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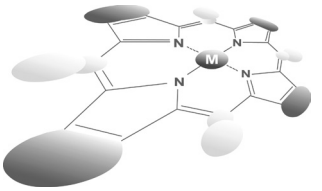

Coordination and electrochemistry of new substituted manganese phthalocyanines

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Dedicated to Professor Tebello Nyokong on the occasion of her 60th birthday

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ABSTRACT: A number of substituted manganese phthalocyanines PcMn have been synthesized from the corresponding phthalonitriles with rather good yields (up to 67%) and high purity. All complexes were characterized by elemental analysis, electronic absorption spectra, and some of them by redox potentials. Three coordination forms — PcMn(II), PcMn(III)X and $[LPcMn(III)]_2O$ were fixed for all complexes. The equilibrium of three electronic isomers — $Pc^{+\cdot}$ Mn(I) × L, PcMn(II) × L_n and $Pc^{-\cdot}$ Mn(III) × 2L — has been observed in solutions of all PcMn(II) in the presence of organic base L.

KEYWORDS: manganese phthalocyanines, synthesis, coordination forms, electronic isomers, electronic absorption spectra, electrochemistry.

INTRODUCTION

Metal phthalocyanines (PcM) are a very important class of compounds because of their diverse properties and applications. Interest in manganese phthalocyanine (PcMn) has emerged more than half a century ago and continues till now [1–13]. Major interest in PcMn along with PcFe lies in the high catalytic activity of this compound. Among the last publications on PcMn [14–26] only a few studies deal with coordination properties, although the variety of PcMn coordination and valence forms makes the investigation of its coordination chemistry of considerable importance. We have previously suggested the full scheme of photo and dark transformations of PcMn derivatives in solutions (Scheme 1, [13]). Herein we wish to present the investigation of this scheme validity for the series of new substituted manganese phthalocyanines with diversified electronic and steric peculiarities.

RESULTS AND DISCUSSION

Synthesis of substituted manganese phthalocyanines

The procedure, which is based on the anhydrous manganese acetate heating in sealed tube with corresponding phthalonitriles **1**–**6**, was applied to the synthesis of new substituted in benzene rings PcMn **7**–**12** (where Pc = phthalocyanine dianion Pc^{2-}, Scheme 2). For the first time complex **11** was mentioned [27] simultaneously with our colleagues from South Africa, who studied some properties of this complex in solution and as self-assembled monolayers on gold [14].

In the course of the synthesis species **7**–**12** are formed as Mn(II) complexes PcMn(II) (form **c**, Scheme 1, 2, Table 1**),** which oxidize to the PcMn(III)X (form **a,** Scheme 1, Table 1) during purification in air. Purification was carried out using column chromatography with neutral alumina as column material and $CHCl_3$ or CCl_4 as eluent. Counter-ion X^- in this case is chloride anion.

Complex **10** (Table 1) treatment in air does not lead to complete Mn(II) oxidation but instead results in isolation of stable in air form **c** during **10** purification done by column chromatography with benzene. Our earlier

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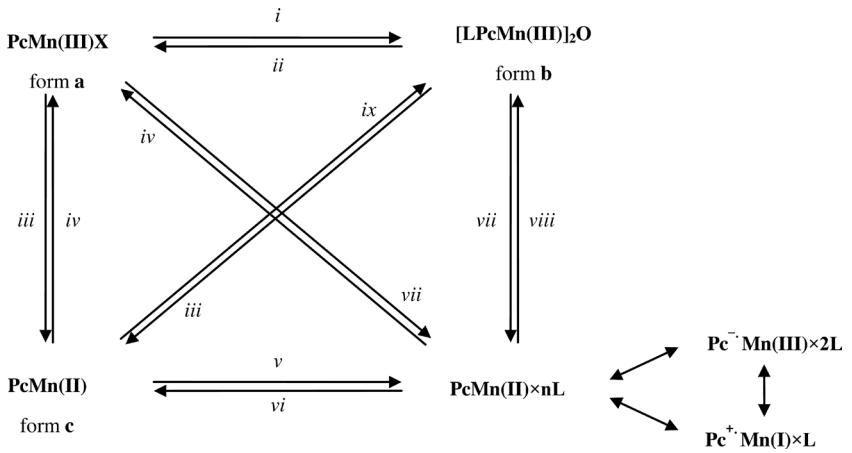


Scheme 1. Transformations of valence and coordination forms of PcMn derivatives in solutions [13]

studies [13, 28] had shown that form **a** is the most stable in non-coordinating solvents under ambient conditions for PcMn bearing neutral and electron-donating groups. It seems that in the case of complex **10** electron-withdrawing substituents stabilize PcMn(II).

Dimeric species $[LPcMn(III)]_2O$ (form **b**, Scheme 1, Table 1) have been also obtained as admixtures during **10** and **12** purification by column chromatography with acetone ($L = C_3H_6O$).

Substituted metal-free Pcs have been isolated as the reaction by-products in compounds **7** and **8** synthesis.

All compounds obtained possess high solubility in non-coordinating organic solvents such as benzene, chloroform and CCl_4.

Since the electronic absorption spectra are the most informative method of Pc characterization, it was chosen as a main research and description mean for our study.

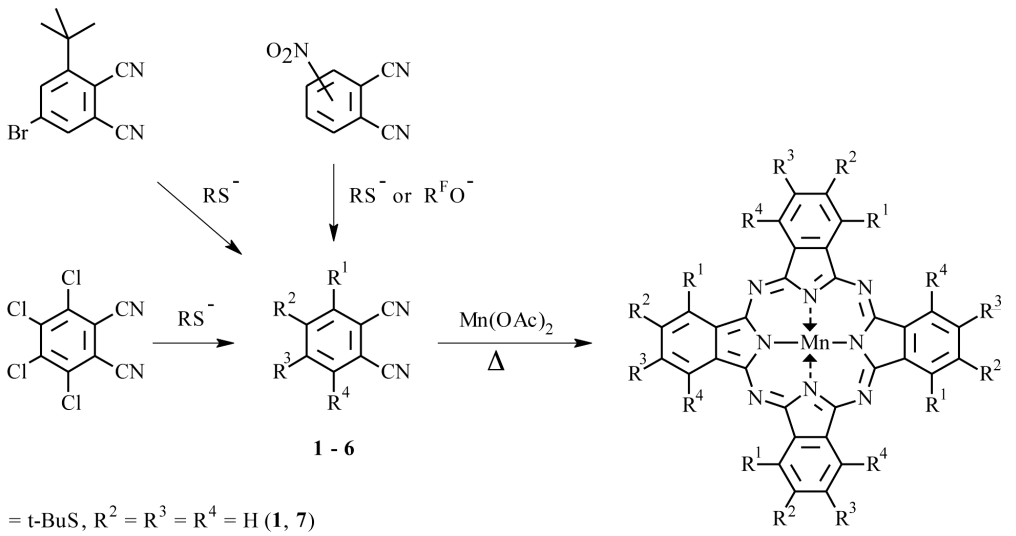
Coordination chemistry of substituted manganese phthalocyanines

Monomeric manganese(III) phthalocyanines 7a–12a. We started our investigation by focusing on the most stable under ambient conditions PcMn form — monomer PcMn(III)X, form **a** (Scheme 1, Table 1).

