Physico-chemical Study of Copper(II) and Cobalt(II) Chelates of Tetra-2,3-pyridinoporphyrazine †

Thomas D. Smith,* John Livorness, and Helen Taylor
Chemistry Department, Monash University, Clayton, Victoria, 3168, Australia
John R. Pilbrow and Geoffrey R. Sinclair
Physics Department, Monash University, Clayton, Victoria, 3168, Australia

The electronic and e.s.r. spectral data of the copper(II) and cobalt(II) chelates of tetra-2,3-pyridinoporphyrazine show that the electronic environment provided by the ligand is similar to that of the phthalocyanines. Potentiometric pH, spectrophotometric, and e.s.r. spectral measurements show that the water soluble *NN'N''N'''*-tetramethyl quaternized tetracationic forms of the copper(II) and cobalt(II) tetra-2,3-pyridinoporphyrazinates are free of solute–solute interactions, stable in a wide range of acidic solutions, but give rise to some decomposition in slightly alkaline solution. The cobalt(II) chelate forms five- and six-co-ordinate complexes with certain heterocyclic nitrogen ligands. The e.s.r. spectrum due to the imidazole complex of cobalt(II) *NN'N''N'''*-tetramethyltetra-2,3-pyridinoporphyrazinate indicates an unusual ground state of cobalt(II) in these circumstances. Spectrophotometric and e.s.r. spectral data indicate that the cobalt(II) chelate in aqueous solution undergoes a one-electron reduction of the metal centre as a result of reaction with ascorbic acid. The d.c. polarographic behaviour of the cobalt(II), nickel(II), and copper(II) chelates consists of waves with $E_{\frac{1}{2}}$ in the region of −0.55 and −1.20 V *versus* the saturated calomel electrode. The waves are polarographically irreversible but it has been shown that the first wave is due to a one-electron reduction of the chelates at the dropping mercury electrode.

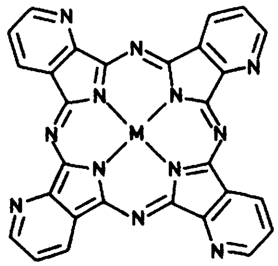
Isologues of the well known class of macrocyclic compounds termed phthalocyanines [1-3] were originally synthesized by Linstead *et al.*,[4] who were interested in synthesizing phthalocyanine derivatives where the outer benzene rings of phthalocyanine were replaced with other heterocyclic rings including thiophene, thionaphthalene, pyridine, and pyrazine. When the outer heterocycle is pyridine the term tetrapyridinoporphyrazine was proposed by Linstead [4] whilst the systematic name tetrabenzoporphyrazine was adopted for phthalocyanine.

Unlike the phthalocyanines, the chemical and physical properties of the tetrapyridinoporphyrazines have received little attention. However, their use as fuel-cell catalysts,[5] and their catalytic role in thiol [6] and cumene [7] autoxidation has been described.

The metal complexes of tetrapyridinoporphyrazines are synthesized by a template procedure analogous to that of phthalocyanine.[1,3,8,9] The most common methods use α-dicyanopyridine or α-dicarboxypyridine. Danzig *et al.*[10] obtained α-dicyanopyridine by dehydration of the diamide using phosgene. Scott [11] prepared the dinitrile by a similar procedure using phosphorus oxychloride at low temperatures. Pure copper complexes of tetra-2,3- and tetra-3,4-pyridinoporphyrazine were obtained by heating the dinitrile with copper powder or copper chloride. Alternatively, several syntheses of metallo-tetrapyridinoporphyrazines using 2,3- or 3,4-pyridinedicarboxylic acid have been reported.[12-18]

The highly organo-soluble tetra-3,4-(6-t-butylpyridino)-porphyrazine chelates of vanadium and cobalt have been prepared.[19] Scott [11] prepared water-soluble cationic tetra-2,3-pyridinoporphyrazines by quaternization of the pyridine nitrogen with dimethyl sulphate at 120 °C in dimethylformamide. If 2,3-pyridinedicarboxylic acid is used as the precursor to the preparation of the tetra-2,3-pyridinoporphyrazine chelate, evidence has been presented for the formation of one isomer of the product, as shown by structure (1).

