Spectroscopic Studies on Some Pyridine and Morpholine Adducts of (meso-Tetraphenylporphyrin)chromium(III) Chloride⁺

Stephen P. Roe, John O. Hill and Robert J. Magee

Department of Chemistry, La Trobe University, Bundoora, Vic. 3083.

Abstract

Infrared, electronic and X-ray photoelectron spectroscopic data are reported for a series of (*meso*-tetraphenylporphyrin)chromium(III) chloride adducts: Cr(tpp)ClL, where L = pyridine, 2-picoline, 4-picoline, 2,6-lutidine, 4-cyanopyridine and morpholine. The data are interpreted in terms of increased symmetry of the porphinato moiety upon metallation and changes to the metal electronic environment resulting from the inductive and steric effects of the axial base-ligand L. A correlation is shown to exist between the $E_b^F(Cr 2p_{3/2})$ binding energy and the band I electronic transition energy for these complexes, which quantifies the influence of the base-ligand L on the electronic environment of the coordinated metal.

Introduction

meso-Tetraphenylporphyrin (H₂tpp) has been widely used as the ligand in metalloporphyrin systems to model the natural haem proteins. Such studies have involved a large number of metals Fe, Mn, Zn, Au, Re, Mg, Co, Ni and others. Studies on chromium porphyrins have, however, been meagre in comparison. As far as the chromium(III) porphyrins are concerned, work on octaethylporphyrin chromium(III) complexes such as $Cr^{III}(oep)OH^{1,2}$ and $Cr^{III}(oep)(OH)(PhOH)^3$ has been reported. Studies on the substitutional lability of $Cr^{III}(tpps)$ complexes, where tpps = *meso*-tetrakis(*p*-sulfonatophenyl)porphine, have shown that the porphyrin ligand has a labilizing effect on Cr^{III} substitution reactions, which are 10^3-10^4 times faster than normal chromium complexes.⁴⁻⁶ Labilization has been attributed to very 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 d³ character. Leipoldt *et al.*,⁵ however, have shown that the lability of Cr^{III} porphyrins is due to the porphyrin ligand promoting a dissociation reaction along the axial ligands.⁷ The empty $d_{x^2-y^2}$

† Dedicated to the memory of Maxwell J. O'Connor.

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⁴ Fleischer, E. B., and Krishnamurthy, M., J. Am. Chem. Soc., 1971, 93, 3784.

⁵ Leipoldt, J. G., Van Eldik, R., and Kelm, H., Inorg. Chem., 1983, 22, 4146.

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and d_{z^2} -orbitals on the chromium are available for σ -bonding with axial ligands and porphyrin macrocycle. Most Cr^{III} porphyrin studies have involved Cr^{III}(tpp)X(L) complexes, where X is a coordinated counterion and L is a neutral axial ligand.⁸⁻¹⁸

Cr^{III}(tpp)Cl complexes do not possess an oxidation state conducive to axial ligation by dioxygen. They do, however, have a high affinity for coordination of a sixth ligand. Further, axial ligation can influence the electronic structure of the metalloporphyrin.

In this paper the effects, brought about by changing axial ligation, on the electronic environment in Cr(tpp)Cl, through the formation of pyridine and morpholine adducts, have been examined by using X-ray photoelectron spectroscopy (XPS), infrared and electronic spectroscopy.

Experimental

All solvents were purified by the methods of Perrin *et al.*¹⁹ meso-Tetraphenylporphine (H_2 tpp) was supplied by Aldrich: the 2-10% meso-tetraphenylchlorin (H2tpc) was removed by refluxing H₂tpp in dimethyl sulfoxide for several hours followed by elution through an alumina (Grade I) column (40 by 12 cm) with chloroform.^{20,21} (meso-Tetraphenylporphyrin)chromium(III) chloride was synthesized and purified according to the method of Adler et al.²² (Found: C, 72.9; H, 4.5; Cl, 4.6; N, 8.9. C47H35ClCrN5O requires C, 73.0; H, 4.6; Cl, 4.6; N, 9.1%) which suggest a stoichiometry of $Cr(tpp)Cl.HCONMe_2$. (*meso*-Tetraphenylporphyrin)chromium(III) base adducts, Cr(tpp)Cl(L), L = pyridine (py), 2-picoline (tpic), 4-picoline (fpic), 2,6-lutidine (lut), 4-cyanopyridine (cypy) and morpholine (mor), were synthesized²³ by recrystallization of the parent complex in the appropriate base, where the following exchange reaction has been suggested to occur:8,10