Electronic absorption spectra of **7a**–**12a** solutions are typical for PcMn(III)X derivatives [10] and demonstrate Q-bands in region 700–800 nm, B-bands in region 300–400 nm and ligand-to-metal charge transfer bands near 500 nm (Table 1, Fig. 1). Spectra of compounds **9a** and **11a** have two charge transfer bands with maxima 449, 525 nm and 464, 534 nm, accordingly (Fig. 1).

The broadening of the Q-band in **10a** spectrum in non-coordinating organic solvents has been observed. This effect is probably caused by the complex aggregation in solution.

As stated in previously reported publications [13, 28] the Q-band position of PcMn(III)X derivatives strongly depends on the electronic nature of substituents and shift could achieve up to 140 nm. Actually, we can see (Table 1,



R^1 = t-BuS, $R^2 = R^3 = R^4$ = H (**1**, **7**)

R^1 = t-BuS, R^3 = t-Bu, $R^2 = R^4$ = H (**2**, **8**)

R^2 = BuS, $R^1 = R^3 = R^4$ = H (**3**, **9**)

$R^1 = R^4$ = Cl, $R^2 = R^3$ = n-$C_{10}H_{21}S$ (**4**, **10**)

$R^2 = R^3$ = PhS, $R^1 = R^4$ = H (**5**, **11**)

R^1 = $H(CF_2)_6CH_2O$, $R^2 = R^3 = R^4$ = H (**6**, **12**)

Scheme 2. Synthetic route for the nitriles **1**–**6** and substituted PcMn **7**–**12**

Table 1. The main bands positions and intensities of **7–12** coordination forms

Compound	R^1	R^2	R^3	R^4	λ_{max}, nm (log ε) /relative intensities/					
								Spectra of electronic isomers in equilibrium mixture		
					PcMn(III)Cl form a in chloroform	**$[LPcMn(III)]_2O$ form b** in pyridine	**PcMn(II) form c** in benzene	**PcMn(II)×nL** n=1, 2 in pyridine	/intensities relative to the intensity of **PcMn(II)×nL** B band/	
									$Pc^{-}Mn(III)×2L$ in pyridine	**$Pc^{+\cdot}Mn(I) × L$** in pyridine
7	t-BuS	H	H	H	359 (4.59), 528 (4.08), 745 (4.85)	330, 654 /1:0.62/	350, 685 /0.60:1/	350, 668 /1:0.88/	483, 840 /0.52/ /0.13/	525, 568, 889 /0.24/ /0.24/ /0.14/
8	t-BuS	H	t-Bu	H	367 (4.63), 535 (4.15), 751 (4.80)	340, 651 /1:0.60/	360, 689 /0.54:1/	350, 668 /1:0.90/	487, 838 /0.70/ /0.19/	524, 568, 887 /0.51/ /0.50/ /0.30/
9	H	BuS	H	H	337 (4.59), 449 (4.41), 525 (4.28), 750 (4.85)	330, 640 /0.8:1/	350, 685 /0.55:1/	350, 640, 670 /1:0.52:0.61/	482, 850 /0.41/ /0.12/	530, 581, 911 /0.24/ /0.27/ /0.17/
10	Cl	$SC_{10}H_{21}$	$SC_{10}H_{21}$	Cl	300 (4.28), 522 (3.71), 787 (4.18)	310, 683 /1:0.61/	304, 723 /1:0.62/	354, 695 /1:0 55/	487, 855 /0.38/ /0.10/	—
11	H	PhS	PhS	H	330 (4.63), 464 (4.43), 524 (4.34), 773 (4.87)	325, 662 /1:0.5/	350, 712 /0.6:1/	355, 687 /1:0.54/	493, 868 /0.33/ /0.09/	550, 916 /0.20/ /0.11/
12	$OCH_2(CF_2)_6H$	H	H	H	355 (4.45), 515 (4.00), 737 (4.70)	330, 636 /1:1/	350, 678 /0.56:1/	350, 645, 671 /1:0.88:0.91/	470, 845 /0.34/ /0.09/	523, 570, 900 /0.31/ /0.35/ /0.20/
Ref.	H	H	H	H	359 (4.18), 504 (3.78), 717 (4.69)[*,**][11]	620 (4.94)[2]	674[*][7]	323, 643, 660[2]	467, 835[2]	520, 557, 880[2]

[*] DMA, [**] X = OH

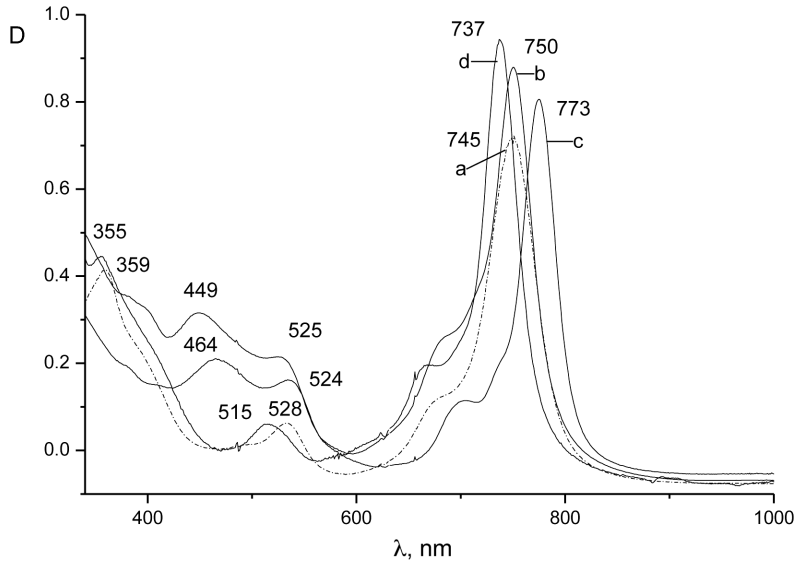


Fig. 1. UV-vis spectra of monomers PcMn(III)Cl: **7a** (a), **9a** (b), **11a** (c), **12a** (d), chloroform, l = 1 cm

Fig. 1) that Q-bands of **7a–12a** are bathochromically shifted relatively unsubstituted analog. It is known [14, 15, 29] that sulfanyl substituents cause more significant red shift as compared with alkoxy groups. Table 1 data represent an unquestionable evidence of this statement: the biggest red shift (71 nm) compared to unsubstituted analog has been registered for compound **10a** bearing eight decylsulfanyl groups and the least shift (20 nm) has been obtained for the complex **12a** substituted with four dodecafluoroheptyloxy groups.

If compared to the spectrum of complex **7a** bearing four *tert*-butylsulfanyl groups in α-positions (λ_{max} in chloroform 745 nm) with its earlier reported β-substituted analog (λ_{max} in chloroform 734 nm [28]), it becomes evident that α-substitution causes the more strong shift of the Q-band in comparison with β-substitution. This observation confirms the known fact that the α-substitution has more strong influence on Pc's properties as compared with β-substitution [30–32].

Q-band of **8a** (λ_{max} in chloroform 751 nm) is red shifted as compared with **7a** (λ_{max} in chloroform 745 nm) due to the additional donating effect of *tert.*butyl groups.

Solvatochromism of Pcs is well known phenomenon [3], which manifests as Pc's Q-band position dependence on the solvent nature. For example, maximum of **12a** Q-band differs from 722 nm in benzene to 732 nm in acetone and to 737 nm in CCl_4 and chloroform.

