Extended X-Ray Absorption Fine Structure Studies on Chloro(phthalocyaninato)cobalt(III) and Chloro(pyridine)(phthalocyaninato)cobalt(III)

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The local coordination about the cobalt atom in chloro(phthalocyaninato)cobalt(III) (PcCoCl) and chloro(pyridine)(phthalocyaninato)cobalt(III) (PyrPcCoCl) has been determined by EXAFS spectroscopy. The cobalt atom in PcCoCl is coordinated to four nitrogen atoms at 1.91(1) Å and one chlorine at 2.24(1) Å. The Co–Cl bond length in PyrPcCoCl is 2.20(1) Å, and the composite Co–N bond length is 1.89(1) Å. The geometry obtained here allows the phthalocyanine ring current model to be tested. The calculated and observed ring current shifts of the ligand protons are now in accord.

The phthalocyaninato macrocycle bears two negative charges and is termed Pc(2 –), here shorted to Pc. Oxidation of transition-metal phthalocyanine complexes. Pc-M(II), gives complexes with the metal in a higher oxidation state, e.g. Co(III) as in this study, and counterions in order to balance the resulting excess positive charge(s). In addition, radical phthalocyaninato(1 –) complexes of some transition metals [Cr(III), Fe(III), Co(III), Zn(II)] have been synthesized and characterised.[1] Particularly relevant to the present study is the cobalt compound with molecular formula Pc(1 –)Co(III)Cl$_2$, which has been studied by X-ray crystallography.[2] The Pc(1 –)M(III)Cl$_2$ formulation with a cationic radical ligand is favoured rather than PcM(IV)Cl$_2$. The metal is positioned at the centre of symmetry, coordinated to the four nitrogen atoms in the phthalocyaninato ring and to two axial chloride anions, with the phthalocyaninato ligand remaining planar. The crystal structures of chloro(phthalocyaninato)cobalt(III) (PcCoCl) and chloro(pyridine)(phthalocyaninato)cobalt(III) (PyrPcCoCl) have not been published. The aim of the present study is to investigate the local environment around the cobalt atom in these compounds using extended X-ray absorption fine structure (EXAFS) spectroscopy.

The precise determination of the coordination geometry of the cobalt(III) phthalocyanine complex is also directly related to the attempts by Abraham et al. to obtain geometrical data from NMR measurements of porphyrins

and related macrocycles.[3-8] In this research the observed NMR ring current shifts of the protons in both the attached ligands and the macrocycle were reproduced by a double-dipole model of the macrocycle ring current.[3,5] The application of the model then allows the determination of porphyrin to ligand distances and ligand geometries for complexes with unknown crystal structures directly from the observed NMR shifts in solution.[4,6,8] The NMR parameters required for this model, i.e. the magnitudes of the ring current equivalent dipoles, can only be obtained from the observed NMR shifts of molecular complexes of known geometry. Several accurate structures for Co(III) porphyrin complexes were known,[3] but none for Co(III) phthalocyanine ligand complexes. Thus, in the extension of the double-dipole ring current model to phthalocyanines it was necessary to assume that the Co(III) to ligand bond length in Co(III) phthalocyanines was the same as the known bond length in the comparable Co(II) complexes.[5] We shall show that this assumption is not accurate and will derive an improved refinement of the previous ring current model based on the Co(III)/ligand geometry given here and by Hedtmann-Rein et al.[9]

Experimental

The reference compound tris(ethylenediamine)cobalt-(III)chloridehydrate [Co(en)$_3$Cl$_3$·3H$_2$O] was purchased from Aldrich Chemical Co. PcCoCl was prepared by the

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method of Barrett *et al.*[10] as given in Ref. 5. The Pyr-PcCoCl complex was prepared by adding equimolar amounts of pyridine to a chloroform solution of PcCoCl and evaporating the resulting solution. NMR experiments on the chloroform solution confirmed that only one pyridine ligand was added to the cobalt.

