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Ruthenium(II) complexes of meso-tetrakis(4-cyanophenyl)porphyrin

Júlio S. Rebouças ^{a,*}, Brian R. James ^{b,*}

^a Departamento de Química, CCEN, Universidade Federal da Paraíba, João Pessoa, PB, 58.051-900, Brazil

^b Department of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Z1

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ABSTRACT

A novel synthesis is presented for the *meso*-tetrakis(4-cyanophenyl)porphyrin complex Ru(T-*p*CN-*P*P)(CO)(H₂O), the first Ru complex with this long-known porphyrin; compared to standard methods reported for other porphyrin analogues via Ru₃(CO)₁₂, extra steps involving addition of pyridine (Py) and its subsequent removal as $[HPy^+]CI^-$ are required. The Py breaks down coordination polymers (as yet uncharacterized) formed via the peripheral *p*-cyanophenyl moiety; these materials may offer potential as porphyrin-based supramolecular solids. Removal of the CO by photolysis in MeCN solution generates Ru(T-*p*CN-*P*P)(MeCN)₂, but attempts to make the bis(thiol) analogues from this precursor were unsuccessful, again due to formation of polymeric species.

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Introduction. We reported recently on just over one hundred $Ru(porp)(RSH)_2$ species formed in situ from the bis(acetonitrile) species, where porp is the anion of the parent porphyrin $H_2(porp)$, and R is an alkyl or aryl group [1,2], the key purpose being to measure the ¹H NMR resonances of the SH proton. The upfield shifts on coordination of the thiol reflect changes in porphyrin ring current, and the measured shifts were analyzed in terms of an empirical model that depicted quantitatively the non-bonding, electronic and steric interactions between the thiol ligands and the porphyrin plane. Steric factors were found to dominate the upfield shifts within variation of the thiol, whereas electronic factors were most important within the porphyrins used. More generally, such interactions are typically involved in small-molecule recognition within metalloporphyrin systems, and the findings offer an insight into this complex feature of many metalloporphyrin-containing protein systems [1]. One series of porphyrins studied was meso-tetraphenylporphyrin (H₂TPP) and its *p*-substituted-tetraphenyl analogues (H₂T-*p*X-*P*P, where X is OMe, Me, F, Cl, CO₂Me, and CF₃), the electronic nature of the X substituent, as listed, going from electron-donor to increasingly electron-withdrawing properties; more quantitatively, the Hammett σ factor increases within this series from -0.28 to +0.53 [3]. In an attempt to extend the electronic properties within this series, the X = CN species with a greater electron-withdrawing ability (σ = 0.71 [3]) was an attractive candidate. A further interest in using H₂T-pCN-PP was the possibility of synthesizing coordination polymers and networked structures of porphyrin-based supramolecular solids, which have been formed via the N-atom of the linear -CN function within Cu^{II} and Zn^{II} systems with this porphyrin [4].

There are no previous reports on $\text{Ru}/\text{H}_2\text{T}$ -pCN-PP chemistry, except for an oblique, non-detailed mention of Ru(T-pCN-PP)(MeCN)_2 in our recent paper [1]. This current paper describes the lengthy, non-routine synthesis of the required precursor *meso*-tetrakis(4-cyanophenyl)porphyrin complex Ru(T-pCN-PP)(CO)(H₂O), the synthesis of Ru(T-pCN-PP)(MeCN)_2, and our unsuccessful efforts to make the corresponding bis(thiol) complexes likely due to formation of supramolecular species.

Experimental section. Reactions and manipulations were carried out under anaerobic conditions. Ar (Praxair, 99.996%) was passed through an active Ridox column (Fisher Scientific), and N₂ (Praxair, 99.995%) was dried with Drierite (W.A. Hammond Co.). MeCN (Fisher Scientific, HPLC grade) was stored over activated molecular sieves (4 Å); C₆H₆ (Fisher Scientific) was treated with Na/benzoquinone, distilled under N₂, and used immediately. Other solvents were reagent grade and were deoxygenated by purging with Ar. Deuterated NMR solvents were obtained from Cambridge Isotope Laboratories, Inc. Ru₃(CO)₁₂ [5] and chlorin-free H₂T-*p*CN-*P*P [4,6] were made by reported methods.