$Cr(tpp)Cl(HCONMe_2) + L \rightarrow Cr(tpp)Cl(L) + HCONMe_2$

Cr(tpp)Cl(py): (Found: C, 75.1; H, 4.5; Cl, 4.1; N, 8.0. C₄₉H₃₃ClCrN₅ requires C, 75.5; H, 4.3; Cl, 4.6; N, 9.0%). Cr(tpp)Cl(lut): (Found: C, 75.1; H, 4.6; Cl, 4.1; N, 8.9. C₅₁H₃₇ClCrN₅ requires C, 75.9; H, 4.6; Cl, 4.4; N, 8.7%). Cr(tpp)Cl(mor): (Found: C, 72.9; H, 4.8; Cl, 4.1; N, 8.7. C₄₈H₃₇ClCrN₅O requires C, 73.2; H, 4.7; Cl, 4.5; N, 8.9%).

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¹⁸ Bottomley, L. A., and Kadish, K. M., J. Chem. Soc., Chem. Commun., 1981, 1212.

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²² Adler, A. D., Longo, F. R., Kampas, F., and Kim, J., J. Inorg. Nucl. Chem., 1970, **32**, 2443.

²³ Buchler, J. W., in 'Porphyrins and Metalloporphyrins' (Ed. K. M. Smith) p. 212 (Elsevier: Amsterdam 1975).

Infrared spectra in the range $4000-250 \text{ cm}^{-1}$ were recorded on a Perkin-Elmer 457 grating infrared spectrophotometer by using the KBr disc method, with band calibration relative to polystyrene. Far-infrared spectra, in the range $500-200 \text{ cm}^{-1}$, were recorded on a Perkin-Elmer 180 grating infrared spectrophotometer by using the Nujol mull technique with polythene cylindrical plates and a Nujol reference.

Ultraviolet and visible spectra were recorded on a Shimadzu UV-240 recording spectrophotometer with l-cm matched quartz cells and chloroform as solvent.

Elemental analyses were obtained from the Australian Microanalytical Service, Melbourne.

X-Ray photoelectron spectra were recorded on a spectrometer previously described by Kemeny et al.²⁴ using Al K α photons of 1486.6 eV energy. 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 $(932.5 \text{ eV})^{25}$ of the reversible copper sample holder, relative to the spectrometer Fermi Level. The copper metal surface was scraped and passivated in air for 1–2 min prior to exposure to vacuum (10^{-7} hPa) . The XPS spectra were checked for surface charging effects on the core level binding energies by varying the intensity of the Al K α X-rays (50–300 W, Leybold–Heraeus RQ 10/63 X-ray source). The copper sample holder with adhered sample were situated inside a cylindrical metal housing. The X-rays entered through a slot in the side of the cylinder and the photoelectrons passed through a fine slit in the same cylinder prior to entering the energy analyser. No surface charging effects were observed with variation of X-ray intensity which suggests that the generation of secondary electrons inside the housing was sufficient to act as a 'flood-gun' for the sample surface. Hence, no correction to binding energies for a 'floating' Fermi edge was necessary. The overall uncertainty associated with reported E_b^F is $\pm 0.3 \text{ eV}$.

Results and Discussion

X-Ray Photoelectron Spectroscopy (XPS) Investigations

The study of porphyrins and metalloporphyrins by XPS has been limited²⁶⁻³² with investigations restricted, in the main, to the nitrogen 1s core electron binding energies. These investigations showed that the $E_b^F(N \ 1s)$ was a very sensitive probe in analysing the charge distribution in the porphyrins. A number of workers have reported²⁶⁻³⁰ two types of nitrogen atoms in porphyrin free bases, namely, the aza- and pyrrole-types, where $E_b^F(N \ 1s)$ is approximately 398 eV and 400 eV, respectively. On metallation, the four nitrogen atoms become equivalent with an $E_b^F(N \ 1s)$ value of 399 eV. Thus, replacement of free base protons by a metal ion to form a metalloporphyrin increases the symmetry of the molecule²⁷ and introduces, what is, in fact, an electron-withdrawing group into the centre of the ligand.