The resonance-Raman spectrum of dilute aqueous solutions of a quaternized copper(II) complex of tetra-2,3-pyridinoporphyrazine arises from the tetrapositive cation which is essentially of symmetry C_{4h}.[20]



(1)

Critical electrolyte concentration studies by Scott [11] of Alcian blue [21,22] and quaternized copper(II) complexes of tetra-2,3-pyridinoporphyrazines have contrasted the relative affinities of the cationic dyes for cellular polyanions and hence their properties as histochemical dyes.[21-25]

The aim of the present investigation is to outline some features of the axial interactions of the tetra-2,3-pyridinoporphyrazine chelates and the reduction properties of the water soluble tetraquaternized form.

Results

*Tetra-*2,3-*pyridinoporphyrazinatocopper*(II).—The solubility of tetra-2,3-pyridinoporphyrazinatocopper(II), [Cu(tppa)], in organic solvents is exceedingly low. However, solutions of the chelates can be obtained in 60% v/v of concentrated sulphuric acid in water. Elemental analysis of the product obtained upon precipitation by addition of water showed that four molecules of acid are associated with one molecule of the copper(II) porphyrazine. The result suggests that quaternization of the pyridino-nitrogens occurs in strong acid media thereby rendering the porphyrazine soluble. The e.s.r. spectra due to a frozen solution (60% H_2SO_4–H_2O v/v) is typical of a monomeric copper(II) species.

The e.s.r. spectrum was computer simulated using an axial model including both quadrupole and ligand hyperfine interaction terms. The latter arise from the four in-plane ($d_{x^2-y^2}$)

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† Tetra-2',3'-pyrido[*b,g,l,q*]-5,10,15,20-tetra-azaporphyrin.

Table 1. Magnetic parameters of copper(II) chelates of tetra-2,3-pyridinoporphyrazine[a]

Copper chelate	$g_\parallel$	$g_\perp$	$10^4A_\parallel$/cm^{-1}	$10^4A_\perp$/cm^{-1}	$10^4A_\parallel^N$/cm^{-1}	$10^4A_\perp^N$/cm^{-1}	Ref.
[Cu(tppa)] in 60% H_2SO_4–H_2O	2.190	2.074	213	5	15	15	This work
[Cu(tmtppa)]$^{4+}$ in 5% dmf–H_2O	2.189	2.074	209	<20	15	15	This work
[Cu(tspc)]$^{4-}$ in 75% dmf–H_2O	2.189	2.056	210	1	15	15	28
[Cu(tspp)]$^{4-}$ in 100% dmf	2.204	2.069	208	<20	14	16	*b*

[a] Fitting errors: g values (±0.005); $A_\parallel$ ($\pm5 \times 10^{-4}$ cm^{-1}), $A_{\parallel,\perp}^N$ ($\pm2 \times 10^{-4}$ cm^{-1}). Errors in $A_\perp$ may be quite large because of inadequacy of perturbation theory simulations when $A_\perp$ *ca.* 0. [b] J. De Bolfo, T. D. Smith, J. F. Boas, and J. R. Pilbrow, *J. Chem. Soc., Dalton Trans.*, 1975, 1523.

nitrogen atoms, which were assumed to be identical, although allowance was made for the angular variation of the ligand splittings of the lines. This spectrum can be described by the following Hamiltonian with $S = \frac{1}{2}$ and $I = \frac{3}{2}$, where $g_\parallel$, $g_\perp$,

$$\mathscr{H} = g_\parallel\beta B_zS_z + g_\perp\beta[B_xS_x + B_yS_y] + A_\parallel S_zI_z + A_\perp[S_xI_x + S_yI_y] + \sum_{i=1}^{4}[A_\parallel^N S_{z_i}I_{z_i}^N + A_\perp^N(S_{x_i}I_{x_i}^N + S_{y_i}I_{y_i}^N)] \quad (1)$$

$A_\parallel$, and $A_\perp$ refer to copper(II) [or later to cobalt(II)] and $A_\parallel^N$ and $A_\perp^N$ refer to in-plane nitrogen ligands with $I^N = 1$. The z_i direction points along the ith metal–nitrogen bond. The spin-Hamiltonian parameters used to fit the experimental spectrum are shown in Table 1.

