ requires C 77.56, H 7.98, N 4.95. MS (MALDI-TOF) *m/z*: 2199.52 [(3,5-*di*-$^tBuPhO)_8PcMn]^+$ (calcd. for $C_{144}H_{176}N_8O_8Mn$ 2199.0).

Results and Discussion

Synthesis

The UV-vis spectra of (*m*-$CF_3Ph)_8TAPH_2$ (**1**) in DMF 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 CH_2Cl_2 and its UV-vis spectrum was found to be similar to that of $Ph_8TAPMn^{III}(Cl)$ described earlier[25] (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

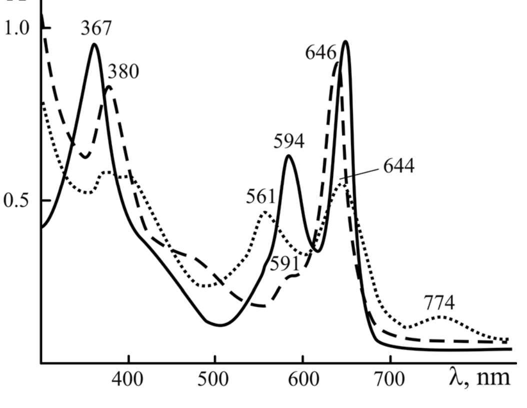


Figure 1. UV-vis (298 K) spectra of (*m*-$CF_3Ph)_8TAPH_2$ (**1**) in DMF (solid line), after the successive addition of $Mn(OAc)_2$ (dotted line) and AcOH (dashed line).

same spectral changes with two bands at final spectrum were also observed in the reaction of octaphenyltetraazaporphyrin Ph_8TAPH_2 and octa(*p*-bromophenyl)tetraazaporphyrin (*p*-BrPh)$_8$TAPH$_2$ respectively with $Mn(OAc)_2$ in pyridine at room temperature,[25] as in the case when reaction of **1** with $Mn(OAc)_2$ is proceeding in pyridine.

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

Complex	Solvent	$\lambda_{max,}$ nm (lgε)
1a	CH_2Cl_2	406 (4.57), 461 (4.32), 654 (4.71)
2a	CH_2Cl_2	413 (4.42), 493 (4.38), 674 (4.58)
$Ph_8TAPMn(Cl)$[25]	$CHCl_3$	413 (4.40), 475(4.12), 665 (4.43)
3a	CH_2Cl_2	392 (4.52), 525 (4.11), 739 (4.82)
4a	CH_2Cl_2	389 (4.52), 515 (4.08), 724 (4.84)
5a	CH_2Cl_2	393 (4.52), 513 (4.16), 735 (4.82)
$^tBu_4PcMn(Cl)$[16]	benzene	351 (4.72), 518(4.23), 725 (5.06)
$^tBu_4PcMn$[16]	benzene	350, 680
$^tBu_4PcMn$[16]	pyridine	350, 480,560, 660, 840, 880

Complexation of porphyrins[26] and azaporphyrins[27] with Mn^{II} salts in solution is commonly accompanied by an instantaneous oxidation of Mn^{II} to Mn^{III} in the presence of air. Thus the compounds $PMn^{III}(X)$, having characteristic electronic absorption spectra, are formed. The spectra of tetraazaporphyrinatomanganese(III) contain one intense *Q*-band at 650-680 nm and an additional but weaker absorption band at 450-480 nm.[27]

The reaction of $TAPH_2$ with $Mn(OAc)_2$ in pyridine yields a product, the electronic absorption spectrum of which in the visible region contains two bands shifted hypsochromically as compared to that of $TAPH_2$.[23,28]

As it was shown by UV-vis spectroscopy for phthalocyanines, the axial coordination of Py causes the formation of manganese(II) complexes $PcMn^{II}\cdot Py$ and $PcMn^{II}\cdot 2Py$.[29] According to paper[16] there is intramolecular electron transfer resulting in the formation of two new forms of Mn^{II} complex - the radical-cation $Pc^{+\bullet}Mn^{I}\cdot n Py$ and radical-anion $Pc^{-\bullet}Mn^{III}\cdot n Py$, which are confirmed by UV-vis spectra (λ_{max} 560, 880 and 480, 840 nm, correspondingly). The possibility of formation of the μ-oxo complex $(MnPcPy)_2O$ was shown in paper[30]. However, it takes place when PcMn is dissolved in pyridine solution, but not in the process of the macrocycle complexation with Mn^{II} salt. We did not observe any spectrum similar to that of μ-oxo complex in our work.

