

Electrochemical and spectroscopic studies on some pyridyl and morpholyl adducts of (*meso*-tetraphenylporphyrin)chromium(III) chloride

S P ROE, R J MAGEE* and J O HILL

Department of Chemistry, La Trobe University, Bundoora (Melbourne), Victoria 3083, Australia

MS received 14 March 1985; revised 30 July 1985

Abstract. The electrochemical behaviour of the adducts $\text{Cr}(\text{TPP})\cdot\text{Cl}\cdot\text{L}$, where TPP = tetraphenylporphyrin; L = pyridine, 2-picoline, 2,6-lutidine, 4-cyanopyridine, morpholine or 4-picoline is reported and the relationship between reduction potentials, the electron band I transition and the binding energy of the Cr $2p_{3/2}$ level examined.

Based on criteria for the differences in oxidation potentials determined in acetonitrile by cyclic voltammetry and reduction potentials determined in DMSO, it is concluded that the adducts behave as normal metalloporphyrins. Further, variations for the different adducts are attributed primarily to different inductive effects from the heterocyclic axial groups. The adduct formed from 2,6-lutidine, however, shows anomalous behaviour which is attributed to a marked steric effect between the ligand and the porphinato-nitrogen atoms.

Keywords. (*meso*-Tetraphenylporphyrin)chromium(III) chlorides; base adducts; electrochemical behaviour.

1. Introduction

Previous studies on chromium porphyrins by spectroscopic techniques (Cheung *et al* 1976; Scheidt *et al* 1979; Jones *et al* 1979; Summerville *et al* 1979) have shown that the porphyrin ligand has a labilising effect on Cr(III) substitution reactions, making them 10^3 - 10^4 times faster than those with normal Cr(III) complexes. This labilisation has been attributed to strong mixing (π -bonding) of the chromium d_{yz} , d_{xz} orbitals and the lowest unfilled porphyrin π^* -orbitals, causing the metal to lose its d^3 character with the empty $d_{x^2-y^2}$, d_{z^2} orbitals being available for σ -bonding with axial ligands and the porphyrin macrocycle.

Considerable interest has centred on the effect of axial ligation. Summerville *et al* (1977), showed that changes in axial ligation of the heme moiety in natural heme proteins causes changes in the biological role of the heme protein.

It has also been pointed out (Inhoffen *et al* 1968) that the properties of a metalloprotein are influenced by the geometry, charge, electronegativity, degree of σ - and π -bonding of the metal porphyrin systems and the degree of σ - and π -bonding of the metal-axial ligand system.

While a number of publications have reported electrochemical studies on porphyrin

* To whom all correspondence should be addressed.

free bases and chromium porphyrin complexes (Fleischer and Krishnamurthy 1971; Fleischer and Srivastava 1971; Bottomly and Kadish 1981; Kelly and Kadish 1984), studies on axial ligation of metalloporphyrins by pyridyl groups has been limited, especially for Cr(III) tetraphenylporphyrin complexes, such as Cr(III)-(TPP)Cl. Bottomley and Kadish (1981) and Larkworthy (1984) suggest, on the basis of electrochemical investigations, that two discrete pathways for electron transfer are possible in the reduction of Cr(TPP)Cl(L), where TPP = tetraphenylporphyrin, L = substituted pyridine.

To investigate the possible inductive and steric factors associated with axial ligation of Cr(III) (TPP)Cl by different substituted pyridine ligands, the electrochemical behaviour of the complexes formed with pyridine, 2-picoline, 2,6-lutidine, 4-cyanopyridine, morpholine and 4-picoline has been determined and the relationship between reduction potentials, the electronic band I transition and the binding energy of the Cr $2p_{3/2}$ level examined.

