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Synthesis and characterization of tetraphenylporphyrin manganese(III) complexes of phenylcyanamide ligands

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Abstract

Several complexes of TPPMn–L, where TPP is the dianion of tetraphenylporphyrin and L is monoanion of 4-methylphenylcyanamide (4-Mepcyd) (**1**), 2,4-dimethylphenylcyanamide (2,4-Me_2pcyd) (**2**), 3,5-dimethylphenylcyanamide (3,5-Me_2pcyd) (**3**), 4-methoxyphenylcyanamide (4-MeOpcyd) (**4**), phenylcyanamide (pcyd) (**5**), 2-chlorophenylcyanamide (2-Clpcyd) (**6**), 2,5-dichlorophenylcyanamide (2,5-Cl_2pcyd) (**7**), 2,6-dichlorophenylcyanamide (2,6-Cl_2pcyd) (**8**), 4-bromophenylcyanamide (4-Brpcyd) (**9**), and 2,3,4,5-tetrachlorophenylcyanamide (2,3,4,5-Cl_4pcyd) (**10**), have been prepared from the reaction of TPPMnCl and thallium salt of related phenylcyanamide. Each of the complexes has been characterized by IR, UV–Vis and ^{1}H NMR spectroscopies.

4-Methylphenylcyanamidotetraphenylporphyrin manganese(III) crystallized with one molecule of solvent $CHCl_3$ in the triclinic crystal system and space group $P\bar{1}$ with the following unit cell parameters of: $a = 11.596(6)$ Å; $b = 11.768(9)$ Å; $c = 17.81(2)$ Å; and α, β, γ are 88.91(9)°, 88.16(7)°, 67.90(5)°, respectively; $V = 2251(3)$ Å^3; $Z = 2$. A total of 4234 reflections with $I > 2\sigma(I)$ were used to refine the structure to $R = 0.0680$ and $R_w = 0.2297$. The Mn(III) shows slightly distorted square pyramidal coordination with the 4-methylphenylcyanamide in the axial position, coordinated from nitrile nitrogen. The reduction of each of the TPPMn–L complexes was also examined in dichloromethane and spectroelectrochemical behavior of (**1**) was investigated and compared to TPPMnCl.

Keywords: Manganese porphyrin; Phenylcyanamide; Axial ligand; Spectroelectrochemistry; X-ray diffraction; ^{1}H NMR

1. Introduction

While unambiguous role of manganese porphyrin in biological process has not been established [1], synthetic manganese porphyrins have been used extensively as models for monoxygenases enzymes [2,3], DNA cleavage agent [4,5] and could also be considered as a potential contrast enhancement agent for magnetic resonance imaging [6]. Effect of axial ligand on the properties of Mn(III)porphyrin is important and has been the center of recent attentions. The most studied synthetic manganese porphyrins are those with halide [7] or pseudo-halide [8], nitrate, perchlorate, carboxylate [9], thiolate [10], phenolate [11], tetrazolate [12], and some other axial ligands [7,13,14]. From these studies in contrast to iron and cobalt analog, Mn(III)porphyrin shows lower affinity for addition of two axial ligands and formation of the low-spin d^4 complexes is very rare. So, most Mn(III)porphyrin complexes are high-spin five-coordinate and coordinated solvents readily displace the anionic ligand to yield solvated complexes [11,15]. Furthermore, molecular materials with special properties,

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such as one or two dimensional electronic based on planar π-conjugated molecules, are very active field today, due to their potential applications in new generation of electronic, magnetic, and/or photonic devices [16]. In this regard, TCNE in [TPPMn][TCNE] · 2PhMe has shown to act as molecule-based magnet [17–20] and phenylcyanamide in (2,5-dimethyl-*N*,*N*′-dicyanoquinonediimine)$_2$Cu has shown to exhibit extremely high conductivity of 500,000 S cm^{-1} at 3.5 K [21]. In spite of these important findings, coordination chemistry of phenylcyanamide has not been fairly explored. However, Crutchley et al. [22] have largely investigated the coordination chemistry of phenylcyanamide ligands, in both neutral and anionic form mostly with Cu and Ru as metals.

Therefore, due to large π-conjugated system in porphyrins and phenylcyanamides and magnetic properties of Mn(III), which is usually high-spin in porphyrin complexes, we have prepared tetraphenylporphyrin manganese(III) with phenylcyanamide derivatives as axial ligand. To the best of our knowledge, there is just one example for complex of Mn with phenylcyanamide [23]. We have shown with the use of NMR spectroscopy as a sensitive probe of spin distribution that cyanamides are capable to transfer spin in long range through conjugated bond. These complexes were characterized by means of electronic, IR spectroscopy and the structure of 4-methylphenylcyanamidotetraphenylporphyrin manganese(III) was determined by X-ray diffraction as well.