Dimeric manganese(III) phthalocyanines 7b–12b. Earlier studies have shown that monomers PcMn(III)X react with coordinating organic bases (L) such as pyridine, 4-aminopyridine, imidazol in the presence of water in air to give quantitative yields of the corresponding μ-oxo species $[LPcMn(III)]_2O$ (form **b,** Scheme 1, Table 1) [5, 6, 11, 13, 32].

Our results for the addition of organic bases L to **7a–12a** solutions are puzzling. Transformation of the form **a** into the corresponding form **b** in this way was achieved only for three complexes — **9b**, **10b** and **12b** (Scheme 1, Table 1). Unexpectedly, in other cases reaction failed. Treatment of compounds **7a**, **8a** and **11a** with coordinating organic bases in air did not lead to the expected products **7b**, **8b** and **11b** and starting materials were recovered in all cases.

Complex **11b** has been obtained only by treatment of **11a** chloroform solution with Et_3N-KOH-acetone mixture in air. It is reasonable to assume that reaction results first in **11c** complex to give then **11b**.

It was rather difficult to obtain compounds **7b** and **8b**. We speculated that the reason of this effect are steric hindrances of the bulky *tert.*butylsulfanyl groups in α-positions of the benzene rings. It is known, for example that PcMn with non-coplanar *ortho*-chlorphenyl groups in α-positions of the benzene rings does not form the corresponding μ-oxo dimer under the described conditions [32]. An efficient synthesis of the μ-oxo dimers **7b** and **8b** has been achieved by addition of hot water to **7a** and **8a** pyridine solutions in the presence of triethylamine in air. Firstly the reduction of form **a** to form **c** by triethylamine takes place and only 24 h later the formation of μ-oxo dimers **7b** and **8b** is observed. Taking into account the difficulty of **7b** and **8b** formation, it is reasonable to assume that these complexes may be of interest as catalysts for the oxidation reactions in weakly alkaline solution where dimerization of PcMn leads to the loss of their catalytic activity.

Dimers **10b** and **12b** have been also obtained in a mixture with **10a** and **12a** in course of **10** and **12** purification done by column chromatography with acetone. The equilibrium between **12a** and **12b** is very mobile; acetone shifts it to dimer and chloroform — to monomer form. Reversible **10b** formation has been observed after isopropanol addition to the **10a** chloroform solution. Back process of monomer formation proceeded on the diluted HCl addition. The last reaction is typical for PcMn(III) μ-oxo dimers and has been observed for all complexes **7b–12b**.

Electronic absorption spectra of **7b–12b** are characteristic of PcMn(III) μ-oxo species [7] and demonstrate broadened Q-bands near 640–680 nm and B-bands near 330 nm (Table 1). Q-bands in **7b–12b** spectra are about 100 nm blue shifted relative to Q-bands of the corresponding forms **a** (Table 1). The dependence of forms **b** Q-bands positions on the substituent nature is rather significant. The biggest red shift (63 nm) relatively

unsubstituted analog has been registered for compound **10b** and the least shift (16 nm) has been obtained for the complex **12a** (Table 1). Interestingly, the same dependence has been observed in the case of forms **a** (see above).

In summary, the results described in this part of the work show that all the six new PcMn **7**–**12** can exist in two PcMn(III) forms: monomeric PcMn(III)X and μ-oxo dimers $[LPcMn(III)]_2O$. Different ways were used for each complex **b** formation. Rather elusive were complexes **7b** and **8b**.

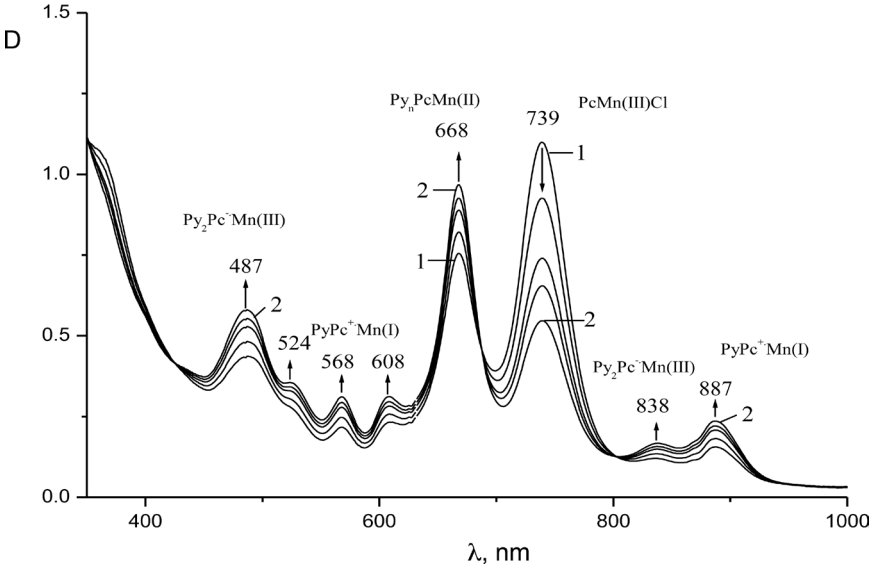


Fig. 2. UV-vis spectrum of PcMn(II) × Py_n formation from **8a** in triethylamine after Py addition, n = 1, 2; 0.5 min (1), 0.5 h (2), l = 1 cm

Manganese(II) phthalocyanines 7c–12c. The next group of PcMn valence forms are PcMn(II) derivatives. The procedure, which is based on the form **a** or form **b** reduction by triethylamine or potassium hydroxide-water-acetone mixture in anaerobic conditions [11, 13, 32], was applied to the synthesis of PcMn(II) (form **c**, Table 1).

As usual these complexes are unstable in air in solutions. We have previously described two compounds which have proved to be resistant to air — complexes with eight strong electron-withdrawing substituents — octanitro- and octa(phenylsulfonyl) substituted PcMn(II) (form **c**) [13]. This property allows use them as catalysts in oxidation processes [33]. These compounds can be converted into the corresponding PcMn(III)OAc (form **a**) by treatment with acetic acid in air.

We now report new stable in air in solution PcMn(II) — compound **10c** bearing electron-withdrawing substituents (Table 1). Complex **10c** has been isolated at **10** reaction mixture purification by column chromatography over neutral alumina with benzene as eluent (see above). The reduction of **10a** or **10b** also results in stable in air in solution complex **10c**. Generally the reduction of PcMn(III) derivatives in air results in back oxidation or in destruction of PcMn(II). Such destruction can be very quick (for compound **12c**) or rather slow (for complex **8c**).

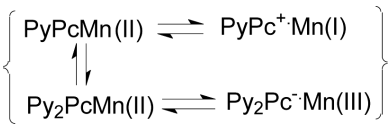
Electronic absorption spectra of **7c**–**12c** in non-coordinating organic solvents are characteristic of PcMn(II) species and demonstrate Q-bands in range 680–720 nm and B-bands in range 300–360 nm (Table 1). Charge-transfer bands at 500 nm are absent in **7c**–**12c** spectra. Q-bands of **7c**–**12c** in non-coordinating organic solvents are about 60 nm blue shifted compared to the Q-bands of **7a**–**12a** (Table 1). The broadening of the complex **10c** spectrum in non-coordinating organic solvents has been observed. Probably, similar to **10a** this effect is caused by the complex aggregation in solution.