X-Ray absorption data were collected at the Daresbury Synchrotron Radiation Source (operating at an energy of 2.0 GeV and an average current of 200 mA) using station 7.1 equipped with an order-sorting Si(III) monochromator that was offset to 50% of the rocking curve for harmonic rejection. Focussing optics were not used. Room temperature cobalt K-edge data ($E = 7710$ eV, $\lambda = 1.608$ 11 Å) were registered over the energy range 7422–8307 eV in the fluorescence mode because the samples were dilute in cobalt. The fluorescence detector used was a NaI scintillation counter. A spectrum of the reference compound was also collected in the transmission mode, the sample being diluted with boron nitride in

order to attain $\log(I_0/I)$ in the range 1–2 just above the absorption edge. The fluorescence sample was also diluted with boron nitride so as to give a suitable fluorescence spectrum. Each sample was finely ground and held between strips of cellotape.

The EXCALIB and EXBACK programs[11] were used to correct for dark currents, to extract background subtracted EXAFS and to convert the data into k-space. The two scans recorded for PyrPcCoCl were summed. The EXAFS χ-curves are shown in Fig. 1. Model fitting was carried out with the EXCURV90 program[11] using curved-wave theory and *ab initio* phase shifts. The central atom (Co) and backscattering atom (N and C) phase shift were calculated within EXCURV90 using a $Z + 1$ 1s core hole correction; they were not iterated in the least-squares fitting process. Fourier transforms were corrected for the phase shifts of the relevant atoms. The low-energy cut-off for all samples was 30 eV. The data were weighted by k^3 in order to compensate for the diminishing amplitude at
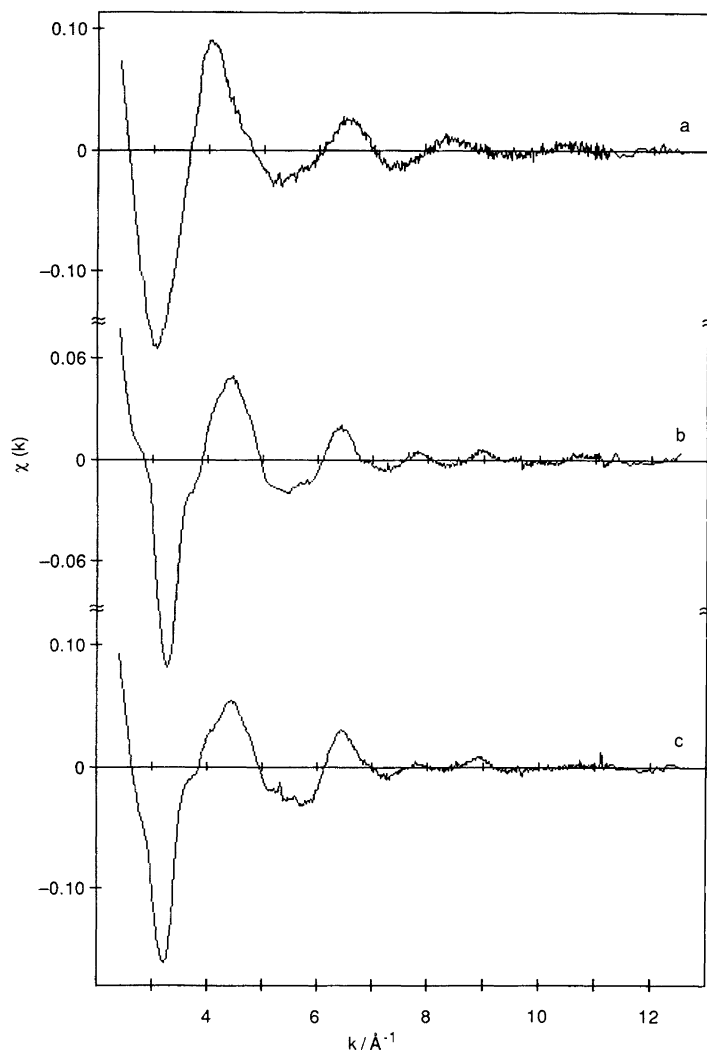