An aqueous solution of the tetracationic derivative *NN′N″N‴*-tetramethyltetra-2,3-pyridinoporphyrazinatocopper(II) [Cu(tmtppa)]$^{4+}$, as its methyl sulphate salt, prepared by quaternization of the pyridine nitrogen atoms with dimethyl sulphate gave rise to a well resolved e.s.r. spectrum from which the magnetic parameters, listed in Table 1, were found to be essentially identical to those for [Cu(tppa)] in 60% H_2SO_4–H_2O. The *S*-band spectrum obtained at *ca.* 2.9 GHz, shown by Figure 1 for [Cu(tmtppa)]$^{4+}$, exhibits improved resolution of the low-field ' parallel ' part of the spectrum, similar to the results reported by Froncisz and Hyde.[26] The solvent conditions of 5% dimethylformamide–H_2O were chosen to decrease the dipolar broadening effect which arises from the interaction between localized concentrations of solute molecules at the interstices of crystallites of frozen aqueous solutions.[27] The absence of any solute–solute interactions in these aqueous solutions contrasts with the behaviour of the tetra-anionic 3,10,17,24-tetrasulphonated phthalocyanine (tspc) chelates where such interactions do occur and where disaggregation of the chelates is achieved by the addition of various amounts of polar organic solvents to their aqueous solutions.[28,29] As seen from Table 1, the parameters for the tetracationic porphyrazines are in the same range as those previously obtained for the monomeric species of [Cu^{II}(tspc)]$^{4-}$ and 5,10,15,20-tetra(*p*-sulphophenyl)porphyrinatocuprate(II), [Cu^{II}(tspp)]$^{4-}$.

In pH conditions of neutral or below an aqueous solution of [Cu(tmtppa)]$^{4+}$ is characterized by a distinct deep blue phthalocyanine-like colour, with a major absorption peak which is split at 638 and 623 nm.[21] With increasing pH the intensity of the major absorption peak decreases and coalesces whilst the solution becomes distinctly violet in colour. The absorption changes were followed by a spectrophotometric titration at 630 nm. In the pH range up to 7.5 the spectral intensity is essentially constant whilst at pH 7.95 there is a sharp drop as the solution becomes decidedly violet in colour.

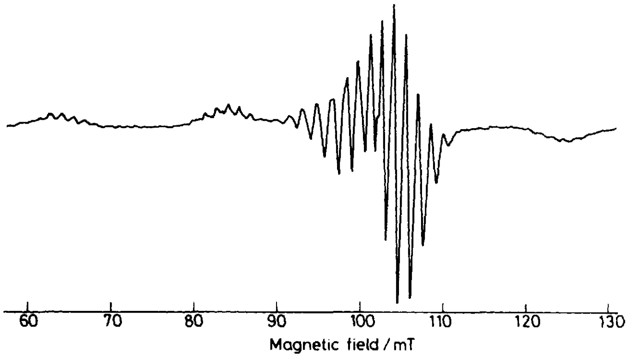

Figure 1. E.s.r. spectrum at 2.885 GHz of [Cu(tmtppa)]$^{4+}$ (0.1 g, 25 cm^3) in 40% dmf-H_2O frozen solution at 77 K. Simulated spectra not given as programs based on perturbation theory unreliable at low frequencies [*cf.* Figure 1(*g*) of ref. 29 for compound with almost identical spectral characteristics]

The colour change is partially reversible at this point but beyond pH 9.5 the porphyrazine changes to a dark brown decomposition product which is no longer water soluble.

The e.s.r. spectrum of the violet coloured aqueous solution at pH 8.5 containing 5% v/v dimethylformamide (dmf) was found to differ greatly from that of a similar solution at pH 6.0. The spectrum shows no sign of in-plane nitrogen super- and hyperfine interaction with the copper nucleus and is reduced markedly in intensity, compared with those in acid solution.