2. Experimental

Electrochemical data (DC cyclic voltammetry, CV, and DC polarography, DCP) were recorded on an AMEL 471 Multipolarograph, 3-electrode system. The reference, auxiliary and working electrodes were the saturated calomel electrode (SCE), platinum wire electrode and either a hanging mercury drop electrode (HMDE) (CV) or a dropping mercury electrode (DME) (DCP), respectively. All solutions were of concentration 1.5×10^{-3} M, with 0.2 M tetrabutylammonium perchlorate as supporting electrolyte together with 50 μ l of 0.1% Triton-X100 surface active agent. The solvent for cyclic voltammetry was either acetonitrile or dimethylsulphoxide. The latter solvent was used exclusively for DC polarography.

X-ray photoelectron spectra were recorded on a spectrometer previously described by Kemeny *et al* (1973), using AlK α photons of 1486.6 eV energy. The powdered samples were adhered to a copper sample holder with double-sided adhesive tape. All core level binding energies (E_b^f) were calibrated relative to the Cu $2p_{3/2}$ core level binding energy (932.5 eV) of the reversible copper sample holder, relative to the spectrometer Fermi Level, in accordance with the procedure of Barr (1978). The copper metal surface was scraped and passivated in air for 1–2 min prior to subjection to a vacuum reaching 10^{-7} HPa (torr) in approximately 20 min. Determination of surface charging effects was made by the standard method (Kohiki *et al* 1983), which involves variation of the intensity of the AlK α x-rays (50–300 W, Leybold-Heraeus RQ 10/63 x-ray source). No surface charging effects were detected which suggests that the generation of secondary electrons inside the spectrometer housing was sufficient to act as a 'flood-gun' for the sample surface. As a result, no correction for a 'floating' Fermi edge was necessary in calibrating core level binding energies. The associated error with E_b^f is (± 0.3 eV).

Ultraviolet and visible spectra were recorded on a Shimadzu, UV-240 Recording Spectrophotometer using 1 cm matched quartz cells and purified chloroform as solvent.

Chemicals: TPPH $_2$: this was purified according to the procedure of Datta-Gupta and Williams (1971);

Cr(TPP)Cl: The metalloporphyrin was synthesised according to the method of Adler *et al* (1970).

Elemental analysis: *Found*: C, 58.70; H, 3.79; N, 7.36%; *Calcd*: (as CrC₄₇H₃₅N₅ClO 1.5HCl₃) C, 58.72; H, 3.72; N, 7.00%.

The Cr(TPP)CL adducts, where L = pyridine, 2-picoline, 2,6-lutidine, 4-cyanopyridine, morpholine and 4-picoline, were prepared according to the following general procedure.

The heterocyclic ligand, L, was added in excess (10 cm³) to a solution of Cr(TPP)Cl (0.5 g) dissolved in purified chloroform (50 cm³) and stirred at ambient temperature for 3 hours. Slow evaporation of the solvent afforded the Cr(TPP)Cl(L) adducts, with an average yield of 95% after washing with anhydrous, purified chloroform. The 4-cyanopyridine adduct was prepared by adding 4-cyanopyridine (9.5 g) in benzene (30 cm³) to Cr(TPP)Cl (0.5 g) in chloroform (50 cm³), followed by slow evaporation of the solvents.

The elemental analysis for the Cr(TPP)Cl(Pyridine) adduct is as follows: *Found*: C, 75.50; H, 4.20; N, 9.00%; *Calcd*.: C, 75.52; H, 4.27; N, 8.98%.

3. Results and discussion

Electrochemical data for the Cr(TPP)Cl adducts with the following axial ligands—pyridine, 2-picoline, 2,6-lutidine, 4-cyanopyridine, morpholine and 4-picoline are shown in table 1, along with electrochemical data for selected chromium porphyrins extracted from the literature for comparative purposes. The xps E_b^f (Cr 2p_{3/2}) binding energies and near infrared Band I [$a_{2u}(\pi)$, $a_{1u}(\pi) \rightarrow e_g(\pi^*)$] electronic transitions are recorded in table 2.

Elemental analyses yielded results which indicated that the (meso-tetraphenylporphyrin)chromium(III) chloride dissolved in dimethylformamide had the formula Cr(TPP)Cl(DMF). However, in the formation of the pyridyl and morpholyl adducts, a dissociative exchange mechanism: Cr(TPP)Cl(DMF) + L \rightleftharpoons Cr(TPP)Cl(L) + DMF takes place, where L = an axial base ligand.