Fig. 1. Fluorescence EXAFS χ-curves of (a) the reference compound, tris(ethylenediamine)cobalt(III)chloride, diluted with BN, (b) PcCoCl and (c) PyrPcCoCl.

high k due to the decay of the photoelectron wave. The initial analysis was carried out on Fourier-filtered data $(1.0-5.0 \text{ Å})^{12}$ using a Gaussian window function, but the final fitting to the model parameters was performed on data Fourier-filtered over a much wider range (1.0–25.0 Å). The latter filter removes low-frequency contributions to the EXAFS below 1 Å, but does not remove noise, i.e. the spectrum is not smoothed. Only those shells significant at the 99% level[13] were included in the final models. Details of the final models are listed in Table 1, which gives interatomic distances (r_n), Debye–Waller-like factors $(2\sigma^2)$ and the multiplicities (N), i.e. the number of atoms in a given shell n. The fits are shown in Figs. 2 and 3.

The validity of the ab initio phase shifts were checked against the reference compound, tris(ethylenediamine)-cobalt(III) chloride,[14,15] and the EXAFS-analysis parameters, AFAC and VPI[16] were refined using data from that compound. These parameters model the proportion of

Table 1. Results of EXAFS curve-fitting for PcCoCl and Pyr-PcCoCl.

	Multiplicity	$r/\text{Å}$	$2\sigma^2/\text{Å}^2$	E_0/eV	$R(\%)$
PeCoCl					
Co–N	4	1.907(3)	0.0117(5)	12.0(3)	27
Co–Cl	1	2.239(3)	0.0036(5)		
Co···C	8	2.944(7)	0.022(2)		
Co···N	4	3.269(12)	0.020(3)		
Co···C	8	3.926(6)	0.008(1)		
Co···C[a]	6	3.694(10)	0.012(2)		
PyrPcCoCl					
Co–N[b]	5	1.891(3)	0.0080(4)	15.9(6)	28
Co–Cl	1	2.201(6)	0.008(1)		
Co···C	10	2.927(5)	0.012(1)		
Co···N	4	3.219(9)	0.010(3)		
Co···C	8	3.876(18)	0.002(5)		

[a] Consistent with intermolecular distance to light atoms.
[b] Composite of several overlapping distances.

Each distance $(r$, Co–X for bonding and Co···X for nonbonding) is associated with a multiplicity (or coordination number) and thermal vibration (Debye–Waller-like factor, $2\sigma^2$). E_0 is the refined correction to the threshold energy of the absorption edge. The multiplicities are assigned on structural chemical grounds and the spectra Fourier-filtered using a Gaussian window function, 1.0–25.0 Å.

The standard deviation in the least significant digit as calculated by EXCURV90 is given in parentheses. However, note that such estimates of precision overestimate the accuracy, particularly in cases of high correlation between parameters. The estimated standard deviations for distances are 0.01 Å at small r and 0.10 Å at large (ca. 4 Å) R, with $\pm 20\%$ accuracy for $2\sigma^2$.

Residual index R was calculated as

$$R = \frac{\sum_i \{k^3 (\chi_i^{obs} - \chi_i^{calc})\}^2}{\sum_i \{k^3 \chi_i^{obs}\}^2}$$
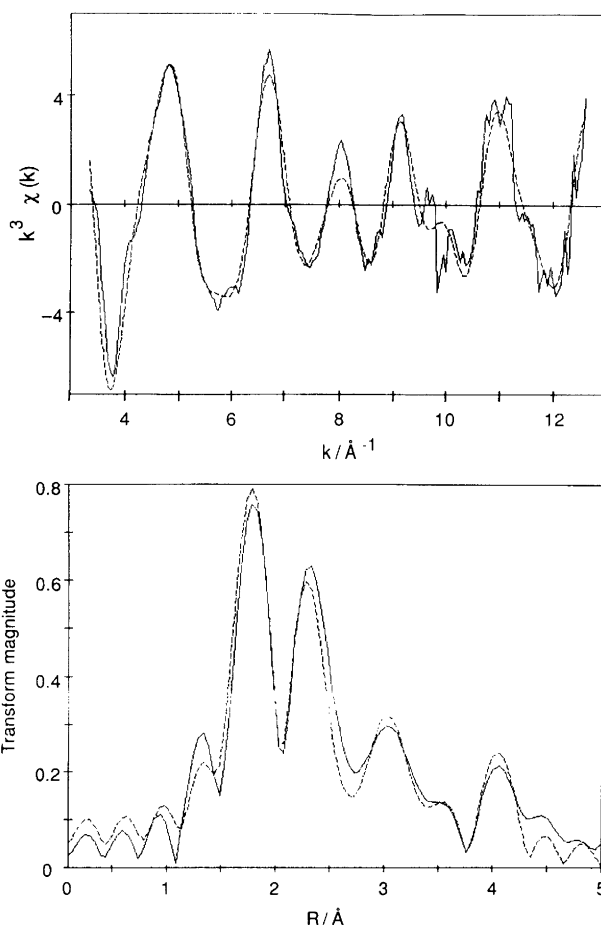