2. Experimental

2.1. Reagents and physical measurements

UV–Vis spectra were obtained on a shimadzu 2100 spectrometer in a 1 cm cell in chloroform at room temperature. Infrared spectra (4000–600 cm^{-1}) of solid samples were taken as 1% dispersion in KBr using a Shimadzu-470 spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker AC-250 MHz spectrometer operating in the quadrature mode. The spectra were collected over a 50-kHz band width with 16 K data points and a 5-μs 45° pulse. For a typical spectrum, between 1000 and 5000 transients were accumulated with a 50-ms delay time. The signal-to-noise ratio was improved by apodization of the free inducting decay. Cyclic voltammetry was performed using a BAS CV-27 voltammograph and plotted on a BAS XY recorder. The sample cell consisted of a double-walled glass crucible with an inner volume of ~15 ml, which was fitted with a Teflon lid incorporating a three-electrode system and argon bubbler. The cell temperature was maintained at (25.0 ± 0.1) °C by means of a HAAKE D8 recirculating bath. BAS 2013 Pt electrodes (1.6 mm diameter) were used as the working and counter electrodes. A silver wire functioned as a pseudo-reference electrode. Ferrocene was used as an internal reference [24]. An optically transparent thin-layer electrode (OTTLE) cell was used to perform the spectroelectrochemistry [25,26]. The cell had interior dimensions of roughly 1 × 2 cm with a path length of 0.2 mm and was fitted with a silver/silver chloride (Ag/AgCl) as reference electrode and an ITO (indium-tin oxide) coated glass used for the working and counter electrodes. $E_{1/2}$ for all complexes was measured with differential pulse polarography using a Metrohm-746 VA Trace Analyzer in 10^{-3} M concentration in the presence of 0.1 M of (TBAH) electrolyte.

2.2. X-ray structural determination of [TPPMn(4-Mepcyd)] · $CHCl_3$ (1)

Dark red block-shape crystals of [TPPMn(4-Mepcyd)] · $CHCl_3$ were grown by slow evaporation of $CHCl_3$ solution in the temperature range of 0–4 °C under N_2 atmosphere. Crystal data are presented in Table 1. Data were collected on an Enraf-Nonius-CAD-4 diffractometer using the SHELXS-97 [27] with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) and operating in the ω–2θ scan mode. Cell parameters were obtained from 25 accurately centered reflections in the 2θ range. The space group was confirmed by XPREP routine [28] in SHELXTL program [29]. Data reduction was performed using a locally modified version of the NRC-2 program [30]. The structure was solved by direct method using SHELXS-97 and difmap synthesis using SHELXL-97 [31]. All non-H atoms were refined with anisotropic thermal parameters. H atoms constrained to the parent site using a riding model; SHELXL-97 defaults, C–H 0.93–0.98 Å. The isotropic factors, U_{iso}, were adjusted to 20%

Table 1
Crystal data for [TPPMn(4-Mepcyd)] · $CHCl_3$ (**1**)

Empirical formula	$C_{52}H_{35}MnN_6 \cdot CHCl_3$
Formula weight	918.17
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	11.596(6)
b (Å)	11.768(9)
c (Å)	17.81(2)
α (°)	88.91(9)
β (°)	88.16(7)
γ (°)	67.90(5)
V (Å^3)	2251(3)
Z	2
$D_{calc.}$ (Mg m^{-3})	1.355
T (°C)	20
λ (Mo Kα) (Å)	0.71073
Maximum and minimum transmission	0.9300 and 0.8500
R factor[a]	0.0680
R_w factor[b]	0.2297

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$.

[b] $R_w = \left(\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\right)^{1/2}$.

higher value of the parent site. A final verification of possible voids was performed using the VOID routine of the PLATON program [32].

2.3. Materials

Dichloromethane, *N*,*N*-dimethylformamide, methanol, *p*-chloranil, *n*-hexane, benzaldehyde, benzophenone, I_2, Na, and Mg were of reagent grade and purchased from Merck, pyrrole and tetrabutylammonium hexafluorophosphate was from Fluka and Aldrich, respectively. Dichloromethane and methanol were pre-dried and distilled over P_2O_5 and Mg + I_2, respectively, prior to use. *n*-Hexane was pre-dried and distilled over Na and benzophenone. Tetrabutylammonium hexafluorophosphate (TBAH) was twice recrystallized from ethanol:water (1:1) and vacuum dried at 110 °C. All manipulations involving phenylcyanamide coordination to manganese(III)porphyrin were carried out under nitrogen using standard Schlenk technique. Tetraphenylporphyrin ($TPPH_2$) and TPPMnCl were synthesized by Lindsey [33] and Adler's method [34], respectively. Extra care to exclude trace of impurity of μ-oxo dimer and pre-treatment of TPPMnCl with HCl was necessary. Preparation of the thallium salts of phenylcyanamide ligands ($pcyd^-Tl^+$) has been previously reported [35]. *Caution*: Thallium is toxic.