Tetra-2,3-*pyridinoporphyrazinatocobalt*(II).—As in the case of the copper(II) chelate, [Co(tppa)] is sparingly soluble in organic solvents. On the other hand, the tetramethylated cationic form of the chelate is water soluble. The e.s.r. spectra of a frozen aqueous solution of [Co(tmtppa)]$^{4+}$ as its methyl sulphate salt and containing 5% v/v of dmf is shown by Figure 2.

The magnetic parameters, listed in Table 2, were obtained by computer simulation using an orthorhombic model by methods previously outlined.[29,30] The e.s.r. spectrum of monomeric [Co(tmtppa)]$^{4+}$ may be described by the spin Hamiltonian (2). It may be supplemented when necessary by the ligand hyperfine term due to ' *n* ' ligands [equation (3)].

$$\mathscr{H} = \beta(g_xS_xB_x + g_yS_yB_y + g_zS_zB_z) + A_xS_xI_x + A_yS_yI_y + A_zS_zI_z \quad (2)$$

$$\mathscr{H}_L = \sum_{i=1}^{n}[A_x^N S_{x_i}I_{x_i}^N + A_y^N S_{y_i}I_{y_i}^N + A_z^N S_{z_i}I_{z_i}^N] \quad (3)$$

Table 2. Magnetic parameters of cobalt(II) chelates of tetra-2,3-pyridinoporphyrazine

Cobalt chelate	$g_{\parallel}$	$g_{\perp}$	$10^4A_{\parallel}/cm^{-1}$	$10^4A_{\perp}/cm^{-1}$	Ref.
$[Co(tmtppa)]^{4+}$ in 5% dmf–H_2O	2.0116	g_x = 2.2313 g_y = 2.1720	85	A_x = 23 A_y = 10	This work
[Co(tppa)] in 60% H_2SO_4–H_2O	2.0110	g_x = 2.2315 g_y = 2.170	85	A_x = 23 A_y = 11	This work
$[Co(tspc)]^{4-}$ in 5% dmf–H_2O	2.014	2.270	98	*ca.* 0	28

Fitting errors: see Table 1.

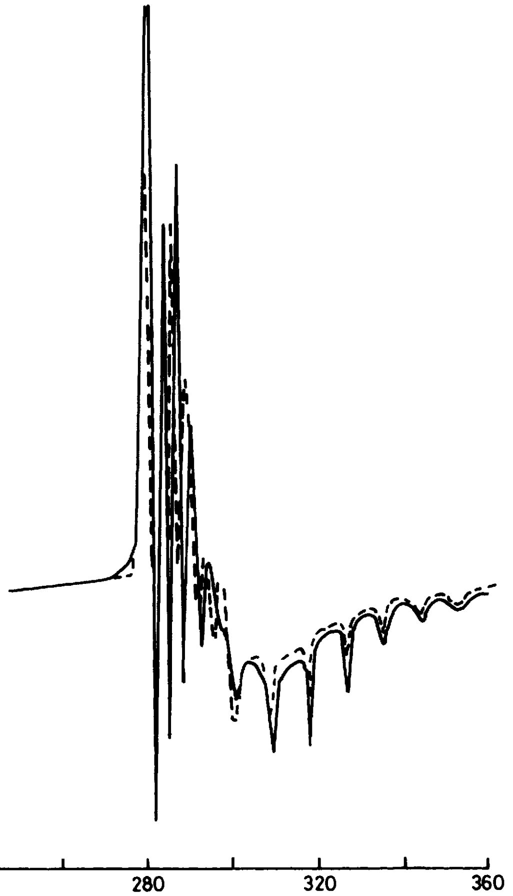

Figure 2. E.s.r. spectrum due to frozen (−140 °C) 5% dmf–H_2O (v/v) solution of $[Co(tmtppa)]^{4+}$ (1.0×10^{-3} mol dm^{-3}). Dashed line represents computer simulation of the spectrum using the magnetic parameters outlined in Table 2. Microwave frequency 9.147 GHz

In these equations all the terms have their usual meaning. For low-spin cobalt(II), $S = \frac{1}{2}$ and $I = \frac{7}{2}$ while for nitrogen, $I^N = 1$. In contrast to equation (1) lower symmetry is allowed for in the nitrogen ligand hyperfine splitting (h.f.s.). The x_i, y_i, and z_i axes are individually defined for each nitrogen nucleus.