Fig. 2. Observed (——) and calculated (----) k^3-weighted χ-curves (Fourier-filtered 1.0–25.0 Å) and their Fourier transforms for PcCoCl; parameters in Table 1.

absorption that leads to EXAFS and the magnitude of inelastic effects represented by an imaginary potential so as to reproduce the known multiplicities about the metal atoms. AFAC and VPI were then transferred into the analyses for the compounds being investigated, thereby reducing any residual systematic error in the multiplicities. The estimated standard deviations (e.s.d.) for distances derived by EXAFS are 0.01 Å at small r and 0.10 Å at large r (ca. 4 Å), with $\pm 20\%$ accuracy for $2\sigma^2$.

Results and discussion

The results are listed in Table 1, and the fits are shown in Figs. 2 and 3. As a result of the relatively rigid macrocyclic system, contributions from more distant atoms in the phthalocyanine ring are seen in the Fourier transforms. The multiplicities and approximate distances for these atoms were calculated from reported crystal structures (Table 2). It should be noted that distances extracted from EXAFS are often shorter than those obtained from crystallography.[17] This is largely due to the inexact treatment in the theory, coupled with the lack of
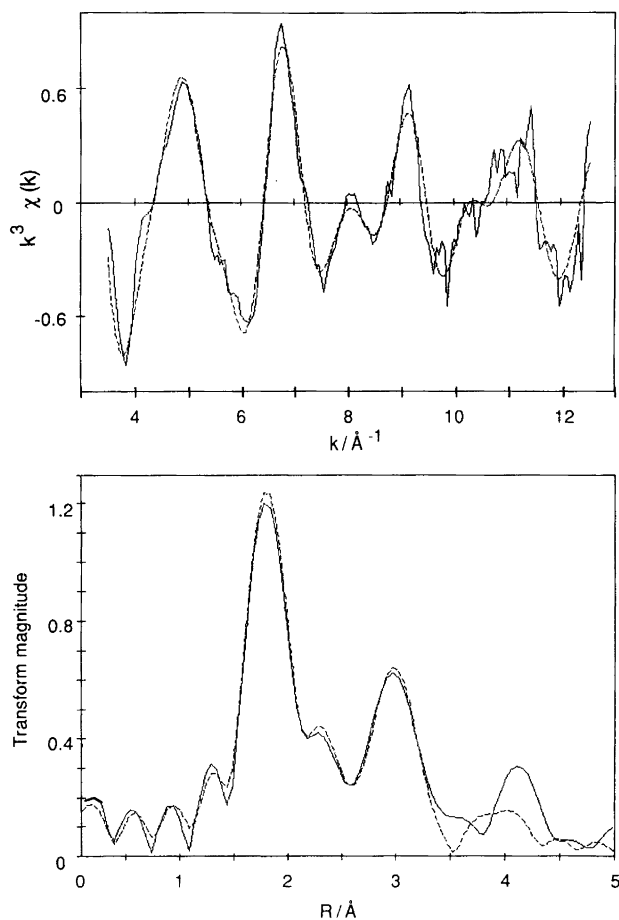
Fig. 3. Observed (——) and calculated (----) k^3-weighted χ-curves (Fourier filtered 1.0–25.0 Å) and their Fourier transforms for PyrPcCoCl; parameters in Table 1.

resolution of similar distances [i.e. the Co–(N$_4$) and Co–L distances are represented by a composite distance].