2.4. Preparation of TPPMn(4-Mepcyd) (*1*)

80 mg of powders of TPPMnCl (0.11 mmol) and 200 mg of thallium salt of 4-Mepcyd (0.59 mmol) were placed together in a two-neck round-bottom flask. After 30 min of vacuum and then under nitrogen atmosphere, 50 ml dry methanol was transferred to the reaction flask and stirred for 24 h. Then, the solvent was removed under reduced pressure and the residue was dissolved in dry dichloromethane and filtered under Schlenk technique. The volume of filtrate was reduced to 10 ml and then 50 ml of dried *n*-hexane was added in portion while solution was stirring. The precipitate was removed by filtration and dried in air. Other compounds were prepared by the above procedure except that 4-Mepcyd was replaced by related phenylcyanamide derivatives. The IR, UV–Vis data and the yields of products are summarized in Table 2.

3. Results and discussion

The synthesis of compounds (**1**–**10**) were achieved according to metathesis reaction at ambient temperature (Scheme 1).

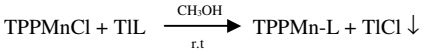
This reaction is very sensitive to moisture and in less extent to O_2, so existence of water results in the formation of μ-oxo dimer, TPPMn–O–MnTPP, during preparation. μ-Oxo dimer impurity is hard to remove, since chromatography on silica gel or aluminium oxide may lead to its additional formation. The reaction yields were quantitative, although during the process of precipitation 20–30 percent of the products were lost. Compounds (**1**–**10**) are slightly sensitive to moisture or oxygen. No effort was made to exclude air for NMR, IR and electronic spectroscopy, but crystals of (**1**) were grown under N_2 atmosphere. All compounds have fair solubility in all solvents except saturated hydrocarbons. Addition of HCl, gas or solution, completely converts the phenylcyanamide derivative complexes to TPPMnCl.

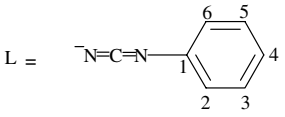
IR spectroscopy is a proper tool for characterisation of phenylcyanamide metal complexes. It can differentiate nitrile versus amine coordination in both anionic and neutral form of phenylcyanamides [36]. Neutral phenylcyanamide has shown υ(C≡N) around 2225–2249 cm^{-1}

Table 2
UV–Vis electronic absorption[a] and IR data[b] for TPPMn–L complexes and thallium salts of phenylcyanamide

Complex	UV–Vis[c]		υ(NCN)[d,e]		Yield (%)
	Soret band	Q bands	Thallium salt	Complex	
TPPMn(4-Mepcyd)	473	575, 609	2060	2090	80
TPPMn(2,4-Me_2pcyd)	474	580, 617	2060	2075	75
TPPMn(3,5-Me_2pcyd)	470	576, 612	2095	2115	76
TPPMn(4-MeOpcyd)	471	578, 614	2065	2090	72
TPPMn(pcyd)	473	581, 619	2055	2090	76
TPPMn(2-Clpcyd)	477	582, 620	2080	2095	73
TPPMn(2,5-Cl_2pcyd)	481	584, 620	2110	2120	73
TPPMn(2,6-Cl_2pcyd)	479	583, 620	2045	2110	74
TPPMn(4-Brpcyd)	475	581, 619	2045	2085	78
TPPMn(2,3,4,5-Cl_4pcyd)	482	583, 620	2095	2110	76

[a] In nm.
[b] In cm^{-1}.
[c] In chloroform.
[d] KBr disk.
[e] Strong.





(1)	2,3,5,6 H	4 Me
(2)	3,5,6 H	2,4 Me
(3)	2,4,6 H	3,5 Me
(4)	2,3,5,6 H	4 MeO
(5)	2,3,4,5,6 H	
(6)	3,4,5,6 H	2 Cl
(7)	3,4,6 H	2,5 Cl
(8)	3,4,5 H	2,6 Cl
(9)	2,3,5,6 H	4 Br
(10)	6 H	2,3,4,5 Cl

Scheme 1. Metathesis reaction.

