Pseudohalogeno-Bonding of Thallium(III) Porphyrins, Stabilisation of Isocyano Bonding. Crystal Structure of Isocyano(5,10,15,20-tetraphenylporphyrinato)thallium(III)[†]

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Thallium(III) porphyrin complexes of the type [TI(por)X] [por = 5,10,15,20-tetraphenyl- (tpp) or 2,3,7,8,12,13,17,18-octaethyl-porphyrinate(2-) (oep); X = N₃, SCN or NC] have been prepared. The stereochemistry of the metal has been established by IR and ¹H NMR spectroscopy and isocyano bonding in [TI(tpp)(NC)] confirmed by X-ray diffraction methods using Mo-K_a radiation. Crystals are monoclinic, space group $P2_1/n$, with a = 10.061(8), b = 16.161(12), c = 21.173(15) Å, $\beta = 90.80(6)^\circ$ and Z = 4; R = 0.023 and R' = 0.028 for 4833 observed reflections. The thallium atom is five-co-ordinated by the four nitrogen atoms (N_p) of the porphyrin plane and one nitrogen atom, N(25), of the isocyano group: mean TI-N_p 2.222(10), TI-N(25) 2.260(3) Å, N(25)-TI-N_p 110.4(1) TI-N(25)-C(26) 175.3(4)°.

The relationship between metalloporphyrin stereochemistry and the biochemical functions of haemoproteins has been the subject of extensive investigations.¹⁻³ Studies of acyl isocyanide^{4,5} binding to metalloporphyrins were of particular interest in exploring the structure at the binding site in natural haemoproteins. Recently hydrocarbon oxidations with oxometalloporphyrinates have been reported extensively.⁶⁻¹⁰ In a similar approach, Groves and Takahashi¹¹ have demonstrated that a reactive nitridomanganese(v) porphyrin complex induces direct oxidative amination of hydrocarbons. Other nitridometalloporphyrins¹²⁻¹⁵ and nitrido-bridged metalloporphyrin dimers¹⁶⁻¹⁹ have been reported, the precursors often being the corresponding azido derivatives.

The main purpose of this paper is to report the synthesis and complete characterization of the isocyano-, thiocyanato- and azido-thallium(III) complexes [Tl(por)X] (X = NC, N₃ or SCN)[‡] and to describe the X-ray crystal structure of [Tl(tpp)(NC)].

Experimental

Preparation of Complexes.—Synthesis. The starting compounds [Tl(por)Cl] were prepared according to the method reported previously.²⁰ The azido- and thiocyanato-complexes were synthesised from [Tl(por)Cl] by two general procedures which are detailed below.

(i) Azido(porphyrinato)- or porphyrinato(thiocyanato)thallium(III). (a) To [Tl(por)Cl] (0.125 mmol) dissolved in dichloromethane (100 cm³) was added NaN₃ or NaSCN (14.5 mmol) in H₂O (10 cm³). The mixture was stirred for 12 h and then washed three times with water (20 cm³). The organic solution was dried, evaporated to dryness, and the residue recrystallised.

(b) To [Tl(por)Cl] (0.125 mmol) dissolved in dichloromethane (100 cm^3) were added NaN₃ or NaSCN (1.125 mmol), 18-crown-6 (1,4,7,10,13,16-hexaoxacyclohexadecane) (1.350 mmol) and H₂O (10 cm^3) . The mixture was stirred for 2 h and then washed and treated as above.

(ii) Isocyano(porphyrinato)thallium(III). The complex [Tl-(por)Cl] (0.125 mmol) was dissolved in CH_2Cl_2 (100 cm³) and NaCN (20.4 mmol) and H_2O (10 cm³) added. After reaction (12 h) the organic phase was washed with water, dried, and the solvent evaporated. The reaction residue was recrystallised.

Recrystallisation of all the complexes was accomplished by a slow diffussion of hexane into saturated toluene solutions by use of an H tube.