An important factor that often appears in EXAFS is the phenomenon of multiple scattering (MS). MS enhances contributions from distant atoms owing to the first shell atoms focussing the electron wave with a concomitant phase shift and a consequent displacement in distance and increased amplitude. This leads to shorter or longer distances and higher multiplicities and/or underestimates for the Debye–Waller factors. MS effects are known to be important for ligands containing ring complexes (such as the present compounds) and near-colinear atomic arrangements.[17] The Debye–Waller-like factors and the errors in the distances out from ca. 3.5 Å are to be regarded in this context (the multiplicities being fixed). That multiple scattering pathways do not significantly affect the results for the first three shells was tested by carrying out parallel calculations on data that were Fourier-filtered to include only these shells. This cut-off can be made without causing large truncation effects, and is one which is not complicated by overlapping Fourier transform shells. It also eliminates complications in data

analysis due to multiple scattering effects which could arise in more distant shells.

The structure of chloro(phthalocyaninato)cobalt(III). As expected for a rigid macrocyclic system, the Fourier transform contains features out to relatively long distances (ca. 4 Å) for the light atoms. In the region between 1.5 and 3.5 Å the transform contains three resolved peaks. The first peak is consistent with four short Co–N distances at 1.91 Å. The coordination is completed by a chlorine atom at 2.24 Å as shown by the second peak. In order to achieve a satisfactory fit (*R*-factor $< 30\%$) distances but out to 3.95 Å were included in the final model (Table 1 and Fig. 2). Table 2 compares the results of the present study with distances reported in the literature for related cobalt phthalocyanines.

The results show that PcCoCl (Fig. 4) has a similar local environment about the metal as the corresponding porphyrin complex chloro-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinato-cobalt(III) (TPPCoCl).[18] A square pyramidal coordination about the metal is also found for PcZnCl.[19] In TP-PCoCl, the cobalt atom is positioned 0.05 Å above the centre of the plane of porphine nitrogen atoms and towards the chlorine atoms. Since the size of the porphyrin prevents close intermolecular contacts between neighbouring porphyrin molecules, the closest carbon to carbon intermolecular contact is 3.64 Å. A similar intermolecular separation is found in PcCoCl, as reflected by the Co$\cdots$C distance at 3.69(5) Å.

A noteworthy feature of PcCoCl, as compared with TPPCoCl, is that the Co–N bonds in the former are significantly shorter [1.91(1) Å] whilst the Co–Cl distance is longer [2.24(1) Å]; the corresponding distances in TP-PCoCl[18] being 1.985(9) and 2.145(6) Å. Repulsion between the chlorine atom and the ring system is manifested by the observed chlorine to ring distance. There are two ways that this can affect the stereochemical relationship between the metal atom and the ring system. The first is that the chlorine atom can drag the metal atom some small distance from the centre of the (N)$_4$ grouping, thereby maintaining a shorter M–Cl distance. Alternatively, the metal to nitrogen bonds are relatively strong, and there is no significant distortion from the planar (N)$_4$ grouping. In this case, the movement away from the ring on the part of the chlorine atom is consistent with a longer metal to chlorine distance. The fact that the latter is observed here, fits in with the general trend that crystal structures of metal phthalocyanines and porphyrins show significantly shorter M–N distances in phthalocyanines.[20]

Provided that the metal atom and its four nitrogen neighbours are planar, the Co–N distances are constrained by the ring system to be 1.91–1.93 Å (Table 2), independent of size and oxidation state. This allows us to conclude that the present structure contains a planar Co(N)$_4$ grouping because the Co–N distances are 1.91(1) Å. This distance is the same within experimental error as the Co–N distances in PcCo(II)[21] [1.908(2) Å], Pyr$_2$PcCo(II)[22] [1.914(8) Å] and Pc(1 –)Co(III)Cl$_2$[2]

Table 2. The intramolecular distances (in Å) obtained for PcCoCl and PyrPcCoCl and selected distances (in Å) reported for PcCo(II), Pc(1-)Co(III)Cl$_2$ and PyrPcCo(III)(SCN).