To distinguish between metal and ligand redox reactions in metalloporphyrins, Furhop (1974) and Felton (1979) established the general pattern that the numerical difference between the half-wave potentials of the first ligand oxidation ($E_{1/2}^{ox}$) in nitrile solvents and the first ligand reduction in DMSO ($E_{1/2}^{red}$), i.e., $\Delta E_{1/2}^{ox/red} = \delta$, equals 2.25 \pm 0.15 V, when the redox processes involve the porphinato moiety and not the metal. Further criteria are that the normal difference between the 1st and 2nd ring oxidations, $\Delta_{ox} = E_{1/2}^{ox}(2) - E_{1/2}^{ox}(1)$ equals 0.29 \pm 0.05 V, while the normal difference between the 1st and 2nd ring reductions $\Delta_{red} = E_{1/2}^{red}(1) - E_{1/2}^{red}(2)$ should lie in the range 0.49 \pm 0.08 V.

From the literature data cited in table 1 for chromium-porphyrin complexes, it is clear that, in general, these complexes exhibit Δ_{ox} and Δ_{red} values within the normally accepted ranges. Further, it would appear that they are, to certain extents, subject to solvation effects and varying inductive and steric effects by the axial ligand groups. Further, the similarity of δ for TPPH₂ and Cr(TPP)Cl would tend to support the view that there is negligible mixing of the ligand (a_{2u}), (a_{1u}) and metal $e_g(d\pi)$ molecular orbitals, as metallation does not significantly affect the value of δ .

Table 1. Electrochemical data for selected chromium porphyrins and TPPH₂ free base.

Complex	CV oxidation (CH ₃ ON)			CV reduction (DMSO)			DCP reduction (DMSO)				
	Ligand		Metal	Ligand		Metal	Ligand		Metal		
	$E_{1/2}$ (2) (V)	$E_{1/2}$ (3) (V)	III → IV (V)	Δ_{ox} (V)	$E_{1/2}$ (2) (V)	$E_{1/2}$ (3) (V)	III → II (V)	Δ_{red} (V)	δ (V)	Ligand $E_{1/2}$ values (V)	III-II (V)
Cr(TPP)-Cl(DMF)	+1.20	+1.42	+0.53	0.22	-1.27	-1.70	-0.75	0.43	2.47	-0.06	-0.37
Cr(TPP)-Cl(Py)	+1.01	+1.20	+0.33	0.19	—	-1.53	-0.80	—	—	-0.1	-0.37
Cr(TPP)-Cl(2-Pic)	+1.06	—	+0.25	—	-1.22	-1.65	-0.42	0.43	2.28	-0.05	-0.38
Cr(TPP)-Cl(2,6-lut)	+1.01	—	—	—	-1.31	—	-0.43	—	2.32	-0.09	-0.25
Cr(TPP)-Cl(4-CyPy)	+0.98	—	—	—	—	-1.25	-1.37	0.12	2.23	-0.02	-0.36
Cr(TPP)-Cl(Mor)	+1.16	—	—	—	-1.24	—	-0.96	—	2.40	-0.03	-0.47
Cr(TPP)-Cl(4-Pic)	+1.08	—	—	—	-0.91	-1.19	-0.73	0.28	1.99	-0.06	—
TPPH ₂ ^a	+1.12	+0.97	—	0.15	—	—	—	—	—	—	—
TPPH ₂ ^b	+1.28	+0.95	—	0.33	-1.05	-1.47	—	0.42	2.33	—	—
Cr(OEP) ^c -(OH) in CH ₂ Cl ₂	+1.22	+0.99	+0.79	0.23	-1.35	—	-1.14	—	2.57	—	—
Cr(OEP) ^d -(OH) in DMSO	+1.22	+0.99	+0.79	0.23	-1.34	—	-1.13	—	2.56	—	—
Cr(TPP) ^e -ClO ₄ in CH ₂ Cl ₂	+1.39	+1.03	—	0.36	-0.81	-1.20	—	0.39	2.20	—	—
Cr(TPP) ^e -(NO) in CH ₂ Cl ₂	—	+0.79	—	—	—	-1.86	—	1.05	—	—	—
[Cr(TPP) ^e -Cl(Py) ₂] ⁺ in CH ₂ Cl ₂	+1.22	+0.95	—	—	—	—	—	—	—	—	—
Cr(TPP) ^e -Cl(Py) in CH ₂ Cl ₂	—	—	—	—	—	—	-0.75	—	—	—	—
Cr(TPP) ^e -Cl in CH ₂ Cl ₂	+1.29	+0.87	—	0.42	-1.01	-1.20	-1.07	0.19	2.30	—	—
Cr(TPP) ^d -in butyronitrile	—	—	+0.79	—	—	—	—	—	—	—	—
Cr(TPP) ^d -Cl in CH ₂ Cl ₂	+1.25	+0.87	—	0.38	-1.06	-1.69	—	0.63	—	—	—
Cr(TPP) ^b -Cl	—	—	+0.79	—	-1.69	—	-1.06	—	—	—	—