Physical Measurements.—Proton NMR spectra were recorded on a Varian FT-80 instrument. Samples (5 mg) were dissolved in CDCl₃ (0.6 cm³) with SiMe₄ as internal reference. Samples for IR measurements were prepared as 1% dispersions in CsI pellets or Nujol mulls and recorded on a Perkin-Elmer 298 spectrophotometer. Electronic absorption spectra were recorded on a Perkin-Elmer 330 spectrophotometer using 5×10^{-3} mol dm⁻³ toluene solutions or on an ORIEL diodearray visible spectrometer.

Crystal and Molecular Structure Determination.—A suitable crystal of [Tl(tpp)(NC)] was obtained by slow diffusion of hexane into a toluene solution of the compound in an H tube.

Crystal data. $C_{45}H_{28}N_5Tl$, M = 843.13, monoclinic, space group $P2_1/n$ (alt. $P2_1/c$, no. 14), a = 10.061(8), b = 16.161(12), c = 21.173(15) Å, $\beta = 90.80(6)^{\circ}$, U = 3442(4) Å³ (by leastsquares refinement, using the setting angles of 18 reflections in the range $15 < 2\theta < 20^{\circ}$, $\lambda = 0.71073$ Å), Z = 4, $D_c = 1.63$ g cm⁻³. Dark violet tablets. Crystal dimensions $0.48 \times 0.92 \times$ 1.04 mm, μ (Mo-K α) = 47.8 cm⁻¹.

Data collection and processing.²⁰ Nicolet P3F diffractometer, 24(1) °C, θ -2 θ technique (graphite-monochromated radiation). The scan rate was 4° min⁻¹ (in 2 θ) and data were collected to a maximum 2 θ of 45°. The scan range (°) was determined as a function of 2 θ to correct for the separation of the K α doublet;^{20a} 2 θ scan width = 2.00 + [2 θ (K α_2) - 2 θ (K α_1)]; 6078 reflections collected of which 6705 were unique and not systematically absent. The slope of the least-squares line through a plot of intensity versus time was -6(5) counts⁻¹, corresponding to a total loss of intensity of 0.2%. A linear decay correction was

[†] Supplementary data available: see Instructions for Authors, J. Chem. Soc., Dalton Trans., 1991, Issue 1, pp. xviii-xxii.

Abbreviations: por = unspecified porphyrinate(2-), oep = 2,3,7,8,12,13,17,18-octaethylporphyrinate(2-), tpp = 5,10,15,20-tetraphenylporphyrinate(2-).