The analysis of the experimental and literature data (Table 1) makes it possible to conclude that reaction of **1** with $Mn(OAc)_2$ in DMF or pyridine yields Mn^{II} complex (λ_{max} = 644 nm) and the corresponding radical-cation (λ_{max} = 561, 774 nm). Finally the product of complexation reaction after addition of AcOH is manganese(III) complex characterized by UV-vis, IR, and MALDI-TOF methods.

The formation of octakis(*m*-trifluoromethylphenyl) phthalocyaninatomanganese(III) acetate (**3a**) and octakis(*m*-trifluoromethylphenoxy)phthalocyaninatomanganese(III) acetate (**4a**) can also be achieved by direct metallation of the corresponding macrocycles. The spectral changes during the reaction of (*m*-$CF_3Ph)_8PcH_2$ (**3**) with $Mn(OAc)_2$ in DMF are 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 $^tBu_4PcMn(Cl)$,[16] that specifies the formation of PcMn(OAc) (**3a**). The spectrum with λ_{max} = 693 nm corresponds probably to $PcMn^{II}$. Proceeding of the analogous comlexation reaction in unaerobic conditions leads to the formation of one product $PcMn^{II}$ [16] (Table 1), and the oxidation of Mn^{II} to Mn^{III} 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.

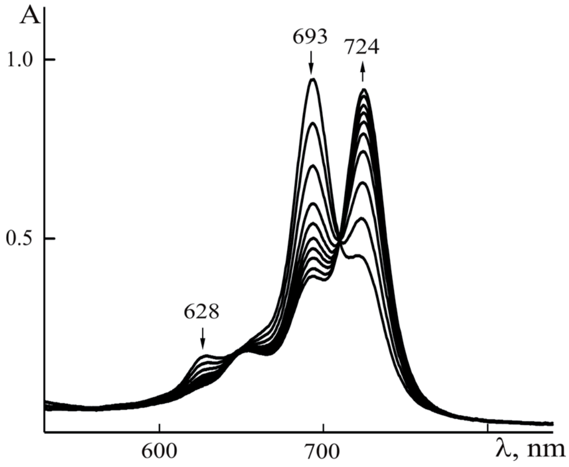


Figure 2. Changes of UV-vis spectra during the reaction of (*m*-$CF_3Ph)_8PcH_2$ with $Mn(OAc)_2$ in DMF at 298 K, $C(PcH_2) = 1.9\cdot 10^{-5}$ mol·l^{-1}, $C(Mn(OAc)_2) = 4.4\cdot 10^{-4}$ mol·l^{-1}. The time between the measurements is 5 min.

(*p*-^{t}BuPh)$_8$TAPMn^{III}(OAc) (**2a**) and (3,5-di-^{t}BuPhO)$_8$PcMn^{III}(OAc) (**5a**) were prepared by cyclotetramerization of the corresponding bis(*p*-*tert*-butylphenyl) fumaronitrile and 4,5-bis(3,5-di-*tert*-butylphenoxy) phthalonitrile in 2-dimethylaminoethanol or hexanol-1, respectively. Direct metallation of octakis(*p*-*tert*-butylphenyl) tetraazaporphyrin (**2**) by manganese(II) acetate did not result in the formation of **2a**, because $TAPH_2$ **2** 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 correspond compounds.

For all the compounds 100% peak of $[PcMn]^+$ (or $[TAPMn]^+$) in mass spectra was detected and no other fragmentation signals were observed (Figure 3). The absence of $[PcMn(OAc)]^+$ (or $[TAPMn(OAc)]^+$) peak indicates the dissociation of the axial ligand under the conditions of MALDI experiment in the case of compounds with both electrofilic (CF_3Ph, CF_3PhO) and nucleophilic (^{t}BuPh, ^{t}BuPhO) groups suggesting electron buffer properties of tetraazamacrocycle in **1a**–**5a**. This result is in agreement with IR (see lower) and UV-vis data.