The dependence of forms **c** Q-bands positions on the substituent nature is less significant in comparison with forms **a** and **b**. The biggest red shift (49 nm) relatively unsubstituted analog has been registered for the compound **10c** and the least shift (4 nm) has been obtained for the complex **12c** (Table 1). The same regularities have been observed in the cases of forms **a** and **b** (see above).

Electronic isomers of manganese(II) phthalocyanines. As part of our continued interest in the PcMn(II) electronic isomers existence [13, 32], we decided to investigate the scope and limitations of this phenomenon for the studied compounds. Complexes **7c**–**12c** were reacted with organic bases in inert atmosphere and this reaction afforded the electronic isomers mixture $Pc^+Mn(I) \times L$, PcMn(II) × L_n and $Pc^-Mn(III) \times 2L$. That manifests as significant changes in **7c**–**12c** electronic absorption spectra (Fig. 2).

Our earlier studies of such multiband spectra [13, 32] and literature data on Pc radical absorption spectra [34–36] had shown that bands at 480 nm and 840 nm correspond to the species $Pc^-Mn(III) \times 2Py$, bands at 570 nm and 880 nm — to the species $Pc^+Mn(I) \times Py$, and the most intensive bands at 660–680 nm correspond to the mixture of PcMn(II) × Py and PcMn(II) × 2Py (Fig. 2, Scheme 3). The intensities of all bands in multiband spectra relatively intensity of the B-band of neutral molecules PcMn(II) × nPy are shown in Table 1.

The phenomenon of electronic isomers mixture existence has a good explanation in terms of the crystal-field theory [32]. The relative intensities of the radical species bands depend on the substituent nature: complexes with electron-donating groups have more intensive cation-radical bands and *vice versa* complexes with electron-withdrawing groups have more intensive anion-radical ones (Table 2, Fig. 3). For example, the



Scheme 3. Equilibrium of electronic isomers in PcMn(II) pyridine solution

Table 2. The relationships of $Pc^{+\cdot}$ Mn(I) × Py ($D_{"570"}$) and $Pc^{-\cdot}$ Mn(III) × 2Py ($D_{"480"}$) bands intensities in spectra **7–12** in pyridine

Compound	**10**	**7**	**11**	**9**	**8**	**12**
σ*	0.55	0.25	0.10	0.05	0.05	-0.1
$D_{"570"}/ D_{"480"}$	0	0.46	0.59	0.67	0.71	1.04

*The sum of Gammet constants for the substituents in one benzene ring.

bands of $Pc^{+\cdot}$Mn(I) × Py are absent in compound **10** spectrum (Table 1).

So, the relationship of anion- and cation-radical bands intensities in electronic absorption spectra of substituted PcMn(II) pyridine solutions can serve for the estimation of the overall electronic influence of all substituents in one benzene ring of Pc macrocycle.

Electrochemical properties of substituted PcMn 7–12

The authors of many articles which are devoted to the electrochemistry of substituted PcMn refer to the controversy of the results obtained [16–26, 37]. The question is: what is the center of the reduction or oxidation? Is it the metal atom or the phthalocyanine ring? For example, in 1972 Clack and Yandle [34] proposed $Pc^{-\cdot}$ Mn(II) as a result of the first step of unsubstituted PcMn(II) electrochemical reduction, based on its spectrum similarity with the spectra of $Pc^{-\cdot}$ Mg and $Pc^{-\cdot}$ Zn. Such situation continued a quarter of century until 1997, when substituted PcMn(I) was obtained by electrochemical reduction of [1,8,15,22-tetrakis(phenylsulfanyl)phthalocyaninato]manganese(II) for the first time [13]. It was shown new species had typical phthalocyanine spectrum. There were no other confirmations of PcMn(I) existence during the decade after this first report. But currently situation is changing, for example, T. Nyokong points that both PcMn(I) and $Pc^{-\cdot}$ Mn(II) can be obtained depending on the substituent nature [17]. The same conclusion follows from the results of the electrochemical investigations of substituted PcMn for the last 7 years (some of them see in Table 3).

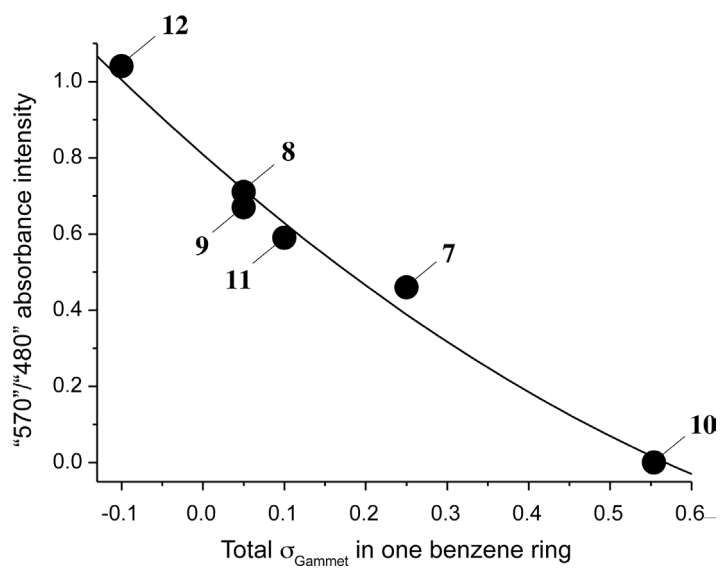


Fig. 3. The dependence of the relationships of $Pc^{+\cdot}$ Mn(I) × Py ($D_{"570"}$) and $Pc^{-\cdot}$ Mn(III) × 2Py ($D_{"480"}$) bands intensities in spectra **7–12** in pyridine on the sum of Gammet constants for the substituents in one benzene ring

It is interesting to note that for complexes from Table 3 in case if the reduction of PcMn(II) leads to PcMn(I) the oxidation of PcMn(III) with the same substituents leads to $Pc^{+\cdot}$Mn(III), and *vice versa*, the reduction of PcMn(II) to $Pc^{-\cdot}$ Mn(II) corresponds to the oxidation of PcMn(III) to PcMn(IV). We can see also that the potentials of Pc ring oxidation to cation-radical are much more higher (~1 V) than these one of Mn(III) oxidation to Mn(IV) (<0.5 V). So we can predict the main redox sequence knowing only the potential of PcMn(III)X oxidation.

It is necessary to note that spectroscopic interpretation of PcMn redox forms, except PcMn(II) and PcMn(III), is not always correct. In some publications spectra of compounds described as PcMn(I) has a maximum in radical region 520–575 nm. Such interpretation causes some doubts. The position of PcMn(IV) Q band also differs in different publications.

In our work electrochemical investigations were carried out for complexes **9**–**12** (Table 4). Pyridine and DMF were chosen as the solvents for the electrochemical study of starting PcMn(III)X. The measurements were made under nitrogen.

The obtained cyclic differential voltammograms (CDV) demonstrate three reduction processes for complexes **9**, **10**, **12** and four — for complex **11** (Table 4).

