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

Nasser Safari [a,*], Behrouz Notash [a], Jafar Mohammad Nezhad [a],
Hossein Chiniforoshan [a], Hassan Hadadzadeh [b], Ali R. Rezvani [b]

[a] *Department of Chemistry, Shahid Beheshti University, 1983963113 Evin, Tehran, Iran*
[b] *Department of Chemistry, Sistan and Baluchestan University, 98135674 Zahedan, Iran*

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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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[*] Corresponding author. Tel.: +98 21 2401765; fax: +98 21 2403041.
E-mail address: n-safari@cc.sbu.ac.ir (N. Safari).

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