	EXAFS results[a]		X-ray		
	PcCoCl	PyrPcCoCl	PcCo(II)[b]	Pc(1-)Co(III)Cl$_2$[c]	PyrPcCo(III)(SCN)[d]
4 CO–N(Pc)	1.91(1)	1.89(1)	1.908(2)	1.925(3)	1.928(4)
1 Co–N(Pyr)	–	–	–	–	2.016(4)
n Co–X[e]	2.24(1)	2.20(1)	–	2.261(1)	2.269(2)
2 Co···C	2.94(2)	2.93(2)	2.928(4)	2.950(3)	2.951[f]
2 Co···C	2.94(2)	2.93(2)	2.930(3)	2.956(3)	2.951[f]
2 Co···C	2.94(2)	2.93(2)	2.955(2)	2.956(3)	2.951[f]
2 Co···C	2.94(2)	2.93(2)	2.956(3)	3.140(4)	2.951[f]
2 Co···C	–	2.93(2)	–	–	2.953(4)
2 Co···N	3.23(3)	3.22(3)	3.335(3)	3.362(4)	3.355(3)
1 Co···N	3.23(3)	3.22(3)	3.370(4)	3.370(3)	3.361(2)
1 Co···N	3.23(3)	3.22(3)	3.370(4)	3.370(3)	3.372(4)
2 Co···C	3.93(5)	3.88(5)	4.170(4)	4.203(3)	4.187[g]
2 Co···C	3.93(5)	3.88(5)	4.181(5)	4.203(3)	4.187[g]
2 Co···C	3.93(5)	3.88(5)	4.181(5)	4.215(4)	4.187[g]

[a] This study, with e.s.d.s in parentheses. [b] Ref. 21. [c] Ref. 2. [d] Ref. 9. [e] X=Cl, SCN, and n is the required multiplicity. [f] Average of eight distances within the range 2.399–2.964 Å. [g] Average of eight distances within the range 4.176–4.195 Å. The non-bonding interatomic distances in the crystal structures were calculated from the atomic coordinates.

[1.925(3) Å]. In all of these compounds the Co(N)$_4$ atoms are also coplanar. For Pc(1 -)CoCl$_2$ the Co–Cl distance is 2.261 Å, which agrees well with our findings, 2.24(1) Å.

The structure of chloro(pyridine)(phthalocyaninato)-cobalt(III). The distances in the model for PyrPcCoCl (Fig. 4) are obtained from PcCoCl by adding the required distances for a pyridine ligand and subtracting the intermolecular Co···C contact at 3.69(5) Å (Table 1 and Fig. 3). Co(III) porphyrins can form either a complex with one amine ligand and one chloride counter ion in the axial coordination sites or a complex salt in which both axial sites are occupied by amine ligands. However, complex salts of cobalt(III) phthalocyanines were not formed by the addition of base to PcCoCl.[5]
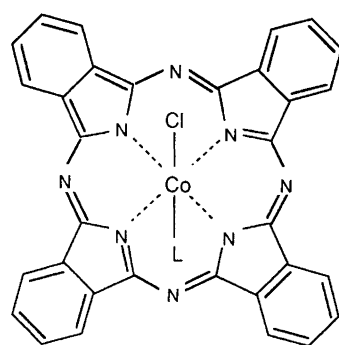
a) L not included.
b) L = pyridine (pyr)

Fig. 4. The structures of (a) chloro(phthalocyaninato)cobalt-(III) (PcCoCl) and (b) chloro(pyridine)(phthalocyaninato)-cobalt(III) (PyrPcCoCl).