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
TI	0.333 47(1)	0.315 78(1)	$0.152\ 33(1)$	C(52)	0.285 0(4)	0.616 3(3)	-0.0116(2)
N(21)	0.457 9(3)	0.310 6(2)	0.240 0(1)	C(53)	0.232 8(5)	0.679 9(3)	-0.0473(2)
N(22)	0.476 0(3)	0.2204(2)	0.120 0(1)	C(54)	0.103 7(6)	0.704 4(3)	-0.0387(2)
N(23)	0.351 4(3)	0.360 9(2)	0.054 5(1)	C(55)	0.030 1(5)	0.664 5(3)	0.005 2(3)
N(24)	0.324 8(3)	0.450 9(2)	0.1747(1)	C(56)	0.079 8(5)	$0.601\ 2(3)$	0.041 0(2)
N(25)	0.1317(3)	0.2610(2)	0.172 3(1)	C(61)	0.397 6(4)	0.494 0(2)	0.346 7(2)
C(1)	0.443 6(4)	0.364 2(2)	0.290 0(2)	C(62)	0.284 7(5)	0.515 4(3)	0.380 0(2)
C(2)	0.498 1(4)	0.325 0(3)	0.344 8(2)	C(63)	0.295 1(5)	0.560 5(3)	0.434 9(2)
C(3)	0.544 1(4)	0.249 9(3)	0.327 8(2)	C(64)	0.415 3(5)	0.586 4(3)	0.456 6(2)
C(4)	0.519 8(4)	0.241 2(2)	0.261 1(2)	C(65)	0.526 2(5)	0.566 6(3)	0.423 9(2)
C(5)	0.558 8(4)	0.172 7(2)	0.224 5(2)	C(66)	0.517 9(4)	0.521 3(3)	0.369 5(2)
C(6)	0.540 9(4)	0.164 8(2)	0.158 9(2)	H(2)	0.500(4)	0.352(3)	0.385(2)
C(7)	0.593 1(4)	0.100 0(3)	0.120 6(2)	H(3)	0.578(4)	0.215(2)	0.349(2)
C(8)	0.561 2(4)	0.116 2(3)	0.059 7(2)	H(7)	0.638(4)	0.059(2)	0.135(2)
C(9)	0.487 6(4)	0.192 6(2)	0.058 6(2)	H(8)	0.584(3)	0.086(2)	0.025(2)
C(10)	0.439 6(4)	0.233 5(2)	0.005 6(2)	H(12)	0.352(4)	0.335(2)	-0.093(2)
C(11)	0.378 3(4)	0.310 8(2)	0.003 4(2)	H(13)	0.259(4)	0.458(2)	-0.056(2)
C(12)	0.340 4(4)	0.354 9(3)	-0.052 9(2)	H(17)	0.223(4)	0.642(3)	0.147(2)
C(13)	0.291 3(4)	0.427 5(2)	-0.035 0(2)	H(18)	0.307(4)	0.601(2)	0.261(2)
C(14)	0.298 8(4)	0.433 5(2)	0.032 3(2)	H(32)	0.501(4)	0.030(2)	0.281(2)
C(15)	0.264 0(4)	0.502 5(2)	0.068 4(2)	H(33)	0.604(5)	-0.081(3)	0.317(2)
C(16)	0.281 7(4)	0.510 8(2)	0.133 7(2)	H(34)	0.812(5)	-0.053(3)	0.324(2)
C(17)	0.267 6(4)	0.585 9(2)	0.169 4(2)	H(35)	0.935(4)	0.058(2)	0.298(2)
C(18)	0.300 0(4)	0.569 6(2)	0.229 7(2)	H(36)	0.802(3)	0.151(2)	0.256(2)
C(19)	0.336 8(4)	0.484 1(2)	0.233 6(2)	H(42)	0.277(6)	0.137(4)	-0.073(3)
C(20)	0.389 7(4)	0.444 2(2)	0.287 7(2)	H(43)	0.300(4)	0.116(3)	-0.179(2)
C(26)	0.035 7(5)	0.239 7(3)	0.183 8(2)	H(44)	0.505(5)	0.118(3)	-0.231(2)
C(31)	0.635 9(4)	0.106 0(2)	0.257 7(2)	H(45)	0.693(5)	0.188(3)	-0.160(2)
C(32)	0.574 2(5)	0.035 9(3)	0.279 4(2)	H(46)	0.668(4)	0.227(3)	-0.058(2)
C(33)	0.644 1(6)	-0.027 4(3)	0.308 6(2)	H(52)	0.366(4)	0.599(2)	-0.014(2)
C(34)	0.779 6(6)	-0.0186(3)	0.3149(2)	H(53)	0.280(4)	0.705(2)	-0.075(2)
C(35)	0.842 5(5)	0.050 4(4)	$0.294\ 5(2)$	H(54)	0.068(5)	0.749(3)	-0.069(3)
C(36)	0.769 6(5)	0.112 2(3)	$0.266\ 2(2)$	H(55)	-0.023(3)	0.6/2(2)	0.014(1)
C(41)	0.464 8(4)	0.195 8(2)	-0.0578(2)	H(56)	0.046(3)	0.585(2)	0.070(2)
C(42)	0.362 4(5)	0.158 1(3)	-0.0918(2)	H(62)	0.210(4)	0.501(3)	0.303(2)
C(43)	0.384 0(5)	0.131 9(3)	-0.1532(2)	H(03)	0.214(4)	0.570(2)	0.439(2)
C(44)	0.505 4(6)	0.142 5(3)	-0.1809(2)	H(04)	0.419(4)	0.014(3)	0.493(2)
C(45)	0.606 2(6)	0.1787(3)	-0.146 9(2)	H(05)	0.390(3)	0.578(2)	0.432(2)
C(46)	0.587 4(5)	0.205 3(3)	-0.085 4(2)	H(00)	0.585(4)	0.510(2)	0.343(2)
C(51)	0.209 7(4)	0.5755(2)	0.0330(2)				

