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

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ABSTRACT

A novel synthesis is presented for the *meso*-tetrakis(4-cyanophenyl)porphyrin complex Ru(T-*p*CN-*PP*)(CO)(H_2O), the first Ru complex with this long-known porphyrin; compared to standard methods reported for other porphyrin analogues via $Ru_3(CO)_{12}$, extra steps involving addition of pyridine (Py) and its subsequent removal as $[HPy^+]Cl^-$ 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-*PP*)$(MeCN)_2$, but attempts to make the bis(thiol) analogues from this precursor were unsuccessful, again due to formation of polymeric species.

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 (H_2T*PP*) and its *p*-substituted-tetraphenyl analogues (H_2T-*p*X-*PP*, where X is OMe, Me, F, Cl, CO_2Me, and CF_3), 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 ($\sigma = 0.71$ [3]) was an attractive candidate. A further interest in using H_2T-*p*CN-*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 Ru/H_2T-*p*CN-*PP* chemistry, except for an oblique, non-detailed mention of Ru(T-*p*CN-*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-*p*CN-*PP*)(CO)(H_2O), the synthesis of Ru(T-*p*CN-*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 N_2 (Praxair, 99.995%) was dried with Drierite (W.A. Hammond Co.). MeCN (Fisher Scientific, HPLC grade) was stored over activated molecular sieves (4 Å); C_6H_6 (Fisher Scientific) was treated with Na/benzoquinone, distilled under N_2, 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. $Ru_3(CO)_{12}$ [5] and chlorin-free H_2T-*p*CN-*PP* [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 C_6D_6 (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 H_2T-*p*CN-*PP* (103 mg, 0.14 mmol) in *o*-dichlorobenzene (15 mL),

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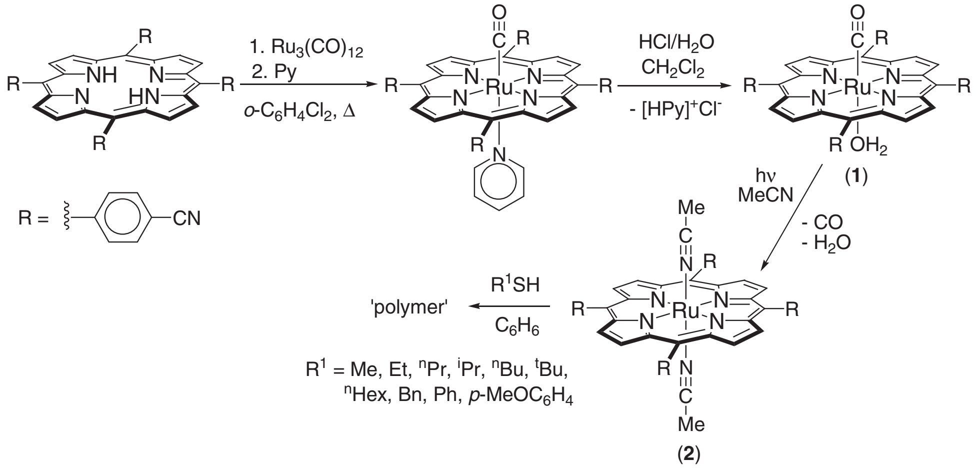
$Ru_3(CO)_{12}$ (138 mg, 0.22 mmol) was added portion-wise (~5–10 mg) over 2.5 h. Pyridine (4 mL) was then added, and the refluxing continued for a further 20 min. The solvent was then removed, the residue suspended in CH_2Cl_2, and the resulting suspension was transferred to a neutral Al_2O_3 column containing CH_2Cl_2. The eluent was changed to a 4:1 CH_2Cl_2/MeCN mixture and the running band was collected. This fraction was taken to dryness and dissolved in CH_2Cl_2; the UV–vis spectrum of this solution showed a band at 608 nm, due to a chlorin contamination [7]. The CH_2Cl_2 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 ($\lambda_{max} = 258$ nm); non-detection implied the absence of Py in the CH_2Cl_2 solution, which was then washed with water until the pH of the aqueous phase was neutral. The organic phase was separated, dried with Na_2SO_4, filtered, and taken to dryness. To remove the chlorin, the residue was dissolved in a mixture of toluene (15 mL), CH_2Cl_2 (20 mL), and MeCN (5 mL); 2,3-dichloro-5,6-dicyano-benzoquinone (DDQ, 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 Na_2SO_4, filtered, and taken to dryness. The resulting red solid was dried overnight in an Abderhalden pistol (H_2O), and then exposed to the atmosphere for ~5 h to give **1**. Yield: 70.2 mg (57%). Anal. Calcd for Ru(T-*p*CN-*P*P)(CO)(H_2O), $C_{49}H_{26}N_8O_2Ru$: 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′*-C_6H_4CN), 8.26–8.21 (m, 12H, *o′*- (or *o*-), *m*-, and *m′*-C_6H_4CN). UV–vis (in DMF): 414 nm (log ε/L mol^{-1} 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/z* 814 (100 %, $[Ru(T\text{-}pCN\text{-}PP)(CO) - CO]^+$).