Potentiodynamic curve of compound **9** in pyridine has a complicated form (Fig. 4), where waves **II** and **III** demonstrate on two poorly separated peaks. This phenomenon may occur due to some reasons. According to literature data it can be chemical reaction following the electroreduction process, counterion and ligand bonding, complex aggregation in solution [15, 17, 25]. In our opinion, existence of electronic isomers in PcMn(II) pyridine solutions also can cause overlap of some processes in this region of potentials.

Table 3. Literature data on substituted PcMn electrochemistry

Substituents				1st oxidized form	- e → $E_{1/2}$, V	Starting compound	+ e → $E_{1/2}$, V	1st reduced form	+ e → $E_{1/2}$, V	2nd reduced form	Ref.
R^1	R^2	R^3	R^4								
$(CH_3)_3CCH_2O$	$(CH_3)_3CCH_2O$	$(CH_3)_3CCH_2O$	$(CH_3)_3CCH_2O$	PcMn(IV)	0.23	PcMn(III)	-0.9	PcMn(II)	-1.69	Pc^{-} Mn(II)	26
H	$OH(CH_2)_2S$	$OH(CH_2)_2S$	H	Pc^{+}Mn(III)	~1.00	PcMn(III)	~ -0.10	PcMn(II)	~-0.70	PcMn(I)	16
H	$Cl(CH_2)_2S$	$Cl(CH_2)_2S$	H	Pc^{+}Mn(III)	~1.00	PcMn(III)	~ -0.10	PcMn(II)	~-0.70	PcMn(I)	16
H	$C_6H_5CH_2S$	H	H	PcMn(IV)	~0.3	PcMn(III)	-0.08	PcMn(II)	-0.84	Pc^{-} Mn(II)	17
H	$CH_3(CH_2)_{10}CH_2S$	H	H	PcMn(IV)	~0.3	PcMn(III)	-0.26	PcMn(II)	-0.98	Pc^{-} Mn(II)	17
H	NH_2	H	H	PcMn(IV)	0.43	PcMn(III)	-0.30	PcMn(II)	-0.98	Pc^{-} Mn(II)	18
H	4-(3-thienyl)-phenoxy	4-(3-thienyl)-phenoxy	H	Pc^{+}Mn(III)	1.05	PcMn(III)	0.010	PcMn(II)	-0.86	PcMn(I)	20
H	2-naphtoxy	H	H	Pc^{+}Mn(III)	1.04	PcMn(III)	-0.16	PcMn(II)	-0.95	PcMn(I)	21
$CH_3(CH_2)_3CH_2S$	H	H	$CH_3(CH_2)_3CH_2S$	PcMn(IV)	0.47	PcMn(III)	-0.46	PcMn(II)	-1.24	Pc^{-} Mn(II)	22
H	$Et_2N(CH_2)_2S$	H	H	PcMn(IV)	0.40	PcMn(III)	-0.29	PcMn(II)	-0.71	Pc^{-} Mn(II)	24
$Et_2N(CH_2)_2S$	H	H	H	PcMn(IV)	0.52	PcMn(III)	-0.32	PcMn(II)	-0.72	Pc^{-} Mn(II)	24

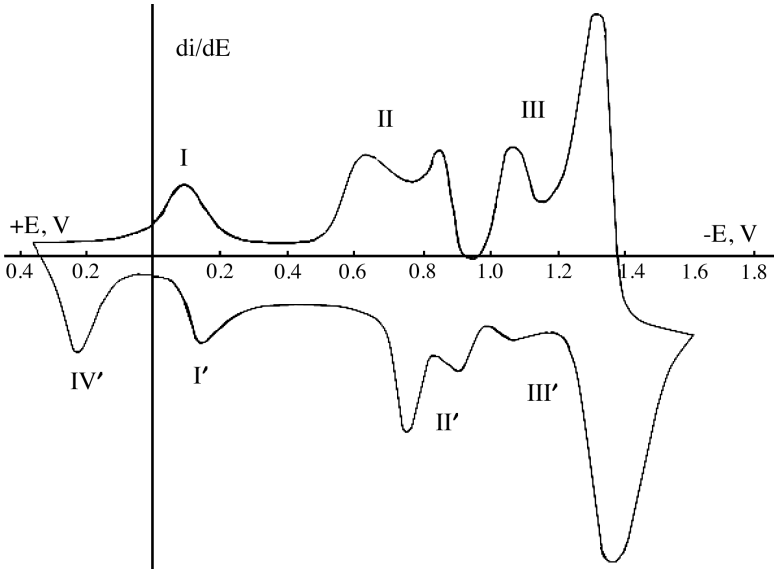


Fig. 4. CDV of the compound **9** in pyridine, 2.5×10^{-4} M, 0.1 TBAP. Scan rate 20 mV/s *vs.* $HgCl_2$

Process **I** is reversible, relationship $i^c_{1/2}/i^a_{1/2}$ is about 1 and the difference of the wave potentials at the forward and reverse scan is less 100 mV (Fig. 4).

Compound **12** in DMF demonstrates three reduction waves. Increase of **12** concentration (curves 1, 2, and 3 Fig. 5a) slightly changes the limiting current of the process I, while the current of the reverse process I′ increased proportionally to **12** concentration. Scanning to the anodic range from -0.5 to 0.0 V and back without electrode clearance showed the intensities of waves I and I′ been equal (Fig. 5b). It means that process I′ is irreversible **12** electrooxidation. The processes II and III are reversible.

The processes I–IV registered at the **11** potentiodynamic curve are reversible. Reversibility was illustrated by the similarity in the forward and reverse CDV scans (Fig. 6) with $i^c_{1/2}/ i^a_{1/2}$ relationship equal 1 and independent on the potential scan rate.

The UV-vis spectrum (Fig. 7-2) of the product which has been obtained at the first stage of **11a** electroreduction in pyridine (Fig. 6, peak I) showed its identity with the spectrum of chemically obtained **11c** in pyridine (Fig. 8-2). So, the first stage ($E_{1/2}$ = -0.05 V) corresponds to the pair PcMn(III)/PcMn(II). The presence of Mn(III) species in spectrum (Fig. 7–2) was caused by back oxidation reaction even in nitrogen atmosphere. It was shown earlier that deep vacuo required to prevent this reaction for complexes with electron-donating substituents [13]. Unfortunately, other products were not stable at UV-vis spectra registration out of electrochemical cell and their identification requires further study.

Peak separations of the first and second reduction processes for studied complexes are limited by the range 0.50–0.59 V (Table 4). According to published data [16, 25] this fact supports the metal-based assignment of the second reduction leading to PcMn(I) formation. Reliable determination of these and others products requires further spectroelectrochemical studies.

EXPERIMENTAL

Materials

4-nitrophthalonitrile, tetrachlorophthalonitrile, 1-butanethiol, 2-methyl-2-propanethiol, 1-decanethiol, triethylamine were obtained from Sigma-Aldrich, 2,2,3,3,-4,4,5,5,6,6,7,7-dodecafluoroheptan-1-ol was obtained from Fisher Scientific and used as received. The synthesis and characterization of 3-bromo-5-*tert*-butylphthalonitrile has been reported before [38]. Substituted PcMn (**7**–**12**) have been prepared by heating anhydrous manganese acetate with the corresponding phthalodinitrile in a sealed tube. The time and the temperature of the reactions varied for different compounds within 1 h–1 h 40 min and 175–250 °C. All organic solvents used for the synthesis were of analytical grade and used as received without further purification.