Table 1 Fractional atomic coordinates for [Tl(tpp)(NC)] with estimated standard deviations in parentheses

applied. The correction factors on F ranged from 1.000 to 1.001 with an average value of 1.001. Lorentz and polarization corrections were applied, the linear absorption coefficient was 47.8 cm⁻¹, and a numerical absorption correction was made.^{20b} Relative transmission coefficients ranged from 7.45 to 23.19 with an average value of 17.31. A secondary extinction correction was applied,^{20b} and the final coefficient refined in least-squares (1.2×10^{-8} absolute units). The agreement factors for the averaging of the 606 observed and accepted reflections were 2.2 (I) and 1.9°_{0} (F_{e}) respectively.

Structure analysis and refinement. Direct methods program SHELXS 86.20c A total of 32 atoms were located from an electron-density map, and the remaining atoms located in succeeding difference Fourier syntheses. Hydrogen atoms were located, and the structure was refined by full-matrix least squares where the function minimized was $\sum w(|F_o| - |F_c|)^2$ and w = $4F_o^2/\sigma(F_o^2)^2$. The standard deviation on intensities, σ -(F_o^2)², is defined by $[S^2(C + R^2B) + (pF_o^2)^2]/L_p^2$ (S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, B = total background count, L_p Lorentz-polarization factor, p = factor introduced to downweight intense reflection = 0.030). Scattering factors were taken from Cromer and Waber.^{20d} Anomalous dispersion effects were included in $F_{c}^{,20e}$ the values for $\Delta f'$ and $\Delta f''$ were those of Cromer,^{20f} only 4833 reflections having intensities $I > 3\sigma(I)$ were used. An alternative refinement with N(25) treated as carbon and C(26) as nitrogen gave unsatisfactory thermal parameters for these atoms. Final R and R' values were 0.023 and 0.028, with an estimated error based on $\sigma(F)^{20g}$ of 0.08. All calculations were performed on VAX 11/750 and VAXstation 3100 computers using SDP/VAX.^{20h} Fractional atomic coordinates of the non-hydrogen atoms are given in Table 1 and selected bond distances and angles in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Results and Discussion

Reaction of NaN₃ or NaSCN at room temperature with the thallium(III) porphyrin complexes [Tl(por)Cl] (por = oep or tpp) afforded compounds [Tl(por)(N₃)] or [Tl(por)(SCN)] respectively. The yields of the azido complexes were high (85-91%) and independent of the nature of porphyrin. The yields of the thiocyanato complexes were satisfactory (70-88%). The method of Abraham and co-workers^{21,22} was not used to prepare cyanothallium(III) porphyrin complexes but instead a direct substitution reaction of [Th(por)Cl] by CN- was employed. However the compounds actually obtained were not the cyano complexes but the isocyanothallium(III) porphyrin complexes (yield 75-84%) as established after examination of the spectroscopic data. The axial-substitution reactions of the chlorothallium(III) porphyrin complexes are summarised in Scheme 1. Purification of the complexes by chromatography (either with alumina or silica gel) was not performed owing to significant ligand exchange (with traces of water or chloro ions).

Table 2 Selected bond distances (Å) and angles (°) for [Tl(tpp)(NC)]

TI-N(21)	2.225(3)	TI-N(24)	2.236(3)
T1-N(22)	2.221(3)	T1-N(25)	2.260(3)
Tl-N(23)	2.206(3)		
N(21)-TI-N(22)	82.7(1)	N(22)-TI-N(24)	140.4(1)
N(21)-TI-N(23)	138.0(1)	N(22)-TI-N(25)	111.8(1)
N(21) - Tl - N(24)	83.3(1)	N(23)-TI-N(24)	83.1(1)
N(21) - TI - N(25)	109.0(1)	N(23)-TI-N(25)	113.0(1)
N(22)–Tl–N(23)	83.0(1)	N(24)-TI-N(25)	107.8(1)



Scheme 1 $R^1 = Et$, $R^2 = H$ (por = oep); $R^1 = H$, $R^2 = Ph$ (por = tpp); $X = N_3$ or SCN. (i) NaX, CH_2Cl_2 ; (ii) NaX, 18-crown-6, CH_2Cl_2 ; (iii) NaCN, CH_2Cl_2