The lgε 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, lgε values of **1a** and **2a** are lower than those found for axially coordinated indium complexes with octakis(*m*-trifluoromethylphenyl) tetraazaporphyrin and octakis(*p*-^{t}butylphenyl)tetraazaporphyrin (with opposite electron effect of substituents).[24] The specificity of functional groups and coordination center in Mn^{III} complexes explains this regularity. Obviously, electron –*I* effect of *m*-CF_3Ph-, *m*-CF_3PhO- groups gradually disappears along the chain of atoms and the positive effect of the conjugation of *p*-^{t}BuPh-, 3,5-di-^{t}BuPhO- groups is not observed because the dative π-bonds $Mn(3d^4) \leftarrow N$ taking place in manganese(III) porphyrin complexes[31] 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 $\pi \rightarrow \pi^*$ 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:[32] annelation of benzene rings to the porphyrazine macrocycle results in the π-MOs destabilization, which increases in the order $a_{1u} < e_g^* < a_{2u}$. Similar bathochromic shift of the *Q*-band was observed in the order of *m*-CF_3Ph- > *m*-CF_3PhO- > *p*-^{t}BuPh- > 3,5-di-^{t}BuPhO- 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,[24,33] 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 CF_3^- groups in peripheral aromatic rings, along with the mixed ν_{C-F} 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 phthalo- and naphthalocyanines,[34–36] but not in works [37,38].

The preliminary investigation of light stability of some of the prepared compounds was carried out in chloroform or dichlormethane 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

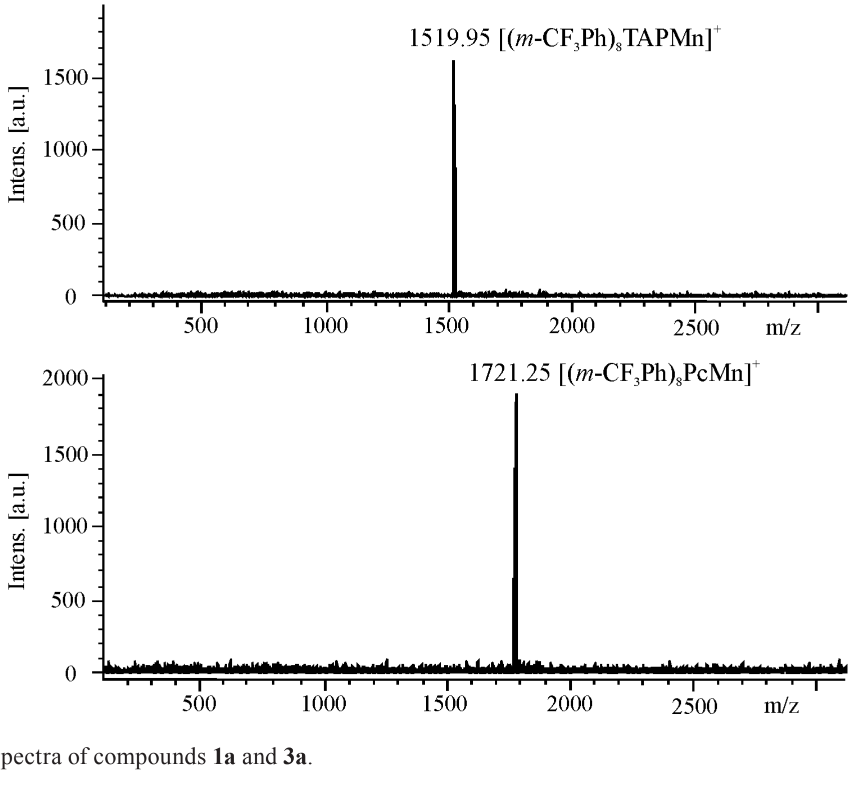


Figure 3. MALDI-TOF spectra of compounds **1a** and **3a**.

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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