The results obtained in the present study are shown in Table 1. It will be seen that for H_2 tpp, only one value for $E_b^F(N \ 1s)$ at 391.0 eV is observed.

For the chromium metalloporphyrins, chromium $2p_{1/2,3/2}$ core electron binding energies are reported for the pyridine and morpholine Cr(tpp)Cl adducts and also Cr(tpp)Cl(HCONMe₂) and CrCl₃.6H₂O.

²⁴ Kemeny, P. C., Maclachlan, A. D., Battye, F. L., Poole, R. T., Leckey, R. G. G., Liesegang,

J., and Jenkin, J. G., Rev. Sci. Instrum., 1973, 44, 1197.

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²⁷ Karweik, D. H., and Winograd, N., Inorg. Chem., 1976, 15, 2336.

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³¹ Falk, H., Hofer, O., and Lehner, H., Monatsh. Chem., 1974, 105, 366.

³² Karweik, D., Winograd, N., Davis, D. G., and Kadish, K. M., J. Am. Chem. Soc., 1974, 96, 591.

The $E_b^F(N \ 1s)$ and $E_b^F(Cl \ 2p_{1/2,3/2})$ levels for all adducts of Cr(tpp)Cl were not observed due to the low population of those atoms in the metalloporphyrins. In general, steric hindrance by an axial ligand group is reflected in the decreased E_b^F levels for the central metal ion. Further, extensive delocalization of the porphinato π -electron system is reflected in the decreased $E_b^F(Cr \ 2p_{1/2,3/2})$ levels of Cr(tpp)Cl(HCONMe₂) (580.4 eV and 570.8 eV, respectively) compared to those levels in CrCl₃.6H₂O (581.6 eV and 572.3 eV, respectively), since the decrease in $E_b^F(Cr \ 2p)$ levels is too large for only lattice energy considerations.

Com- pound	$E_{b}^{F}(N \ 1s)$ (see footnotes)	$E_{b}^{F}(Cl 2p_{1/2,3/2})$ (this work)	$E_{b}^{F}(Cr 2p_{1/2})$ (this work)	$E_b^F(\operatorname{Cr} 2p_{3/2})$ (this work)
H ₂ tpp	400 · 3, 398 · 5 ^A 399 · 2, 397 · 2 ^B 398 · 2 ^C 397 · 2 ^D 391 · 0 ^C			
$H_4(tpp)Cl_2$	399.1 ^D			
H ₂ pc	398.9, ^C 397.9 ^D			
CrCl ₃ .6H ₂ O		190.6	581.6	572.3
Cr(tpp)Cl(py)			581.8	572.2
Cr(tpp)Cl(tpic)			581.1	571.5
Cr(tpp)Cl(fpic)			578.7	569.1
Cr(tpp)Cl(lut)			579.8	569.9
Cr(tpp)Cl(cvpv)			581.2	571.6
Cr(tpp)Cl(mor)			582.9	573.3
Cr(tpp)Cl(dmf)			580.4	570.8

Table 1. XPS binding energy (eV) data for selected porphyrins and Cr(tpp)ClL complexes pc = phthalocyanine, dmf = dimethylformamide

^A From ref. 9. ^B From ref. 10. ^C From ref. 11. ^D From ref. 12.

From a comparison of the XPS data for the pyridine and morpholine adducts with those for the dimethylformamide adduct, it is proposed that the increased binding energies for the pyridine, 2-picoline and 4-cyanopyridine adducts are consistent with an electron-donating effect from the dimethylformamide and electron-withdrawing effects of the pyridyl groups. Minor variations are likely to be due to variations in steric hindrance (strain) factors.

The decreased $E_b^F(Cr 2p)$ levels for Cr(tpp)Cl(fpic) and Cr(tpp)Cl(lut), relative to the $E_b^F(Cr2p)$ levels of Cr(tpp)Cl(HCONMe₂), are caused primarily by steric factors, such as axial ligand influence on the porphinato core, and to the lattice energy of the crystalline solids.

The morphyl adduct, Cr(tpp)Cl(mor), exhibits high $E_b^F(Cr 2p)$ levels at 582.9 eV (Cr $2p_{1/2}$) and 573.3 eV (Cr $2p_{3/2}$) as a result of the electron-withdrawing effect of the morpholine ligand.