[22], and coordinated nitrile in [TPPMn][TCNE]·2PhMe was reported at 2192 cm^{-1} [18], where coordination of anionic phenylcyanamide ligand seems to occur via nitrile nitrogen and produce a strong bond in the frequency lower than 2150 cm^{-1}. The υ(N=C=N) frequencies for thallium salts and compounds (**1**–**10**) are listed in Table 2. In each case, the υ_{CN} absorption is consistent with the presence of N^{-}=C=N–C_6H_5 entity. Fig. 1 shows UV–Vis spectrum of (**1**) in dichloromethane in comparison to TPPMnCl. This spectrum and the results for other compounds (**1**–**10**) in Table 2 indicate similarity of electronic spectra of prepared compounds, and confirm existence of Mn(III) oxidation state, since the UV–Vis spectra of metalloporphyrins are sensitive to oxidation state of metals. Fig. 1 also indicates higher absorption coefficient of (**1**) in comparison to TPPMnCl, which is expected for coordination of long π-conjugated axial ligand.

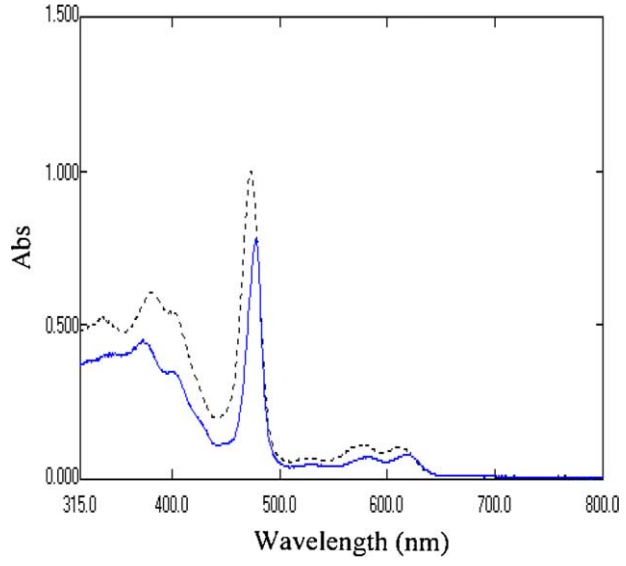


Fig. 1. UV–Vis spectra of TPPMnCl (—) and TPPMn(4-Mepcyd) (---), 1.25×10^{-5} M in dichloromethane.

3.1. NMR studies

Proton NMR spectroscopy is found to be highly informative in terms of evaluation of the axial phenylcyanamide derivatives (**1**–**10**). The ^{1}H NMR spectra of chloro substituted phenylcyanamide complexes and methyl substituted phenylcyanamide complexes are shown in Figs. 2 and 3, respectively. Full assignment of signals for compounds (**1**–**10**) is presented in Table 3. Assignments are made on the basis of:

(i) previous assignments for Mn(III)tetraarylporphyrin complexes,
(ii) relative intensity and line width of the signals,
(iii) comparison of the pattern of signals in phenylcyanamide complexes (**1**–**10**).

For i.e. trace of (**10**) in Fig. 2 shows a signal at 13.9 ppm which arises from the only hydrogen present in ortho position of phenylcyanamide, when compound (**10**) is replaced by (**8**), two kinds of hydrogen, meta and para in the ratio of 2:1 were assigned in 15.3 and −11.9 ppm, respectively, see trace of (**8**) in Fig. 2. These assignments were reconfirmed with the ^{1}H NMR spectrum of (**6**) in Fig. 2 and also in comparison to (**1**–**5**,

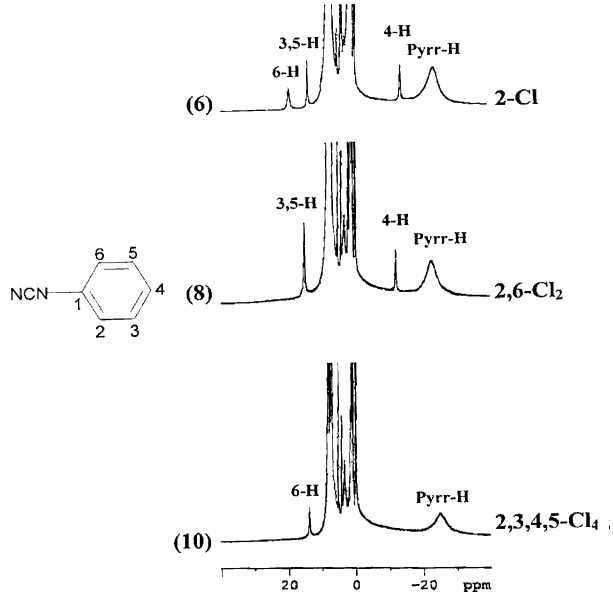


Fig. 2. ^{1}H NMR spectra of manganese(III)porphyrin complexes: TPPMn(2,3,4,5-Cl_4pcyd) (**10**), TPPMn(2,6-Cl_2pcyd) (**8**), and TPPMn(2-Clpcyd) (**6**), in $CDCl_3$ at 300 K.