^aFuhrhop (1974); ^bFelton (1979); ^cFuhrhop *et al.* (1973); ^dNewton and Davis (1975); ^eKelly and Kadish (1984).

Abbreviations: DMF = dimethylformamide; DMSO = dimethylsulphoxide; OEP = octaethylporphyrin; Py = pyridine; 2-Pic = 2-picoline; 2,6-lut = 2,6-lutidine; 4,6-CyPy = 4-cyanopyridine; Mor = morpholine; 4-Pic = 4-picoline.

Table 2. E_f^I (Cr 2p_{3/2}) binding energies and electronic band I [$a_{2u}(\pi)$, $a_{1u}(\pi)$, $e_g(\pi^*)$] transitions for DMF, pyridyl and morpholine adducts of Cr(TPP)Cl and average $E_{1/2}$ (III-II) reduction potentials.

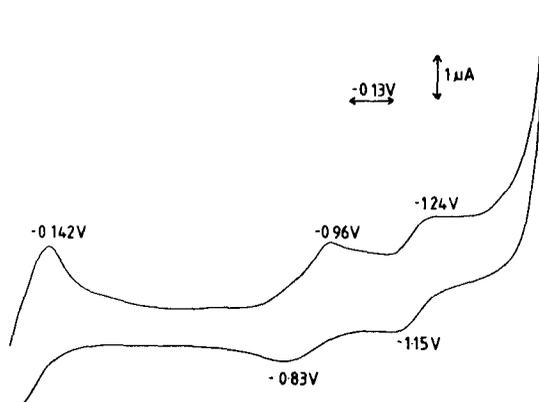
No.	Complex	xps* E_f^I (Cr 2p _{3/2}) (eV)	UV-vis* band I ($a_{2u}(\pi)$, $a_{1u}(\pi) \rightarrow e_g(\pi^*)$) (nm)	/ $E_{1/2}^{red}$ (III-II)/(V)*
1	Cr(TPP)Cl(DMF)	570.8	810.0	-0.75
2	Cr(TPP)Cl(Py)	572.2	788.0	-0.83
3	Cr(TPP)Cl(2-Pic)	571.5	809.5	-0.56
4	Cr(TPP)Cl(4-Pic)	569.1	830.0	-0.46
5	Cr(TPP)Cl(2,6-lut)	569.9	811.0	-1.09
6	Cr(TPP)Cl(4-CyPy)	571.6	795	-0.91
7	Cr(TPP)Cl(Mor)	573.3	806	-0.68

* Errors: xps (± 0.3 eV); band I (± 1.0 nm); $E_{1/2}^{red}$ (III-II) (± 0.05 V); abbreviations: refer table 1, foot note.

As representatives of the voltammograms obtained for the reduction of the different Cr(TPP)·Cl·L adducts, those for the morpholine (Mor) and pyridine (Py) adducts are shown in figures 1 and 2, respectively. From the voltammograms, the values of δ and Δ_{red} were obtained. For the oxidation of the adducts in acetonitrile, the values of δ and Δ_{ox} were also obtained. All values are listed in table 1, which in addition contains the DC polarographic data in DMSO for Cr(TPP)Cl·DMF and the six adducts of Cr(TPP)Cl.