Infrared Investigations

The infrared spectral data are recorded in Table 2. Metallation appears to reduce the number and intensity of the observed porphyrin vibrational bands, as a result of increased symmetry of the porphinato moiety. Summerville *et al.*⁸ have shown by e.p.r. studies on Cr(tpp)ClL complexes that axial ligation by chloride ion moves the chromium slightly out of the porphinato plane. The influence of the axial amine ligand is markedly reflected in the γ (Cr–Cl) stretching vibrations of the 4-substituted pyridine adducts, namely, in Cr(tpp)Cl(fpic) and Cr(tpp)Cl(cypy), where γ (Cr–Cl) is 339.5 cm⁻¹ and 266.5 cm⁻¹, respectively. All other adducts exhibit γ (Cr–Cl) at approximately 298 cm⁻¹. The electron-withdrawing nature of the cypy ligand augments the electron-withdrawing nature of the chromium, thus reducing the electron charge distribution in the Cr–Cl bond and reducing the frequency of the band. The reverse is the case in the 4-picoline adduct, Cr(tpp)Cl(fpic).

L ^A	$\nu_{C=N}^{\nu}C_{C=C}^{B}$	δ _{CH} ν ₉	δ _{CH} ν ₁₀	$\delta_{CH}_{\nu_{C=C},\nu_{12}}$	$\stackrel{\delta_{CH}}{A_{2u}}$	$\pi_{\rm CH}$	v _{Cr-N} D, E	$\nu_{\rm Cr-N}^{\rm A}$	$\delta_{Cr-N}{}^D$	${\nu_{\rm Cr-Cl}}_{{\rm F}}$	$\delta_{Cr-N}{}^A$
dmf	1 596s	1350s	11 6 0m	1075s	850w	803s	447.5s	408 · 5m	341 · 0m	2983	-
ру	1568w	1342m		1068m		799s	449 · 0s	404 · 0m	322m -	298s	
tpic	1568s	1342m	1148m	1068m	_	800s	445 · 5s	406 · 5m	340m	310m	332m
fpic	1570m	1340m	1150w	1070s	_	800s	449 · 5m	_		339.5m	372m
lut	1570s	1342s	1152m	1065s	850w	832w	449.0s	407.0w	338w	298.5m	318.5w
суру	1572w	1342m	_	1070m	_	800s	448.5s	407 · 7m	342 · 5m	266 · 5m	375.5m
mor	1590m	1342m	1155w	1068s	850w	800s		—	—		

 Table 2.
 Infrared spectral data for Cr(tpp)ClL complexes

^A Axial base-ligand. (Abbreviations are as in Experimental section; dmf = dimethylformamide.) ^B Pyrrole. ^C Phenyl. ^D Porphyrin. ^E In plane. ^F Out of plane.

The porphinatochromium in-plane stretching mode $\gamma(Cr-N)$ occurs, in all the adducts at 448.0 ± 1.0 cm⁻¹, which suggests no significant influence of the axial ligands on the chromium Cr-porphyrin bond strengths.

It is interesting to note that repeated exposure of the Cr(tpp)Cl(cypy) adduct to infrared radiation over a period of 30 min resulted in the loss of the γ (Cr-N) band of the Cr-cypy moiety with concomitant decrease in the Cr-porphinato mode δ (Cr-N) from 342.5 to 339.5 cm⁻¹. This indicates decomposition of the adduct by loss of the 4-cyanopyridine ligand and subsequent loss of its inductive effect on the Cr-porphinato moiety.

Electronic Spectra

The electronic spectral data for the adducts studied and also literature data reported for similar adducts are recorded in Table 3.

The data suggest variation in the electronic bands due to solvent effects and changing axial ligands. The spectra of all the adducts studied in the present work are consistent with those for hyperporphyrins.¹³ Prominent near-ultraviolet bands are, therefore, attributed to $a_{2u}(\pi), a_{1u}(\pi) \rightarrow e_g(d\pi)$ -allowed charge-transfer transitions; the visible bands Q(0,0), Q(1,0) and Soret B(0,0) bands to $a_{2u}(\pi), a_{1u}(\pi) \rightarrow e_g(\pi^*)$ transitions.