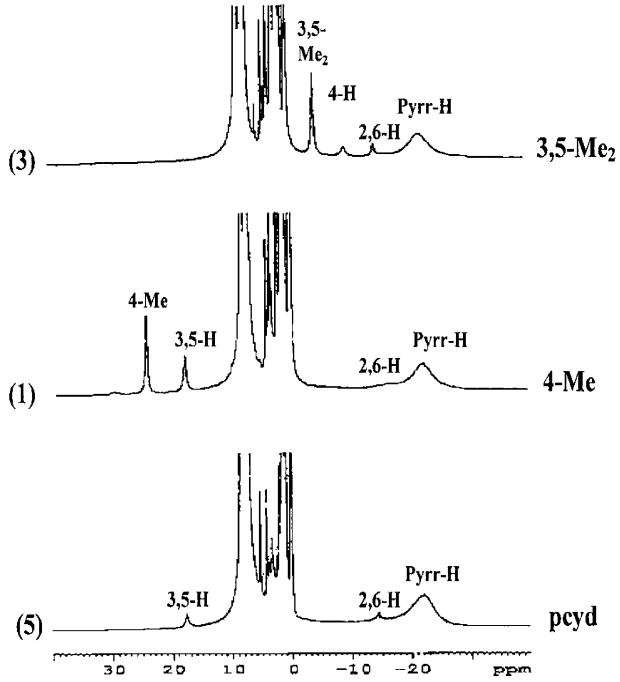


Fig. 3. ^{1}H NMR spectra of manganese(III)porphyrin complexes: TPPMn(pcyd) (**5**), TPPMn(4-Mepcyd) (**1**), and TPPMn(3,5-Me_2pcyd) (**3**), in $CDCl_3$ at 300 K.

7, **9**) compounds. Syntheses of these ten substituted phenylcyanamide complexes and comparison of ^{1}H NMR of them unambiguously confirm our assignments. The pyrrole-H signals of the TPP complexes appear as broad peaks and are located at −21 to −25 ppm. Resonances for the meta, ortho and para-H of phenyl in TPP are seen in the range of 7.5–8.3 ppm. These data prove that Mn in these complexes is Mn(III) and high-spin ($S = 2$) [8,10,37]. The position of pyrrole peaks indicates that phenylcyanamides are pseudo-halide ligands [22], since the same isotropic shift has been shown to exist for TPPMn(III)–X (X stand for F, Cl, Br and I). The pyrrole-H shift increases upfield when more electron-withdrawing groups are present in the phenylcyanamide. This increase in the pyrrole-H contact shift reflected an increase in Por → Mn(III) π charge-transfer as expected. The same trend has been shown for halide coordination to Mn(III) tetraphenylporphyrin [8,10].

The axial protons of phenylcyanamides (L) are clearly resolved and all have smaller line width than pyrrole protons. The alternating upfield–downfield shift pattern (+30 to −20 ppm) for L in TPPMn–L is indicative of contact interaction, which is dominant mechanism in Mn(III) porphyrin [38]. The contact term arises from the presence of unpaired electron density on the ligand. This is an interesting system in which spin delocalisation from Mn reaches to hydrogen that is more than 10 Å away.

3.2. Electrochemistry and spectroelectrochemistry

The electrochemistry of compounds (**1**–**10**) involves many oxidation/reduction processes. Half-wave potentials for the reduction of Mn^{III}/Mn^{II} in 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) in dichloromethane are given in Table 4, and a typical cyclic voltammogram in the ranges of 82 to −1168 mV is presented in Fig. 4. Here, we concentrate on the first reduction/oxidation waves.