In addition to absorptions normally observed in thallium(III) porphyrin complexes, the IR spectra of $[Tl(por)(N_3)]$ and [Tl(por)(SCN)] show characteristic absorptions of their respective pseudohalide ligands (Table 3). The azido derivatives exhibit four bands which are normally assigned to the asymmetric stretching (2048-2035), symmetric stretching (1370–960), and Tl–N₃ stretching (465–445 cm⁻¹). The last may be due to the mixing of the Tl-N₃ and Tl-por stretching modes. These data suggest that the TI-NNN bond is not linear.^{23,24} Similar behaviour has been observed for the analogous azidogallium(III) porphyrin complexes and confirmed by an Xray structural study of $[Ga(oep)(N_3)]^{25}$ Analysis of the IR spectra for the thiocyanoto complexes is more complicated but each complex exhibits generally four bands and a structural diagnosis between the bonding modes of the SCN group is possible.^{24,26} In general, Class A metals (first-row transition series, such as Cr, Mn, Fe, Co, Ni, Cu or Zn) form M-N bonds, whereas Class B metals (second half of the second- and thirdrow transition series, such as Rh, Pd, Ag, Cd, Ir, Pt, Au or Hg) form M-S bonds.²⁷ However, other factors, such as the oxidation state of the metal, the nature of other ligands present, and steric considerations can influence the mode of coordination. Several empirical criteria have been developed to determine the bonding mode of NCS in metal complexes.² ¹ The high CN-stretching frequency (2160-2150 cm⁻¹), and the low



Fig. 1 ORTEP view of [Tl(tpp)(NC)]

intensity of several bands near 420 cm⁻¹ are consistent with the presence of Tl-SCN thiocyanato bonding. In the far IR region some bands can be distinguished from v(Tl-N) (arising from the porphyrin) and are attributed to v(Tl-S) vibrations (280 cm⁻¹). These observations and the analogy with other thiocyanato thallium complexes²³ lead us to propose TI-SCN bonding. The elucidation of the bonding of the cyano group in [Tl(por)(NC)] is very difficult on the basis of IR spectroscopy. As is known, the -CN ion acts as both a σ donor and a π acceptor. σ -Donation tends to raise v(CN) since electrons are removed from the 5σ orbital, which is weakly antibonding, while π back-bonding tends to decrease v(CN) because the electrons enter into the antibonding $2p_{\pi}^*$ orbital. In general –CN is a better σ donor and a poorer π acceptor than CO. Thus v(CN) values in complexes are generally higher than that of free cyanide. Compared with the intensity of v(CN) of NaCN, the intensity of this band in [Tl(por)(NC)] is higher. The soft thallium(III) ion forms very strong complexes. For example, its chloride and bromide complexes are amongst the strongest metal-ion halide complexes known. The soft cyanide ion, as mentioned above, is a very important complexing ligand and forms strong complexes with most of the transition elements and with d¹⁰ ions. The Hg^{II} ion, which is isoelectronic and has similar properties to Tl^{III}, likewise forms very strong cyano complexes. The IR spectra of [Tl(por)(NC)] show a major band at 2160-2150 cm⁻¹, *i.e.* at higher wavenumber than for the free ligand (2100 cm⁻¹), indicating a higher bond order in the complex than for the free ligand.²⁸ These results are consistent with the presence of a positive formal charge on the carbon in the complex indicating isocyano (cyano-N) bonding. The increase in bond order is attributed to the better donor properties of isocyanides towards Tl^{III} and the concomitant decrease in the σ^* population of the CN bond. It is sometimes assumed that thallium does not form cyanide complexes²⁹ {with the possible exception of $[Tl(CN)_4]^-$, because $\hat{T}l^{III}$ is reduced to Tl^I. However, in the present system binding of cyanide is clearly shown. To establish with certainty whether cyano (Tl-C) or isocyano (Tl-N) bonding occurs an X-ray crystal structure determination of [Tl(tpp)(NC)] was undertaken (see below).