The near-infrared and visible (Q) bands in the adducts exhibit a variation in energy with changing axial ligands, which suggests significant influence from the inductive effects of the axial ligands on the overall electron density of the chromium, reflected in the $a_{2u}(\pi), a_{1u}(\pi) \rightarrow e_g(\pi^*)$ transition energy. Further, it is suggested that, as the electron-withdrawing inductive effect of the axial ligand decreases, the degree of $a_{2u}(\pi), a_{1u}(\pi) \rightarrow e_g(\pi^*)$ transition increases and vice versa, which is the consequence of an effective increase in electron density on the chromium and leads to decreased electron withdrawing by the chromium on the porphinato nitrogen atoms.

				Table	3. Ele	etronic	spectral	data for	Cr(tpp)	XL com	lexes						
Compound		Vear-i.	_		Vis	ible ban	sb		Soret B	bands		Ncar-1	J. V.		Solvent	$pK_{a}(L)$	Ref.
	Ì			II	III	IV			۷	ΝI	-		, 	-		, , , ,	
H ₂ tpp				645.8	589	549	514	482	414	400	371	351	301	284	CHC13		¥
Cr(tpp)Cl				648.5	592.5	548	515	481	418.5						C ₆ H ₆		20
Cr(tpp)Cl				1	600	560	520		448	394					С ₆ Н ₆		22
Cr(tpp)Cl					601	562	523		447.5						cň, či,		∞
Cr(tpp)Br(py)		LLL	I	640	608	573	528	ļ	461,	409			328		PhMe ⁻		×
									443	373							
Cr(tpp)Cl(py)		LLL	700	667	611	570	527		458,	404	364	343	327		PhMe		×
									410	372							
Cr(tpp)Cl(py)	788	746		627	598.5	560	522		436	395	360	319	308	289	CHCl ₃	5.17	۷
Cr(tpp)OH.2H,O				664.5	591	552.7	522.1	514.2	449.9	397.6					CHC1,		11
Cr(tpp)Cl(thtp) ^B		760	690	668	605	567	527		447,	394	362	337	320		PhMe		×
									408								
Cr(tpp)Cl(Me2CO)		764	692	658	605	566	524		447	394	357	337	1	1	PhMe		∞
Cr(tpp)Cl(thf) ^C	808	758	690	662	009	562	523		447	394	362	338	322	289	PhMe		∞
Cr(tpp)Cl(BuOH)	810	755	700	657	601	562	525	495	447	393	362	338	322	287	CHCl ₃		13
Cr(tpp)Cl(dmf)	810	762		627.5	599	560	517		436	394	357.5	334	319.5	288	CHCl ₃		V
Cr(tpp)Cl(tpic)	809.5	762		631	603	565	522		448.5	396	362	337	322.5	290	CHCl ₃	5.97	V
Cr(tpp)Cl(fpic)	830	778		633	609	570	523		449.5	398-5	371	337	324	290	CHCl ₃	6.02	V
Cr(tpp)Cl(lut)	811	764	ļ	633	603	564.5	521	I	449	396	363	337.5	322-5	290	CHCl ₃	6.75	V
Cr(tpp)Cl(cypy)	795	752		629	599	562	521	-	444.5	394	363	335.5	320	288	CHCl ₃		<
Cr(tpp)Cl(mor)	806	754		651	600	562.5	522	1	445	395	362	336	322	289	CHCl ₃	8.33	V

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A This work. B thtp \equiv tetrahydrothiophen. C thf \equiv tetrahydrofuran.



Fig. 1 represents the relationship between $E_b^F(\operatorname{Cr} 2p_{3/2})$ as determined by XPS measurements and the near-infrared electronic band I (Table 3). The results reflect an increase in $E_b^F(\operatorname{Cr} 2p_{3/2})$ with decrease in the band I electronic transition $a_{2u}(\pi), a_{1u}(\pi) \rightarrow e_g(\pi^*)$ and concomitantly a decrease in electron density on the chromium. Fig. 1 also reflects the degree of delocalized π -electron density over the central metal from the porphinato ligand. The deviation of Cr(tpp)Cl(mor), and to some extent Cr(tpp)Cl(lut) and Cr(tpp)Cl(tpic) from the line of best fit in Fig. 1, may, it is suggested, be due to the combination of steric and inductive effects.

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