A similar spectrum was obtained from a frozen solution of [Co(tppa)] dissolved in 60% v/v H_2SO_4. The magnetic parameters obtained are listed in Table 2 together with those previously obtained for monomeric $[Co(tspc)]^{4-}$.[29] A distinguishing feature of the cobalt porphyrazinate is the enhanced resolution obtained in the g_z component compared with the $[Co(tspc)]^{4-}$ e.s.r. spectrum.[29]

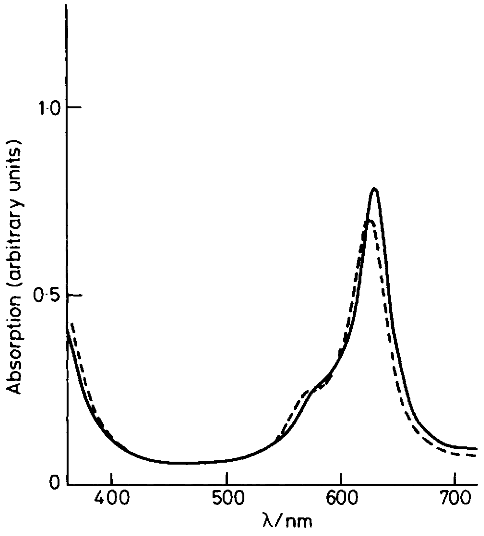

Figure 3. Absorption spectra in the visible region of a solution of [Co(tppa)] (2.0×10^{-5} mol dm^{-3}) in 3-methylpyridine (——) and pyridine (– – –). 1-cm Glass cells

In aqueous solution, $[Co(tmtppa)]^{4+}$ has a strong absorption in the visible region at 616 nm and a broad shoulder at 575 nm. The acid–base behaviour of the spectra was found to be similar to that previously described for the copper(II) chelate. The change in the colour of the chelate from blue to violet which occurs as a result of additions of sodium hydroxide to its aqueous solution occurs at pH 8.65.

Axial Interactions.—The biological functions of the metallic centre in naturally occurring substances such as metalloporphyrins are often determined by the nature of, or exchange of, labile extraplanar ligands or by the variable oxidation states of the metal. Of particular interest in recent years has been the reactivity of metal chelates towards molecular oxygen in a manner which models natural oxygen carriers.

A number of studies on macrocyclic cobalt(II) chelates have shown that the electronic structures of the cobalt(II) ion are sensitive to axial crystal-field distortions.[30–42]

In the present investigation, the effect of extraplanar ligands, particularly heterocyclic bases, on the electronic state of [Co(tppa)] in non-aqueous and $[Co(tmtppa)]^{4+}$ in aqueous media has been studied. It is apparent from the e.s.r. measurements that both five- and six-co-ordinate base adducts can be readily formed.

[Co(tppa)]. Although [Co(tppa)] is relatively insoluble in most organic solvents, it was found that solutions of suitable concentration for e.s.r. measurement (*ca.* 10^{-4} mol dm^{-3}) could be obtained by gently warming, under nitrogen, [Co(tppa)] in pyridine and its derivatives. It was found that substitution at the α-carbon (2-position) of the heterocycle

Table 3. Magnetic parameters of cobalt(II) tppa pyridine base adducts

Base	g_x	g_y	g_z	$10^4A_x^{Co}/cm^{-1}$	$10^4A_y^{Co}/cm^{-1}$	$10^4A_z^{Co}/cm^{-1}$	$10^4A_x^{N}/cm^{-1}$	$10^4A_y^{N}/cm^{-1}$	$10^4A_z^{N}/cm^{-1}$
Pyridine	2.2810	2.2750	2.0075	13	14	89	1	2	15
4-Methylpyridine	2.2710	2.2691	2.0080	16	1	92	2	2	14
3-Methylpyridine	2.2800	2.2750	2.0075	12	12	95	2	2	14
Isoquinoline	2.2800	2.2800	2.0120	19	19	95	1	1	15

Fitting errors: see Table 1.