The first reduction of TPPMn–L (**1**–**10**) in dichloromethane occurs at $E_{1/2}$ values between −0.31 and −0.38 V with a peak potential separation, $|E_a - E_c|$, of 100–150 mV for a potential scan rate of 0.1 V s^{-1}. The cyclic voltammograms are quasi-reversible and as seen from Table 4 the reduction of TPPMn–L becomes more difficult by 70 mV as electron-donating substituents replace electron-withdrawing groups on the phenylcyanamides. Kelly and Kadish [39] have shown that Mn^{III}/Mn^{II} reduction depends on the binding strength of anionic ligands in TPPMn–X. Comparison of these half-wave potentials to that of tetraphenylporphyrin manganese(III) bearing other anionic ligands indicates

Table 3
^{1}H NMR spectral data of TPPMn–L complexes[a,b]

Complex	pyrr-H	*m*-H	*p*-H	H_2	H_3	H_4	H_5	H_6
TPPMn(4-Mepcyd)	−22.3	8.20	7.50	−16.2	17.8	24.2	17.8	−16.2
TPPMn(2,4-Me_2pcyd)	−21.8	8.20	7.50	17.6	14.4	24.3	14.4	21.1
TPPMn(3,5-Me_2pcyd)	−22.2	8.30	7.70	−14.6	−4.4	−9.6	−4.4	−14.6
TPPMn(4-MeOpcyd)	−22.2	8.20	7.50	−15[c]	17.3	10	17.3	−15[c]
TPPMn(pcyd)	−22.2	8.20	7.50	−14.4	17.6	[d]	17.6	−14.4
TPPMn(2-Clpcyd)	−23.2	8.30	7.70		14.1	−13.4	14.1	19.8
TPPMn(2,5-Cl_2pcyd)	−24.3	8.20	7.60		13.4	−12.3		−20[c]
TPPMn(2,6-Cl_2pcyd)	−22.8	8.20	7.70		15.3	−11.9	15.3	
TPPMn(4-Brpcyd)	−23.3	8.30	7.70	−16[c]	17.2		17.2	−16[c]
TPPMn(2,3,4,5-Cl_4pcyd)	−25.0	8.20	7.70					13.9

[a] In $CDCl_3$, data in ppm vs. TMS reference at 0.00 ppm at 300 K.
[b] The *o*-H peak is not clearly resolved, but appears to occur as a very broad resonance near $CDCl_3$.
[c] Very broad.
[d] Not observed.

Table 4
The first half-wave potentials[a] ($E_{1/2}$) measured by DPP for TPPMn–L complexes

Complex	Mn(III/II)
TPPMn(4-Mepcyd)	−360
TPPMn(2,4-Me_2pcyd)	−360
TPPMn(3,5-Me_2pcyd)	−340
TPPMn(4-MeOpcyd)	−380
TPPMn(pcyd)	−330
TPPMn(2-Clpcyd)	−340
TPPMn(2,5-Cl_2pcyd)	−310
TPPMn(2,6-Cl_2pcyd)	−340
TPPMn(4-Brpcyd)	−340
TPPMn(2,3,4,5-Cl_4pcyd)	−310

[a] In mV vs. Ag/AgCl, at 25 °C. In dichloromethane (TBAH 0.1 M) at a scan rate of 100 mV s^{-1}.

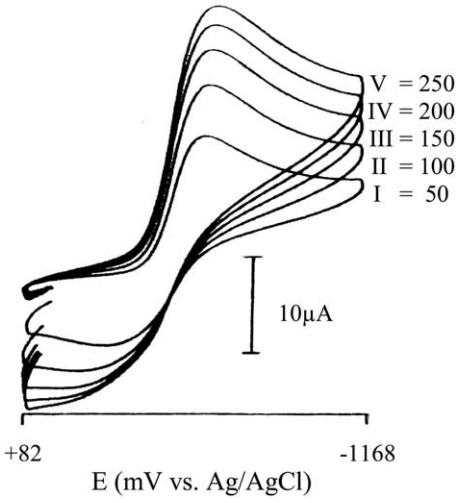


Fig. 4. Cyclic voltammogram of (**1**), 10^{-3} M in dichloromethane shows Mn(III/II) couple in the range of 82 to −1168 mV, between scan rates of 50–250 mV s^{-1} (I–V).

that phenylcyanamide derivatives used in this work have binding ability similar to I^-, SCN^-, Br^- and Cl^- anions [39,40], since they have comparable $E_{1/2}$ under the same experimental condition.

Spectroelectrochemical spectrum of compound (**1**) with OTTLE cell under the one electron controlled potential reduction at −1.2 to 0.2 V is shown in Fig. 5. As the reaction proceeds, the intensity of soret band at 473 nm decreases and new bands at 457 and 395 nm appear. The spectral changes, indicated in Fig. 5, were reversible and the spectrum of the original Mn(III) could be fully regenerated upon controlled potential up to 0.2 V. The electrogenerated $TPPMn^{II}$–L derivatives seem to be stable in dichloromethane, so that loss of the axial ligand does not occur on the spectroelectrochemistry time scale (1–2 h). The electrogenerated $TPPMn^{II}$–(X), where X = Cl^-, Br^-, I^-, N_3^-, were sufficiently stable in dichloromethane in spite of quasi-reversible behavior of their cyclic voltammograms [12,39,40]. This is an excellent property that makes these compounds a good candidate as a building block for $metal_a$–L–$metal_b$ interaction, which is important for switching device or material with special magnetic and electronic properties. Synthesize of dicyanamide metalloporphyrins is under consideration in our laboratory.