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 C_6D_6 (~3 mL) was added. ^1H NMR (C_6D_6): δ 8.58 (s, 8H, β-pyrrole), 8.08 (AA′BB′, 8H, *o*-C_6H_4CN), 7.26 (AA′BB′, 8H, *m*-C_6H_4CN), −2.09 (s, 6H, CH_3CN). IR (see text).

Reaction of **2** *with thiols*. To the C_6D_6 solution of Ru(T-pCN-*P*P)(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, ^{n}Pr, ^{i}Pr, ^{n}Bu, ^{t}Bu, ^{n}Hex, Bn, Ph, and *p*-MeOC_6H_4); immediately precipitated was a reddish brown solid that was collected, washed with C_6H_6 and dried in vacuo. Insolubility has thwarted their characterization.

Results and discussion. The syntheses and reactivity of the Ru(T-*p*CN-*P*P) complexes are summarized in Scheme 1 shown below. Although H_2T-*p*CN-*P*P has been known since the 1960s [8], and many Ru complexes containing various T-*p*X-*P*Ps porphyrins (e.g. X = OMe, Me, ^{i}Pr, F, Cl, Br, and CF_3) have been described since the 1970s [9], no reports have appeared on the Ru-metallation of H_2T-*p*CN-*P*P. 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 H_2T-*p*CN-*P*P 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 $Ru_3(CO)_{12}$, 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 CH_2Cl_2, benzene, and DMF, in direct contrast to other neutral Ru(T-*p*X-*P*P)(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-H_2T-*p*CN-*P*P 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 $[Ru(NH_3)_5(H_2O)]^{2+}$ [14]. Reports [15] that self-coordinating 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-*p*CN-*P*P) complexes.

material whose UV–vis spectrum in CH_2Cl_2 showed major bands (at 412 and 530 nm) typical of a Ru(porp)(CO)-containing species [9b], but also a 608 nm band that was attributed to a “Ru chlorin” impurity, often formed in syntheses of such a complex [7] — the metallation was carried out with a chlorin-free porphyrin, and so the chlorin is formed in situ during the metallation. The Py is almost certainly coordinated as the sixth ligand in any Ru(porp)(CO) or Ru(chlorin)(CO) species present, and was considered disadvantageous for the subsequent synthesis of Ru(porp)$(MeCN)_2$, the required precursor for reaction with thiols (see Introduction). Thus, the Py was subsequently removed by a solvent extraction procedure involving treatment of the CH_2Cl_2 solutions of the carbonyl species with aliquots of aqueous HCl; the extraction is conveniently monitored by UV–vis spectroscopy, which also indicates completion when $[HPy^+]Cl^-$ is no longer detected in the aqueous phase. The organic phase was assumed to contain the aqua complex of Ru(T-*p*CN-*P*P)(CO) and a corresponding Ru(chlorin)(CO) complex, but these species were not separated at this stage. The Ru-chlorin was first converted to its parent Ru(porp)(CO) species *via* the oxidative, DDQ-based procedure, but using a toluene-CH_2Cl_2-MeCN mixture in order to dissolve completely the porphyrin material, instead of the usual neat toluene medium [7b,16]. After removal of the chlorin, as indicated by the disappearance of the 608 nm band, the Ru porphyrin complex was purified by reducing the excess DDQ with dithionite and extracting the resulting hydroquinone (the co-product of the chlorin oxidation) with aqueous alkaline solution, followed by washing of the organic phase with water [7b].