In the polarographic reduction of the adducts, 4 polarographic waves were, in general, detected. The half-wave potentials of these waves were found to be in the range (1) -0.06 to -0.1; (2) -0.25 to -0.47; (3) -0.4 to -0.56 and (4) -0.50 to -0.86. Of the four waves obtained in the polarographic investigations, the fourth was found to be dependent on the metal concentration and gave a value of $n \cong 1$ for the number of electrons transferred. It thus relates to the reduction Cr(III) \rightleftharpoons Cr(II). The variation of $E_{1/2}$ for the different adducts reflects the inductive, steric and solvent effects associated with different adducts.

In cyclic voltammetry, as seen from figure 1 for the reduction of the adduct

**Figure 1.** Cyclic voltammogram at HMDE for reduction of Cr(TPP)Cl·Mor adduct. (0 to -1.55 v; scan rate 0.050 v/s; $T = 25^\circ\text{C}$) in DMSO; 0.2 M Bu_4NClO_4 ; 50 μl 0.1% TRX 100.

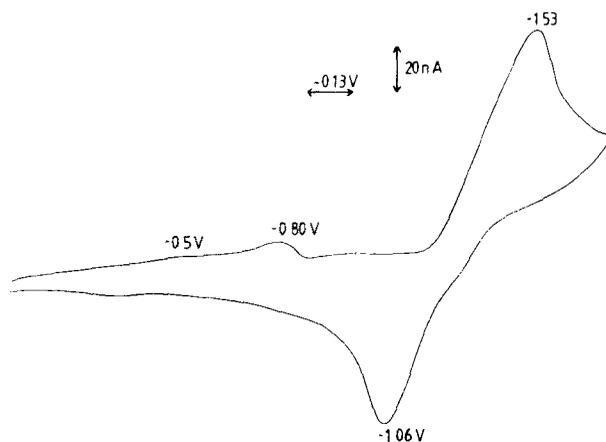


Figure 2. Cyclic voltammogram at HMDE for reduction of $\text{Cr}(\text{TPP})\text{Cl}\cdot\text{Py}$ adduct (0 to -1.17 v; scan rate 0.050 v/s; $T = 25^\circ\text{C}$) in DMSO ; 0.2 M $\text{But}_4\text{NClO}_4$; $20\ \mu\text{l}$ 0.1% TRX 100.

$\text{Cr}(\text{TPP})\text{Cl}\cdot\text{Mor}$ in DMSO , three peaks were found on the cathodic sweep: (1) -0.142 V; (2) -0.96 V; (3) -1.24 V. The peak at -0.96 V was found to be dependent on the concentration of $\text{Cr}(\text{III})$ and thus represents the reduction $\text{Cr}(\text{III}) \rightleftharpoons \text{Cr}(\text{II})$. The peak at -1.24 V does not show the characteristics of an adsorption wave and is not associated with the reduction of the metal. It is, therefore, assigned as a ligand peak. The anodic sweep shows a peak at -1.15 V which corresponds to the cathodic peak at -1.24 V. The peak at -0.142 V appears to be an adsorption wave.

The results obtained with the six adducts (table 1) show accord with the criteria mentioned above and indicate that the system behaves as a normal metalloporphyrin. The variations of δ - and Δ_{red} for the adducts are mainly attributed to different inductive effects from the heterocyclic axial groups. The value of δ reflects the 2.18 eV difference between the e_g and $(a_{1u}), (a_{2u})$ molecular orbitals of the porphinato ligand.