Proton NMR data for the complexes [Tl(por)X] (X = N₃, SCN or NC) are presented in Table 4. All azido, thiocyanato and isocyano derivatives exhibit spectra characteristic of diamagnetic complexes and the NMR data of the three series are very similar. As reported ^{31,32} in the literature, ¹H-^{203,205}Tl couplings are observed (see Table 4) but only between Tl^{III} and the *meso* or pyrrolic proton of the porphyrin macrocycle and the axial ligand proton. The magnitude of the coupling varies with the proton-thallium distance and the *meso* H-Tl and pyrrolic H-Tl couplings are smallest for [Tl(por)(NC)]. This property is in accord with the fact that the central metal atom of

280

290

470

280

TADIC J									
		-N=N=N							
	Compound	V _{asym}	V _{sym}	δ	v(Tl-N)	-C=N	-S-C=N	M-X	
	[Tl(tpp)Cl] [Tl(tpp)(NC)]					2160		278 330	
	$[Tl(tpp)(N_3)]$	2048	1370	635	465				

795

Table 3 IR data for the thallium(III) porphyrin complexes $[Tl(por)X](X = Cl, NC, N_3 \text{ or } SCN)$

2035

1250 960

1308

Table 4 Proton NMR data*

Compound	R¹	R ²	Protons of R ¹	Protons of R ²
[Tl(tpp)Cl] ^b	Ph	Н	o-H m, 8, 7.98; m, p-H, m, 12, 7.42	d, 8, 9.03 (63)
[Tl(tpp)(NC)]	Ph	н	o-H m, 8, 8.19; m, p-H, m, 12, 7.76	d, 8, 8.74 (59)
$[Tl(tpp)(N_3)]$	Ph	Н	o-H m, 8, 8.21; m, p-H, m, 12, 7.75	d, 8, 9.04 (63)
[Tl(tpp)(SCN)]	Ph	Н	o-H m, 8, 8.24; m, p-H, m, 12, 7.78	d, 8, 9.07 (60)
[Tl(oep)Cl] ^b	Н	Et	d, 4, 10.33 (39)	t, 24, 1.79; m, 16, 3.87
[Tl(oep)(NC)]	Н	Et	d, 4, 10.25 (32)	t, 24, 1.96; m, 16, 4.15
$[Tl(oep)(N_3)]$	Н	Et	d, 4, 10.27 (40)	t, 24, 1.95; m, 16, 4.16
[Tl(oep)(SCN)]	Н	Et	d, 4, 10.30 (34)	t, 24, 1.95; m, 16, 4.15

445

2120, 2043

2115, 2035, 1360

2150

^a Spectra recorded in CDCl₃. Data given as multiplicity, intensity, chemical shift. Coupling constants $J(^{1}H-^{203,205}Tl)$ are given in parentheses. ^b Ref. 30.

Table 5 UV-VIS data $\left[\lambda/nm \left(10^{-3} \varepsilon/dm^3 \text{ mol}^{-1} \text{ cm}^{-1}\right)\right]$

[Tl(tpp)(SCN)]

[Tl(oep)(NC)]

 $[Tl(oep)(N_3)]$

[Tl(oep)(SCN)]

[Tl(oep)Cl]

Compound	B(1,0)	B(0,0)	Q(2,0)	Q(1,0) (or α)	Q(0,0) (or β)
[Tl(oep)Cl]	(sh) (225.7)	418 (2.1)	498 (11.8)	545 (10.5)	582
$[Tl(oep)(N_{1})]$	(sh) (253.2)	421 (4.1)	504 (17.9)	547 (13.6)	582
TI(oep)(SCN)]	(sh) (310.2)	427 (1.4)	510 (25.8)	553 (20.7)	588
Tl(oep)(CN)	(sh) (255.7)	433 (0.9)	513 (17.8)	554 (13.2)	591
Tl(tpp)Cl]	(sh) (360.5)	434 (2.7)	520 (13.6)	566 (8.5)	608
[T](tpp)(N ₂)]	(sh) (321.1)	437 (2.3)	523 (15.8)	569 (10.5)	607
[Tl(tpp)(SCN)]	(sh) (399.8)	439 (2.9)	526 (22.3)	572 (11.1)	612
[Tl(tpp)(CN)]	(sh) (442.5)	436	(sh) (17.0)	568 (11.3)	608