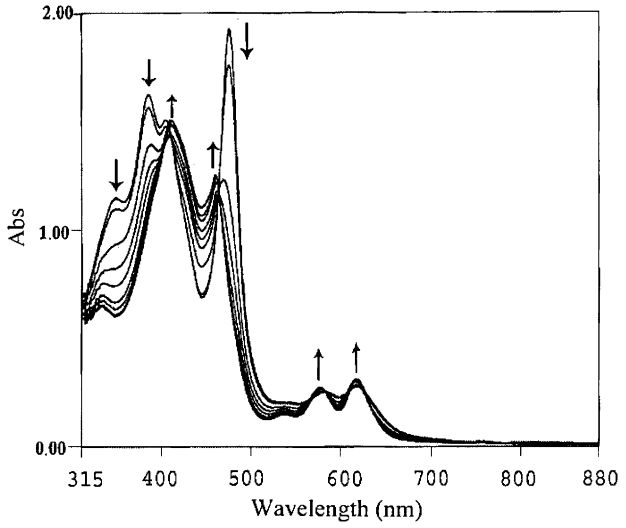


Fig. 5. Optically transparent thin-layer electrode cell electronic spectra of (**1**) (0.1 M TBAH electrolyte) in dichloromethane. Potential range for forward reaction −0.7 to −1.2, for backward reaction −0.3 to +0.2 V vs. Ag/AgCl reference electrode.

3.3. Crystal and molecular structure of [TPPMn(4-Mepcyd)] · $CHCl_3$ (1)

The structure of TPPMn(4-Mepcyd) (**1**) has been studied by X-ray diffraction. Two views of (**1**) are shown in Fig. 6. Selected bond lengths and angles are presented in Table 5. The manganese is five-coordinate and structural parameters are consistent with the parameters observed for high-spin five-coordinate Mn(III) porphyrins. The Mn–N_{porp} distance (average 2.00 Å) is similar to the distance found for TPPMnCl and other nitrosoarene analogous porphyrin complexes [7,14,41]. The equatorial Mn–N_{porp} bond distance is smaller than axial Mn–N(5) bond distance (2.08 Å). This difference in the Mn–N bond distance can be attributed to a spin-state effect. It has shown that manganese has an unoccupied $d_{x^2-y^2}$ and an occupied d_z^2 orbital. The distance from the Mn(III) to the center of the four pyrrole nitrogen plane is 0.24 Å. This distance was reported to be 0.27 Å for TPPMnCl [7].

The phenyl groups in most tetraphenylporphyrin compounds are almost perpendicular to the mean plane of the porphyrin ring, this does not allow any π interaction between the benzene π system and the extensive porphyrin π system. The torsion angle that the phenyl