¹H-NMR spectra (s = singlet, m = multiplet) were measured at room temperature (r.t., ~295 K) on a Bruker AV300 spectrometer, and referenced to residual solvent protons of TMS-free C₆D₆ (δ 7.15). IR spectra in KBr pellets were recorded on an ATI Mattson Genesis Series FT-IR spectrometer. Electrospray ionization mass spectra in the positive ion mode (ESI/MS⁺) were recorded on a Bruker Esquire-LC ion-trap instrument with 0.1% formic acid in MeOH being infused into the ion-source by a syringe pump at a flow rate of 200 µL/min. UV-vis spectra were carried out on a Hewlett Packard 8452 diode array spectrophotometer. Elemental analyses were performed using a Carlo Erba EA1108 elemental analyzer.

Synthesis of $Ru(T-pCN-PP)(CO)(H_2O)$ (1). To a refluxing solution of H₂T-pCN-PP (103 mg, 0.14 mmol) in o-dichlorobenzene (15 mL),

^{*} Corresponding authors.

E-mail addresses: jsreboucas@quimica.ufpb.br (J.S. Rebouças), brj@chem.ubc.ca (B.R. James).

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Ru₃(CO)₁₂ (138 mg, 0.22 mmol) was added portion-wise (~5–10 mg) over 2.5 h. Pyridine (4 mL) was then added, and the refluxing continued for a further 20 min. The solvent was then removed, the residue suspended in CH₂Cl₂, and the resulting suspension was transferred to a neutral Al₂O₃ column containing CH₂Cl₂. The eluent was changed to a 4:1 CH₂Cl₂/MeCN mixture and the running band was collected. This fraction was taken to dryness and dissolved in CH₂Cl₂; the UV-vis spectrum of this solution showed a band at 608 nm, due to a chlorin contamination [7]. The CH₂Cl₂ solution was washed with twelve 10 mL aliquots of 6 M HCl, allowing 5-10 min of phase contact before the aqueous phase was separated. These aqueous phases were analyzed for pyridine hydrochloride ([HPy⁺]Cl⁻) by UV-vis spectroscopy $(\lambda_{max} = 258 \text{ nm})$; non-detection implied the absence of Py in the CH₂Cl₂ solution, which was then washed with water until the pH of the aqueous phase was neutral. The organic phase was separated, dried with Na₂SO₄, filtered, and taken to dryness. To remove the chlorin, the residue was dissolved in a mixture of toluene (15 mL), CH₂Cl₂ (20 mL), and MeCN (5 mL); 2,3-dichloro-5,6-dicyano-benzoguinone (DDO, 15.8 mg) was then added and the solution was refluxed for 30 min. At r.t., 50 mL of an aqueous solution containing sodium dithionite (~100 mg) and NaOH (~500 mg) were then added, and the organic phase was separated, washed with water, dried with Na₂SO₄, filtered, and taken to dryness. The resulting red solid was dried overnight in an Abderhalden pistol (H₂O), and then exposed to the atmosphere for ~5 h to give 1. Yield: 70.2 mg (57%). Anal. Calcd for Ru(T-pCN-PP)(CO)(H₂O), C₄₉H₂₆N₈O₂Ru: C, 68.45; H, 3.05; N, 13.03. Found: C, 68.7; H, 3.2; N, 13.4. ¹H NMR (*d*₆-DMSO): δ 8.55 (s, 8H, β -pyrrole), 8.41–8.38 (m, 4 H, o- or o'-C₆H₄CN), 8.26–8.21 (m, 12H, o'- (or o-), m-, and m'-C₆H₄CN). UV-vis (in DMF): 414 nm (log $\epsilon/L \text{ mol}^{-1} \text{ cm}^{-1} = 5.39$), 532 (4.25), 564 (3.55). IR (cm⁻¹): 3431 (ν_{OH}) , 2227 (ν_{CN}) 1953 (ν_{CO}) . ESI-MS: cluster centered at m/z814 (100 %, [Ru(T-*p*CN-*P*P)(CO)−CO]⁺).