The isolated Ru(T-*p*CN-*P*P)(CO)(H_2O) complex (**1**) was characterized by elemental analysis, UV–vis, IR and ^1H NMR spectroscopies and mass spectrometry, the data resembling closely those of other Ru(T-*p*X-*P*P)(CO)(H_2O) species (X = H and CO_2Me) [9e]. Briefly, metallation is marked by the loss of the 3314 cm^{-1} ν_{NH} stretch in the IR and the ^1H NMR resonance of the NH proton (δ –2.89, $CDCl_3$) of the free-base H_2T-*p*CN-*P*P; the reduced number of bands in the visible region of the UV–vis spectrum compared to that of the free-base is also consistent with metal insertion [17]; the presence of the H_2O, CN and CO moieties is evident in the IR spectra (bands at 3431, 2227 and 1953 cm^{-1}, respectively); the complex ^1H NMR pattern for the phenyl protons, with assignments aided by data for H_2T-*p*CN-*P*P [18], reveals the lack of axial symmetry; the isotopic distribution pattern for the peak cluster seen in the MS spectrum agrees with that calculated for $[Ru(T\text{-}pCN\text{-}PP)]^+$; and the elemental analysis is consistent with the formulation. The use of the Abderhalden pistol (H_2O) and exposure to the atmosphere for a few hours guarantees the presence of the aqua ligand [9].

Complex **1** has thus been isolated for the first time in reasonable yield (57%) via a somewhat lengthy synthesis which, compared to the standard Ru-metallation using $Ru_3(CO)_{12}$, requires two extra steps: the one-pot reaction of the crude product with Py, and the amine extraction with aqueous HCl, which is unnecessary if Ru(T-*p*CN-*P*P)(CO)(Py) were the desired product. All procedures for $Ru_3(CO)_{12}$-based Ru-metallation of porphyrins require chromatographic separation and usually involve chlorine elimination via further chromatography [e.g. ref. 7a] or a DDQ-oxidation [e.g. 7b]. Our synthesis thus represents convenient access to Ru(T-*p*CN-*P*P)(CO)(H_2O), which is particularly interesting for the design of Ru-based multiporphyrin arrays and perhaps polymetallic sensors.

The bis(nitrile) complex, Ru(T-*p*CN-PP)$(MeCN)_2$ (**2**), was synthesized by photolysis of the carbonyl complex **1**. The procedure generally follows reported methods [1,2,19], but neat MeCN was used instead of the C_6H_6:MeCN mixture that we used for other Ru(T-*p*X-*P*P)$(MeCN)_2$ species (X = OMe, H, F, Cl, CO_2Me, CF_3) [20]. Satisfactory elemental analysis was not obtained for **2**, and this is attributed to its air-sensitivity, but the clean ^1H NMR spectra showed the absence of any impurities and establishes the presence of two axial MeCN ligands. An IR spectrum of a sample with limited exposure to air showed no ν_{CO} band, proving that the carbonyl ligand of **1** has been fully photo-dissociated; in the absence of the Al foil, some of the septum was degraded to a yellow product that was extracted by the solvent during the photolysis and led to contamination of **2**.

Room temperature treatment of a C_6D_6 solution of Ru(T-*p*CN-PP)$(MeCN)_2$ with excess of an aliphatic or aromatic thiol yielded solids that were completely insoluble in common solvents, including MeCN. The reactions proceeded with loss of ^1H signals of the bis-nitrile reactant and appearance of the 6-proton signal for free MeCN (δ 0.59). Elemental analyses of the products were extensively variable and of no value for characterization. They are likely to be self-assembled polymers involving coordination of the *p*-cyanophenyl arms of the porphyrin; several types of lattice structures have been reported within Zn^{II}- and Cu^{II}-(T-*p*CN-*P*P) systems, some incorporating benzene as a guest solvent [4]. A thiol does not appear to be a sufficiently strong binding ligand to prevent formation of the polymeric structures, which contrasts with the behavior of Py in disassembling polymer formation during synthesis of Ru(T-*p*CN-*P*P)(CO)(H_2O) (see above). Synthesis of Ru(T-*p*CN-PP)$(MeCN)_2$ by the photolysis procedure implies that MeCN can compete with the peripheral *p*-cyanophenyl as an axial ligand. Thus, the reactivity trend at a Ru^{II}-porp centre appears to be Py > MeCN > porp-C_6H_4-CN > RSH, although a thiol is likely occluded/bonded somewhere in the polymeric, lattice structure. Studies continue on the characterization of the Ru(T-*p*CN-PP)-based coordination polymers and their potential as porphyrin-based supramolecular solids, which are of general interest because of their optical and/or redox properties [4,21].

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