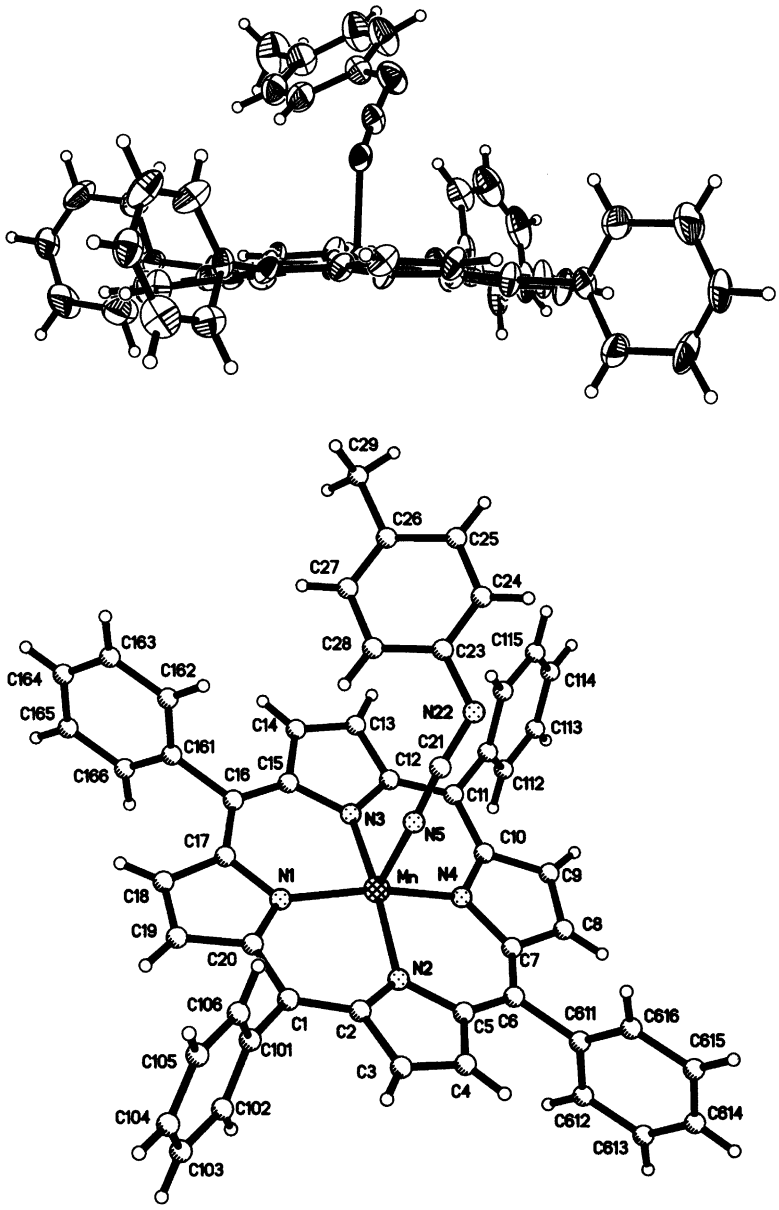


Fig. 6. Thermal ellipsoid plot and numbering scheme of TPPMn(4-Mepcyd). Ellipsoids correspond to 30% probability.

rings make with the porphyrin ring is required to be greater than 70° because of interactions between the phenyl hydrogens and the outer pyrrole hydrogens [42]. These torsion angles for TPPMn(4-Mepcyd) (**1**) are in the range between 87.3° and 91.1°.

The phenylcyanamide has been coordinated to the Mn from nitrile nitrogen and Mn–N(5) distance is 2.08 Å. This is smaller than the distance reported for coordination of anionic phenylcyanamide to Mn(II), 2.15 Å as expected [23]. NCN moiety is almost linear with the N(5)–C(21)–N(22) angle of 174.2°. Also the torsion angle C(21)–N(22)–C(23)–C(28), 13°, shows that the phenyl ring is approximately planar with cyanamide group. This angle was reported to be 12° for {μ-Dicyd-$[(NH_3)_5Ru]_2$}$[ClO_4]$ [43]. Planarity of the phenylcyanamide ligand optimizes the π interaction between the phenyl ring and the cyanamide group. The above crystal structure observation has important consequences to metal–phenylcyanamide coupling.

The angle of metal with axial CN is 135.8°. Crutchley [22] has shown that this angle ranges from 120° to 180°, depending on the amount of contribution from these two resonance forms:

$$\underset{180^\circ}{\text{Ph–N–C}}\equiv\text{N} \leftrightarrow \underset{120^\circ}{\text{Ph–N}}=\text{C}=\text{N}$$

Angle of 135.8° and the N(5)–C(21) distance of 1.17 Å confirm some π donation from phenylcyanamide ligand to manganese d-orbitals [44,45].

Table 5
Selected bond lengths (Å) and angles[a] (°) for [TPPMn(4-Mepcy-d)] · $CHCl_3$ (**1**)

Bond lengths		Bond angles	
Mn–N(1)	1.972(1)	Mn–N(5)–C(21)	135.80(1)
Mn–N(2)	2.010(1)	N(5)–C(21)–N(22)	174.20(1)
Mn–N(3)	2.022(1)	C(21)–N(22)–C(23)	120.70(1)
Mn–N(4)	2.011(1)	N(1)–Mn–N(2)	89.2(5)
Mn–N(5)	2.075(1)	N(2)–Mn–N(4)	90.1(4)
N(5)–C(21)	1.171(2)	N(4)–Mn–N(3)	88.0(4)
C(21)–N(22)	1.250(2)	N(3)–Mn–N(1)	89.5(5)
N(22)–C(23)	1.452(2)	N(2)–Mn–N(3)	169.8(5)
C(23)–C(24)	1.31(2)	N(1)–Mn–N(4)	161.8(4)
C(23)–C(28)	1.382(2)	N(1)–Mn–N(5)	101.3(4)
		N(3)–Mn–N(5)	92.7(5)
		N(4)–Mn–N(5)	96.8(5)

[a] Estimated standard deviations are in parentheses. Torsion angle C(21)–N(22)–C(23)–C(28): 13(2)°.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.ica.2005.03.012.

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