Hedtmann-Rein *et al.*[9] have reported the crystal structure of the closely related compound (thiocyaninato)-(pyridine)(phthalocyaninato)cobalt(III) [PyrPcCo(III)-SCN]. The relevant bond distances are: Co–N(Pc) = 1.928(4) Å, Co–N(pyr) = 2.016(4) Å and Co–S = 2.269(2) Å. The cobalt atom lies slightly above the almost planar Pc ring system in the direction of the pyridine ligand. The axial Co(III)–N bond distances reported in the literature for Co(III)TPP$^+$ complexed with two amine molecules are 1.93(2) Å (imidazole)[23] to 2.030(3) Å (piperidine).[24] The Co–N(pyr) distance in PyrTPPCo(III)Cl is 1.978(8) Å and the Co–Cl distance is 2.251(3) Å.[25] Bearing in mind that distances extracted by EXAFS are often slightly shorter than the crystallographic distances when a peak is a composite of similar distances (see above), the Co–N(pyr) distance can be regarded as similar to the literature values of 2.016(4)[9] and 1.978(8) Å.[25] It is significantly shorter than the axial Co(II)–N amine ligands in, for instance, (piperidine)$_2$TPPCo(II) [2.436(2) Å],[26] (4-methylpyridine)$_2$PcCo(II) [2.322(5) Å][21] and (3-methylpyridine)$_2$(octaethylporphinato)Co(II) [2.386(2) Å].[27]

The proton NMR spectra of a number of Co(III) phthalocyanine complexes show unequivocally that the ring current shifts of the ligand protons are considerably reduced (ca. 30%) as compared with those of equivalent ligands in the Co(III) porphyrin complexes.[5] This could be due either to a decrease in the aromatic ring current of phthalocyanine relative to the porphyrin macrocycle, or to a lengthening of the cobalt to nitrogen bond of the complex in the phthalocyanine with respect to that in the porphyrin complex.

The only data available for the pyridine ligand were for the bis(methylpyridine)PcCo(II) complex in which the Co–N(pyr) bond length was found to be 2.322(5) Å. This bond length is considerably longer than the Co–N(ligand)

bonds in the Co(III) porphyrin complexes investigated in the same NMR study, the above values of 1.978(8) Å (Co–pyridine) and 2.060(3) Å (Co–piperidine) being typical. However, the 0.3 Å difference in the Co–N(ligand) bond length cannot account for the 30% decrease in the observed ring current shifts. Therefore, it was concluded that the observed decrease in the ring current shifts is due to a decrease in the phthalocyanine ring current and not to changes in the ligand geometries.[5] This conclusion is now supported by the present results, which show that the Co–N(pyr) bond length in PyrPcCoCl is much closer to those in the corresponding porphyrin and phthalocyanine complexes. The geometry of the PyrPcCoCl complex obtained here, together with the crystallographic distances, may now be used to both refine and test the ring current model for phthalocyanine, as follows.

The significantly shorter equatorial Co–N distance in the phthalocyanine ring compared to the porphyrin ring (1.91 vs. 1.99 Å) means that repulsive steric interactions between the ligand and the macrocycle are considerably enhanced in the phthalocyanine complexes. In PyrTPP-Co(III)Cl the staggered arrangement of the pyridine ligand is more stable than the eclipsed by ca. 1.6 kcal mol^{-1},[28] owing to the relief of these steric interactions, and this extra stability is enhanced in PyrPcCoCl. Thus, the appropriate model for the calculations is a fixed, staggered orientation of the pyridine and not the free rotation model used previously.

Using this model together with a Co–N(pyr) distance of 2.0 Å, the average of the values quoted above, provides a test of the ring current model. The equivalent dipole parameters given in Ref. 5, together with the present geometry, give calculated (vs. observed) ring current shifts of the pyridine ligand α, β and γ protons of -6.51 (-6.51); -2.03 (-1.98) and -1.57 (-1.57) ppm, respectively. The precise agreement shows that the double-dipole model, when extended to the phthalocyanine ring, is capable of giving a complete description of the ring current shifts of protons in the environment of the phthalocyanine ring. This refined model is thus, in principle, capable of providing useful geometric information directly from NMR data in cases where solid-state studies are not possible.

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