It appeared from this work that the mean half-wave potential for the reduction of the chromium(III) ion has some relationship to the size of the electronic band I ($a_{2u}(\pi), a_{1u}(\pi) \rightarrow e_g(\pi^*)$) transition. To examine this, the experimental value for the electronic band I transition for each adduct was determined and plotted against the corresponding $E_{1/2}$ value. The result is shown in figure 3. The results indicate a direct relationship between electronic band I transition and $E_{1/2}$ with both dependent on the axial ligand. This may be due to changes in the electron withdrawing ability of the chromium ion on the porphinato ring nitrogen atoms, as a direct consequence of changing axial ligands. The deviation of the 2,6-butidine adduct from the line in figure 3 is interesting and may be due to both an axial ligand inductive effect on the chromium ion and steric hindrance between the 2,6-dimethyl groups on the ligand and the porphinato nitrogen atoms.

An approach that may be used to examine the electron density on the chromium as the axial ligand is changed is by means of xps. Consequently, the value of $E_f^{\text{Cr}}(\text{Cr } 2p_{3/2})$ was determined by xps for each $\text{Cr}(\text{TPP})\text{Cl}\cdot L$ adduct and the value obtained plotted against the corresponding $E_{1/2}^{\text{red}}(\text{III-II})$ value. Results are shown in figure 4 and reflect a small increase in the $(\text{Cr } 2p_{3/2})$ binding energy and a small increase in $E_{1/2}$ values with changing axial ligands. It is interesting to note that, in figures 3 and 4, it is the 2,6-butidine ligand which shows a marked deviation from the straight line. It is supposed

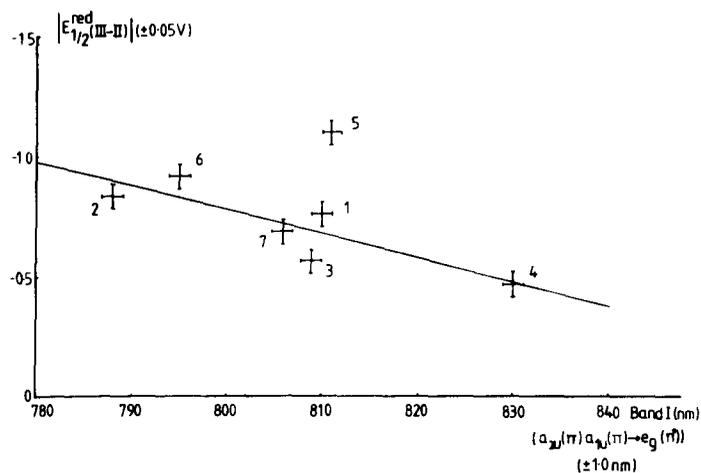


Figure 3. Correlation of $E_{1/2}$ values and the corresponding electronic Band I transitions for the (meso-tetraphenylporphyrin)chromium(III) adducts.

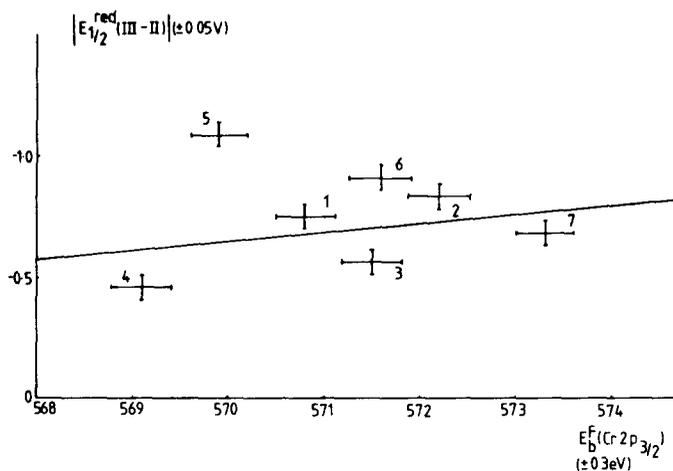


Figure 4. Correlation of $E_{1/2}$ values and the corresponding $E_b^f(Cr 2p_{3/2})$ binding energies for the (meso-tetraphenylporphyrin)chromium(III) adducts.

that the reason for this is that it is reflecting a significant steric interaction of this axial ligand with the porphinato nitrogen atoms. This is confirmed (figure 4) by the large E_b^f range (569–573.5 eV) caused by the steric and inductive influences on the Cr 2p orbitals.

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