[Tl(por)X] is a heavy metal and appears to be more important in influencing deshielding than the electron-donor or -acceptor properties of the axial ligand. Also, the interaction between the meso and pyrrolic protons with the thallium centre is stronger when the axial ligand has some electron-withdrawing ability (Cl, N₃, SCN, NC). The signals of the ethyl groups for the oep complexes show a multiplet for the methylene protons resulting from an ABX₃ coupling with the methyl protons. This behaviour is similar to that observed for oep complexes of gallium or indium^{32,33} and is in accord with five-co-ordination of the Tl^{III} ion which is displaced out of the porphyrin plane.

All the complexes [Tl(por)X] (X = N₃, SCN or NC) exhibit characteristic electronic spectra for 'normal' metallo-porphyrins'.^{34,35} They show an intense Soret band in the region 418-439 nm (see Table 5); three additional bands are red-shifted with respect to the Soret band, the Q(2,0), Q(1,0) and Q(0,0)bands. The spectra are similar to those displayed by all other known thallium(III) porphyrins.

To confirm isocyano bonding of [Tl(por)(NC)] the crystal structure of [Tl(tpp)(NC)] was solved. An ORTEP drawing of the molecule with the numbering scheme used is shown in Fig. 1. As expected the thallium atom is five-co-ordinated by the four nitrogen atoms (N_p) of the porphyrinato group and the nitrogen atom [N(25)] of the isocyano group; the co-ordination polyhedron is an almost perfect square pyramid [mean Tl-N_p 2.222, Tl-N(25) 2.260(3) Å, mean N(25)-Tl-N_p 110.4(1)°]. The

thallium atom lies 0.774 Å from the $4N_p$ plane and 0.905 Å from the porphyrinato core whereas the N(25) atom is 3.032(3) Å above the 4N_p plane. For comparison, the distance of the thallium atom from the $4N_p$ plane is 0.737 Å in [Tl(tpp)Cl],³⁶ 0.974 Å in [Tl(tpp)Me],³⁶ and 2.213(6) Å in [Tl(tpp)F].³⁰ The metal-isocyano angle is almost linear [Tl(1)-N(25)-C(26) $175.3(4)^{\circ}$] (a refinement for the alternative-form, Tl-CN, indicated that the initial refinement was correct and the N and C atoms are correctly assigned). The carbon-carbon and carbonnitrogen bond distances in the macrocycle are normal and there are no short intermolecular distances.

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References

1 A. Bondon, P. Petrinko, P. Sodano and G. Simonneaux, Biochim. Biophys. Acta, 1986, 872, 163.

- 2 A. Bondon, P. Sodano, G. Simonneaux and C. T. Craescu, *Biochim. Biophys. Acta*, 1987, 914, 289.
- 3 G. Simonneaux, A. Bondon and P. Sodano, *Inorg. Chem.*, 1987, 26, 3636.
- 4 M. Le Plouzennec, A. Bondon, G. Simonneaux, *Inorg. Chem.*, 1984, 23, 4398.
- 5 M. Le Plouzennec, A. Bondon, G. Simonneaux and P. Sodano, Inorg. Chem., 1986, 25, 1254.
- 6 J. T. Groves and W. J. Kruper, jun., J. Am. Chem. Soc., 1979, 101, 7613.
- 7 C. K. Chang and M.-S. Kuo, J. Am. Chem. Soc., 1979, 101, 3413.
- 8 C. L. Hill and B. C. Shardt, J. Am. Chem. Soc., 1980, 102, 6374.
- 9 J. T. Groves, W. J. Kruper, jun. and R. C. Haushalter, J. Am. Chem. Soc., 1980, 102, 6375.
- 10 J. T. Groves, R. C. Haushalter, M. Nakamura, T. E. Nemo and B. J. Evans, J. Am. Chem. Soc., 1981, 103, 2884.
- 11 J. T. Groves and T. Takahashi, J. Am. Chem. Soc., 1983, 105, 2073.
- 12 J. W. Buchler, C. Dreher and K. L. Lay, Z. Naturforsch., Teil B, 1982, 37, 1155.
- 13 A. Antipas, J. W. Buchler, M. Gouterman and P. D. Smith, J. Am. Chem. Soc., 1980, 102, 198.
- 14 C. L. Hill and F. J. Hollander, J. Am. Chem. Soc., 1982, 104, 7318.
- 15 J. W. Buchler, C. Dreher, K.-L. Lay, A. Raap and K. Gersonde, *Inorg. Chem.*, 1983, 22, 879.
- 16 W. R. Scheidt, D. A. Summerville and I. A. Cohen, J. Am. Chem. Soc., 1976, 98, 1747.
- 17 D. A. Summerville and D. F. Bocian, J. Am. Chem. Soc., 1983, 105, 1830.
- 18 G. A. Schick and D. F. Bocian, J. Am. Chem. Soc., 1983, 105, 1830.
- 19 D. F. Bocian, E. W. Findsen, J. A. Hoffmann, jun., G. A. Schick, D. R. English, D. N. Hendrickson and K. S. Suslick, *Inorg. Chem.*, 1984, 23, 800.
- 20 (a) Data collection Operation Manual, Nicolet XRD Corp., Madison, WI, 1981; (b) W. H. Zachariasen, Acta Crystallogr., 1963, 16, 1139; (c) G. M. Sheldrick, C. Kruger and R. Goddard, Oxford University Press, 1985, pp. 175–189; (d) D. T. Cromer and J. T. Waber, International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, 1974, vol. 4, Table 2.2B; (e) J. A. Ibers and W. C.