Synthesis of $Ru(T-pCN-PP)(MeCN)_2$ (2). In a Wheaton vial, capped with a rubber septum, complex 1 (5.2 mg, 6.0×10^{-3} mmol) was dissolved in MeCN (18 mL), and the headspace and septum were then completely covered with Al foil. An Ar inlet (stainless steel needle, with the tip placed ~0.5 cm from the bottom of the vial) and outlet (disposable needle, placed in the headspace) were attached, and the Ar flow was adjusted to give a minimal flow of small bubbles through the solution for ~15 min. The solution was then photolysed for 4 h under Ar using a 450-Watt Hanovia Hg lamp (Fisher Scientific) that was water-cooled using a glass jacket. Most of the MeCN evaporates during the photolysis, and the remainder was pumped off at r.t. to yield **2** quantitatively; the septum-sealed photolysis vial was stored under Ar in a glove-box, where **2** was transferred to a J-Young NMR tube to which C₆D₆ (~3 mL) was added. ¹H NMR (C_6D_6) : δ 8.58 (s, 8H, β -pyrrole), 8.08 (AA'BB', 8H, o-C₆H₄CN), 7.26 (AA'BB', 8H, *m*-C₆H₄CN), -2.09 (s, 6H, CH₃CN). IR (see text).

Reaction of **2** *with thiols.* To the C₆D₆ solution of Ru(T-pCN-PP)(MeCN)₂, about a 10-fold excess of RSH was added at r.t., exactly as described previously [2] for the gaseous or liquid RSH (R = Me, Et, ⁿPr, ⁱPr, ⁿBu, ^tBu, ⁿHex, Bn, Ph, and *p*-MeOC₆H₄); immediately precipitated was a reddish brown solid that was collected, washed with C₆H₆ and dried in vacuo. Insolubility has thwarted their characterization.

Results and discussion. The syntheses and reactivity of the Ru(T-pCN-PP) complexes are summarized in Scheme 1 shown below. Although H₂T-pCN-PP has been known since the 1960s [8], and many Ru complexes containing various T-pX-PPs porphyrins (e.g. X = OMe, Me, ⁱPr, F, Cl, Br, and CF₃) have been described since the 1970s [9], no reports have appeared on the Ru-metallation of H₂T-pCN-PP. This likely results from the difficulties in using a standard synthesis of Ru(porp)(CO) from $Ru_3(CO)_{12}$ in various solvents [7a,9e,10]. In decalin, often used for such a synthesis [7a,9e,10a,11], we found no production of a Ru-porphyrin; the H₂T-pCN-PP remained insoluble in this solvent even at refluxing conditions and the isolated purple solid was just free-base porphyrin. To overcome this solubility problem, the reaction was then carried out in refluxing o-dichlorobenzene (also used previously for metallation [12]), which dissolves both the carbonyl and free-base. Upon addition of the Ru₃(CO)₁₂, the color gradually changed from purple to reddish brown concomitantly with the formation of a dark precipitate, and UV-vis analysis of the filtrate indicated almost complete conversion of the free-base porphyrin. The precipitate was insoluble in common solvents, such as CH₂Cl₂, benzene, and DMF, in direct contrast to other neutral Ru(T-pX-PP)(CO) complexes [9], and implies that the product might be polymeric. This product was not investigated further, but likely involves coordination of peripheral *p*-CN groups to some Ru-carbonyl and/or Ru(T-*p*CN-*P*P) moiety - a conclusion based on the facts that (a) benzonitriles are good ligands for Ru-porphyrins [13], (b) Cu- and Zn-H₂T-pCN-PP complexes are excellent synthons for formation of multiporphyrin architectures [4], and (c) the cyano moiety of Co^{II}-porphyrin complexes containing 4-cyanophenyl groups readily replaces the aqua ligand of [Ru(NH₃)₅(H₂O)]²⁺ [14]. Reports [15] that selfcoordinating metalloporphyrin dimers and polymers (including Ru species [15b]), formed within pyridine-substituted porphyrins, can be disassembled into monomers by treatment with exogenous bases prompted us to treat the metallated mixture with excess Py (see Experimental section); indeed, the supposed polymeric solid then dissolved completely within 5 min of reflux to yield a red solution. Chromatographic purification of this solution yielded a solid



Scheme 1. Syntheses and reactivity of the Ru(T-pCN-PP) complexes.

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