Table 4. Voltammetric data for **9**–**12** redox couples on glassy carbon electrode in pyridine, 0.1 M TBAP

Complex	Concentration, M	Half-wave potentials $-E_{1/2}$, V			
		Process I	Process II	Process III	Process IV
9	$2.5 \cdot 10^{-4}$	0.07	0.66, 0.82	1.07, 1.32	—
10	$1.3 \cdot 10^{-3}$	not measured	0.42	1.00	1.54
11	$1.6 \cdot 10^{-4}$	0.05	0.55	1.20	1.50
12	$3.3 \cdot 10^{-4}$	0.09	0.66, 0.75	1.20	—

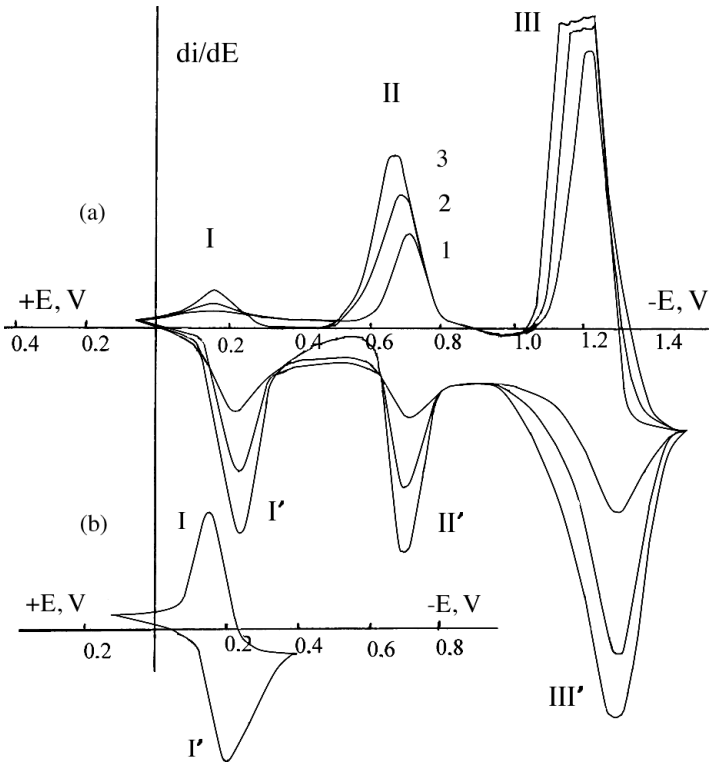


Fig. 5. CDV of the compound **12** in DMF, 0.1 TBAP: 1 – 1.4×10^{-4} M, 2 – 2.7×10^{-4} M, 3 – 3.9×10^{-4} M (a), without electrode clearance (b). Scan rate 20 mV/s *vs.* $HgCl_2$

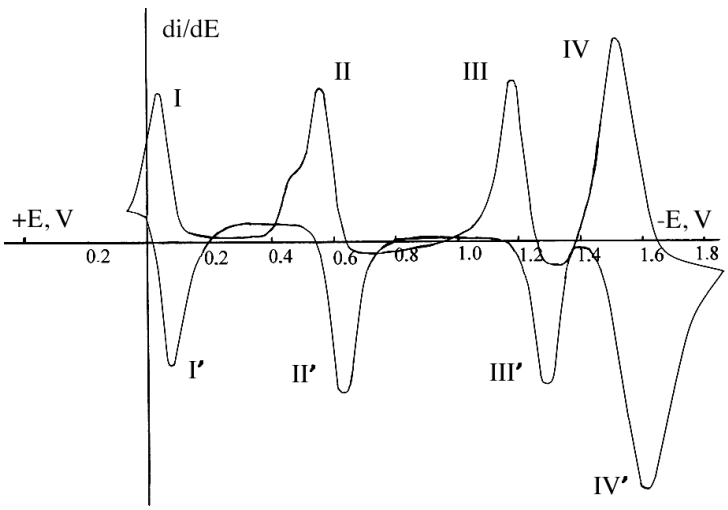


Fig. 6. CDV of the compound **11** in pyridine, 1.6×10^{-3} M, 0.1 TBAP. Scan rate 20 mV/s *vs.* $HgCl_2$

Equipment

Elemental analysis was performed on a Hewlett-Packard HP-185B C,H,N analyzer. IR-spectra were registered on a FMS-1201 FT spectrometer in KBr pellets. The mass spectra (electron impact, 70 eV) were obtained on an MKh-1321 instrument. ^1H and ^{19}F NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer using DMSO-d_6 as solvent and TMS as internal reference. The compositions of reactions mixtures and the purity of isolated compounds were monitored by TLC on Silufol UV-254 plates. The electronic absorption spectra (UV-vis) were recorded by HP 8453 spectrometer. Voltammetry was carried out in three-electrode cell in nitrogen atmosphere. Glassy carbon electrode SU – 2000 prepared by method [39] was used as a working electrode. A standard calomel electrode was used as a reference. Coulometric potentials were generated using polarograph PU-1 and two-coordinate recorder PDS-021. As base electrolyte TBAP (tetrabuthylammonium perchlorate) was used.

Syntheses

Preparation of 3-(*tert*-butylsulfanyl)-phthalonitrile (1). The 3-nitrophthalonitrile (3.46 g, 20.0 mmol) was dissolved in DMF (30 mL), and 2-methyl-2-propanethiol (2.50 mL, 22.2 mmol) was added. After stirring for 5 min triethylamine (3.10 mL, 22.2 mmol) was added in portions during 15 min with efficient stirring. The reaction mixture was stirred at 50 °C for 1 h, cooled to room temperature, poured into ice-water, the formed precipitate was filtered off, washed with water, dried and recrystallized twice from hexane. Yield 3.14 g (72.7%), mp 64–65 °C. Anal. calcd. for $C_{12}H_{12}N_2S$: C, 66.67; H, 5.56; N, 12.96; S, 14.81%. Found: C, 67.10; H, 5.52; N, 12.94; S, 14.87. IR (KBr): λ_{max}, cm^{-1} 2236 (CN). MS: *m/z* 216 $[M]^+$.

Preparation of 5-*tert*-butyl-3-(*tert*-butylsulfanyl)phthalonitrile (2). The phthalonitrile **2** was prepared by method [28], but insted of thiophenol 2-methyl-2-propanethiol was used. The 3-bromo-5-*tert*-butylphthalonitrile (2.63 g, 10.0 mmol) was dissolved in DMF (20 mL), and 2-methyl-2-propanethiol (1.30 mL, 11.5 mmol) was added. After stirring for 5 min triethylamine (1.60 mL, 11.5 mmol) was added in portions during 15 min with efficient stirring. The reaction mixture was stirred at 20 °C for 0.5 h. The mixture was poured into ice-water, the formed precipitate was filtered off, washed with water, dried, dissolved in benzene, purified by column chromatography on silica gel using benzene as eluent and recrystallized from hexane. Yield 1.70 g (62.5%), mp 94–95 °C. Anal. calcd. for $C_{16}H_{20}N_2S$: C, 70.59; H, 7.35; N, 10.29; S, 11.76%. Found: C, 70.61; H, 7.42; N, 10.25; S, 11.68. IR (KBr): λ_{max}, cm^{-1} 2235 (CN). MS: *m/z* 272 $[M]^+$.