- Hamilton, Acta Crystallogr., 1964, 17, 781; (f) D. T. Cromer, International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, 1974, vol. 4, Table 2.3.1; (g) D. W. J. Cruickshank, Acta Crystallogr., 1949, 2, 154; (h) B. A. Frenz, The Enraf-Nonius CAD 4
 SDP – A Real-time System for Concurrent X-Ray Data Collection and Crystal Structure Determination, in Computing in Crystallography, eds., H. Schenk, R. Olthof-Hazelkamp, H. van Konigsveld and G. C. Bassi, Delft University Press, Delft, 1978, pp. 64–71.
- 21 R. J. Abraham, G. H. Barnett and K. M. Smith, J. Chem. Soc., Perkin Trans. 1, 1973, 2142.
- 22 R. J. Abraham, G. H. Barnett, E. S. Bretschneider and K. M. Smith, *Tetrahedron*, 1973, 29, 553.
- 23 E. Maslowsky, jun., Vibrational Spectra of Organometallic Compounds, Wiley, New York, 1977.
- 24 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination compounds, 3rd edn., Wiley, New York, 1978.
- 25 A. Coutsolelos, R. Guilard, A. Boukhris and C. Lecomte, J. Chem. Soc., Dalton Trans., 1986, 1779.
- 26 D. Forster and W. Dew. Horrocks, jun., Inorg. Chem., 1966, 5, 1510.
- 27 S. Ahrhand, J. Chatt and N. R. Davis, Quart. Rev., 1958, 12, 265.
- 28 L. Malateska and F. Bonati, in *Isocyanide Complexes of Metals*, Wiley Interscience, London, 1969, p. 25.
- 29 A. G. Lee, *The Chemistry of Thallium*, Elsevier, Amsterdam, 1971, p. 83.
- 30 A. G. Coutsolelos unpublished work.
- 31 T. R. Janson and J. J. Katz, in *The Porphyrins*, ed. D. Dolphin, Academic Press, New York, 1978, vol. IV, ch. 1 and refs therein.
- 32 A. Coutsolelos and R. Guilard, J. Organomet. Chem., 1983, 253, 273.
- 33 P. Cocolios, R. Guilard and P. Fournari, J. Organomet. Chem., 1979, 179, 311.
- 34 M. Gouterman, *The Porphyrins*, ed. D. Dolphin, Academic Press, New York, 1978, vol. III, p. 1.
- 35 J. W. Buchler, W. Konish and P. D. Smith, *Struct. Bonding (Berlin)*, 1978, 34, 79.
- 36 K. Hendrick, R. W. Matthews and P. A. Tasker, *Inorg. Chem.*, 1977, 16, 3293.

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3417