Preparation of 4-(butylsulfanyl)phthalonitrile (3). The phthalonitrile **3** was prepared by method [28], but

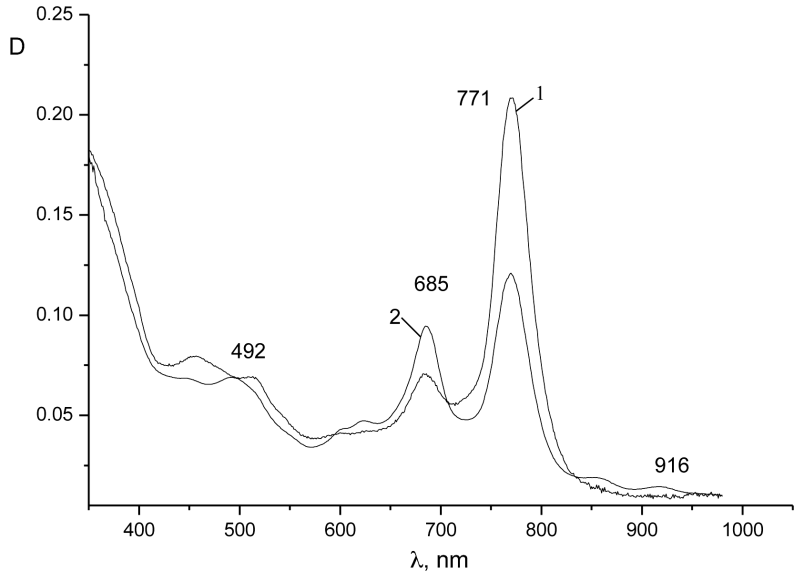


Fig. 7. UV-vis spectrum of the **11a** (1) and the product of the first electroreduction in pyridine, 0.1 TBAP (2), *l* = 1 cm

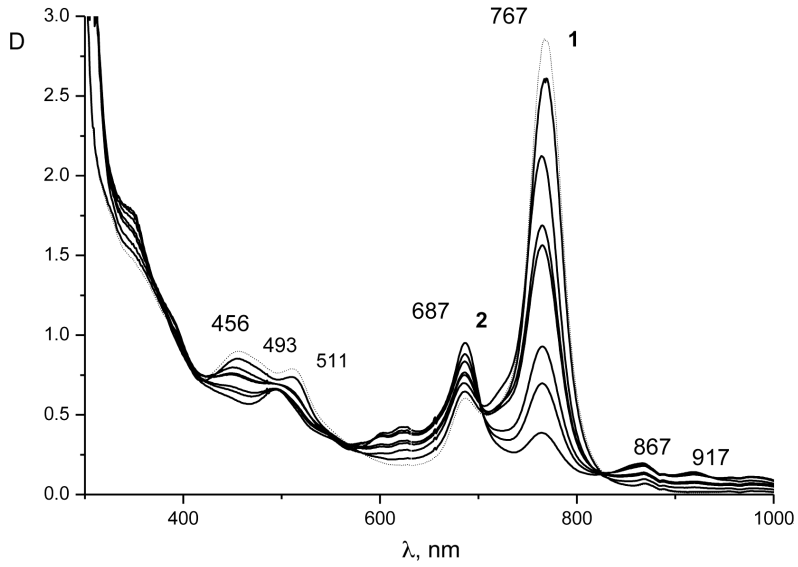


Fig. 8. UV-vis spectrum of **11a** (1) transformation into **11c** (2) in pyridine in the presence of thriethylamine, *l* = 1 cm

instead of 2-methyl-2-propanethiol 1-butanethiol was used. The 4-nitrophthalonitrile (1.73 g, 10.0 mmol) was dissolved in DMF (15 mL), and 1-butanethiol (1.80 mL, 16.8 mmol) was added. After stirring for 5 min triethylamine (2.20 mL, 15.8 mmol) was added in portions during 15 min with efficient stirring. Reaction mixture was stirred at 20 °C for 0.5 h. The mixture was poured into ice-water, the formed precipitate was filtered off, washed with water, dried and recrystallized from hexane. Yield 1.93 g (89.4%), mp 60–61 °C. Anal. calcd. for $C_{12}H_{12}N_2S$: C, 66.67; H, 5.56; N, 12.96; S, 14.81%. Found: C, 66.74; H, 5.60; N, 13.03; S, 14.75. IR (KBr): λ_{max}, cm^{-1} 2234 (CN). MS: *m/z* 216 $[M]^+$.

Preparation of 3,6-dichloro-4,5-bis(decylsulfanyl)phthalonitrile (4). The phthalonitrile **4** was synthesised as previously reported [40]. Isolated yield 87% of yellow oil that very slowly changes to amorphous solid.

Preparation of 4,5-bis(phenylsulfanyl)phthalonitrile (5). The phthalonitrile **5** was synthesised from 4-bromo-5-nitrophthalonitrile by modified method previously reported in the literature [41]. The 4-bromo-5-nitrophthalonitrile (1.26 g, 5.0 mmol) was dissolved in DMF (20 mL), and thiophenol (1.10 mL, 10.8 mmol) was added. After stirring for 5 min triethylamine (1.50 mL, 10.8 mmol) was added in portions during 15 min with efficient stirring. The reaction mixture was stirred at 80 °C for 3 h, cooled to room temperature, poured into ice-water, and the formed precipitate was filtered off, washed several times with water and recrystallized from ethanol. Yield 1.20 g (69.8%), mp 146–148 °C. Anal. calcd. for $C_{20}H_{12}N_2S_2$: C, 69.74; H, 3.51; N, 8.13; S, 18.62%. Found: C, 70.09; H, 3.62; N, 8.00; S, 18.54. IR (KBr): λ_{max}, cm^{-1} 2232 (CN). MS: *m/z* 344 $[M]^+$. ^1H NMR: δ, ppm 7.72 (s, 2H, 3,6-H), 7.51 (d, 4H, *ortho-H of SPh*), 7.43–738 (m, 6H, *meta* and *para-H of SPh*).

Preparation of 3-(2,2,3,3,4,4,5,5,-6,6,7,7-dodecafluoroheptyloxy) phthalonitrile (6). The mixture of 3-nitrophthalonitrile (1.00 g, 5.8 mmol), 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptan-1-ol (1.93 g, 5.8 mmol), anhydrous K_2CO_3 (0.80 g, 5.8 mmol) and DMF (30 mL) was stirred under nitrogen at 120 °C for 2 h. Then the mixture was poured into ice-water, the precipitate was filtered off, washed with water, dried and then recrystallized twice from hexane/benzene (1:1). Yield 2.19 g (82.6%), mp 103–105 °C. Anal. calcd. for $C_{15}H_6F_{12}N_2O$: C, 39.32; H, 1.32; F, 49.76; N, 6.11%. Found: C, 39. 21; H, 1.34; F, 50.01; N, 6.13. IR (KBr): λ_{max}, cm^{-1} 2234 (CN). MS: *m/z* 458 $[M]^+$. ^1H NMR: δ, ppm 7.94 (dd, 1H, 5-H), 7.83 (d, 1H, 6-H), 7.80 (d, 1H, 4-H), 7.18 (tt, 1H, CF_2H; J_{HF} = 51.1 Hz, α-*F*; J_{HF} = 5.3 Hz, β-*F*), 5.20 (t, 2H, CH_2, J_{HF} = 13.4 Hz). ^{19}F NMR: δ, ppm -118.7 (m, 2F), -122.15 (m, 2F), -122.58 (m, 2F), -123.09 (m, 2F), -129.0 (m, 2F), -138.43 (m, 2F).

Synthesis of substituted PcMn 7–12. Substituted PcMn **7**–**12** have been prepared by heating anhydrous manganese acetate with the corresponding phthalodinitriles **1**–**6** and

ammonium molybdate as a catalyst in a sealed tube [28]. Reaction time and temperature are indicated for each complex. Cooled reactive mixture has been dissolved and purified using column chromatography with neutral alumina (silica gel for **10**) as column material. Eluents are indicated for each compound.

Synthesis of chloro[1,8,15,22-tetrakis(*tert*-butylsulfanyl)phthalocyaninato]manganese(III) (7a). The mixture of **(1)** (0.20 g, 0.9 mmol) and manganese(II) acetate (0.078 g, 0.3 mmol), 0.5 h at 175 °C, 1 h at 195 °C. Benzene, washing out yellow colored impurity and blue colored metal-free Pc, chloroform. Yield 0.073 g (30%). Anal. calcd. for $C_{48}H_{48}N_8S_4MnCl$: C, 60.33; H, 5.06; N, 11.72; S, 13.42%. Found: C, 60.01; H, 5.22; N, 11.40; S, 13.17. UV-vis ($CHCl_3$): λ_{max}, nm (log ε) 359 (4.59), 528 (4.08), 745 (4.85).

Synthesis of chloro[3,10,17,24-tetra-*tert*-butyl-1,8,15,22-tetrakis(*tert*-butylsulfanyl)phthalocyaninato]manganese(III) (8a). The mixture of **(2)** (0.15 g, 0.55 mmol) and manganese(II) acetate (0.05 g, 0.20 mmol), 1 h at 180 °C, 15 min at 210 °C, 15 min at 200 °C. Benzene, washing out yellow colored organic impurities and blue colored metal-free Pc, chloroform, collecting red-brown main product. Yield 0.08 g (48%). Anal. calcd. for $C_{64}H_{80}N_8S_4MnCl$: C, 65.14; H, 6.83; N, 9.49; S, 10.86; Cl, 3.00; Mn, 4.65%. Found: C, 65.56; H, 6.85; N, 9.33; S, 10.30; Cl, 3.20; Mn, 4.35. UV-vis ($CHCl_3$): λ_{max}, nm (log ε) 367 (4.63), 535 (4.15), 751 (4.80).

Synthesisofchloro[2,9,16,23-tetrakis(butylsulfanyl)phthalocyaninato]manganese(III) (9a). The mixture of **(3)** (0.34 g, 1.57 mmol) and manganese(II) acetate (0.13 g, 0.53 mmol), 40 min at 170 °C, 40 min at 200 °C, 0.5 h at 210 °C. Benzene, washing out organic impurities, chloroform, collecting red-brown main product. Yield 0.165 g (43.9%). Anal. calcd. for $C_{48}H_{48}N_8S_4MnCl$: C, 60.33; H, 5.06; N, 11.72; S, 13.42; Cl 3.71; Mn, 5.74%. Found: C, 60.69; H, 5.33; N, 11.30; S, 12.98; Cl 3.51; Mn, 5.64. UV-vis ($CHCl_3$): λ_{max}, nm (log ε) 337 (4.59), 449 (4.41), 525 (4.28), 750 (4.85).

Synthesis of chloro[1,4,8,11,15,18,22,25-octachloro-2,3,9,10,16,17,23,24-octakis(decylsulfanyl)phthalocyaninato]manganese(III) (10a). The mixture of **(4)** (0.54 g, 1.0 mmol) and manganese(II) acetate (0.08 g, 0.33 mmol), 1 h at 200 °C, 40 min at 250 °C. Cooled reactive mixture firstly has been washed with isopropanol (100 mL), then has been dissolved in CCl_4 and purified using column chromatography over silica gel (100/160) with benzene, washing out yellow colored organic impurities and some quantity of **10c** and then with CCl_4, collecting brown colored main product **10a**. Yield 0.09 g (16%). Anal. calcd. for $C_{112}H_{168}N_8S_8Cl_9Mn$: C, 59.59; H, 7.50; N, 4.96%. Found: C, 60.41; H, 8.43; N, 4.32. UV-vis (CCl_4): λ_{max}, nm (log ε) 300 (4.28), 522 (3.71), 787 (4.18). Column chromatography performed with acetone as eluent results in **10a** and **10b** mixture isolation.

Synthesis of chloro[2,3,9,10,16,17,23,24-octakis(phenylsulfanyl)phthalocyaninato]manganese(III) (11a). The mixture of **(5)** (0.115 g, 0.33 mmol) and manganese(II) acetate (0.03 g, 0.11 mmol), 40 min at 200 °C, 30 min at 250 °C. Benzene, washing out yellow colored organic impurities, chloroform, collecting cherry colored main product. Yield 0.083 g (67.5%). Anal. calcd. for $C_{80}H_{48}N_8S_8MnCl$: C, 65.44; H, 3.29; N, 7.63; Cl, 2.41; S, 17.46; Mn 3.74%. Found: C, 65.64; H, 3.32; N, 6.92; Cl, 1.95; S, 17.67; Mn, 4.01. UV-vis (CCl_4): λ_{max}, nm (log ε) 330 (4.63), 464 (4.43), 524 (4.34), 773 (4.87).

Synthesis of chloro[1,8,15,22-tetrakis(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyloxyl)phthalocyaninato]manganese(III) (12a). The mixture of **(6)** (0.30 g, 0.65 mmol) and manganese(II) acetate (0.048 g, 0.20 mmol), 30 min at 200 °C, 1 h at 240 °C. Acetone-benzene mixture, benzene, washing out yellow colored organic impurities, acetone, collecting product as mixture of two forms — **a** and **b**. Dried product was dissolved in chloroform, resulting in **12a**. Yield 0.163 g (52%). Anal. calcd. for $C_{60}H_{24}N_8O_4F_{48}MnCl$: C, 37.47; H, 1.25; N, 5.82%. Found: C, 37.77; H, 1.51; N, 5.54. UV-vis (CCl_4): λ_{max}, nm (log ε) 355 (4.45), 515 (4.00), 737 (4.70).

CONCLUSION

New substituted manganese phthalocyanines **7**–**12** have been synthesized from the corresponding phthalonitriles **1**–**6** with rather good yields (up to 67%) and high purity. Main coordination and valence forms: **a** — PcMn(III)X, **b** — $[LPcMn(III)]_2O$ and **c** — PcMn(II) were observed for all complexes. Different ways were used for each complex **b** formation. Rather elusive were complexes **7b** and **8b**. The equilibrium of three electronic isomers: $Pc^{+\cdot}Mn(I) \times L$, $PcMn(II) \times nL$ and $Pc^{-\cdot}Mn(III) \times 2L$ has been observed in the solutions of all PcMn(II) in the presence of organic base L. The relationship of anion- and cation-radical bands intensities in electronic absorption spectra of such solutions can serve for an estimation of the substituent's electronic properties. The electronic absorption spectra of each coordination form in solution for all new compounds were registered. The potentials of electrochemical transformations for complexes **9**–**12** have been obtained.

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