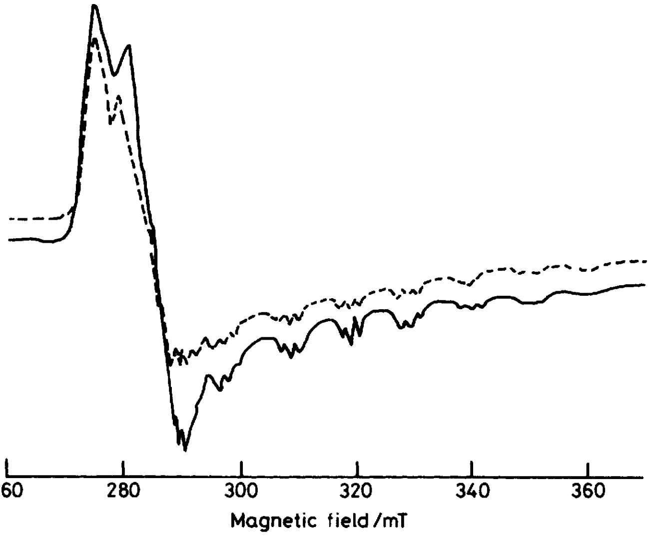

Figure 4. E.s.r. spectrum due to frozen (−140 °C) solution of [Co(tppa)] (1.0 × 10^{-4} mol dm^{-3}) in isoquinoline. Dashed line represents computer simulation of the spectrum using the magnetic parameters outlined in Table 3. Microwave frequency 9.147 GHz

greatly reduced the solubility of [Co(tppa)]. A similar result was found to occur for the cobalt(II) complex of phthalocyanine.[32]

The visible absorption spectra of [Co(tppa)] in pyridine and a methyl substituted pyridine are shown in Figure 3. The presence of these co-ordinating solvents results in a shift to a higher wavelength, 624 nm, compared with that found in solvents such as dimethyl sulphate in which [Co(tppa)] shows a strong absorption at 620 nm.[18]

The e.s.r. spectrum of frozen solutions of [Co(tppa)] in isoquinoline is shown by Figure 4. The spectrum was obtained by dissolving the chelate in warm base under nitrogen and immediately freezing in liquid nitrogen. The spectrum was computer simulated (dashed spectrum) using the magnetic parameters listed in Table 3. The spectrum is described by the spin Hamiltonian [equation (2)] previously described with the appropriate nitrogen spin contribution [equation (3)]. The magnetic parameters obtained from the e.s.r. spectra of [Co(tppa)] in the presence of other nitrogen bases is included in Table 3. In each case the nitrogen superhyperfine interaction with the cobalt(II) centre indicates the formation of a five-co-ordinate complex.

$[Co(tmtppa)]^{4+}$. The co-ordinating properties of heterocyclic bases to the quaternized form of [Co(tppa)] in aqueous solution were found to be similar to those of the parent porphyrazine. When the ratio of $[Co(tmtppa)]^{4+}$ to heterocyclic bases is *ca.* 1 : 20, the e.s.r. spectra, a typical example of which is shown by Figure 5, show the presence of what has been recognized from the overall shape and nitrogen superhyperfine interaction as a five-co-ordinate (Type I) form of the chelate. In comparing the computer simulation with the experimental spectrum in Figure 5 it must be recognized that different combinations of g_x, g_y, A_x, and A_y are able to produce results better in some parts and worse in others than that shown here. This proved a particularly difficult result to simulate and the details must be seen as tentative. In broad outline, however, the results are correct and the hyperfine structure is not nearly as anisotropic as for many of the other examples in this paper. Upon further addition of the base, the e.s.r. spectra, a typical example being shown by Figure 6,

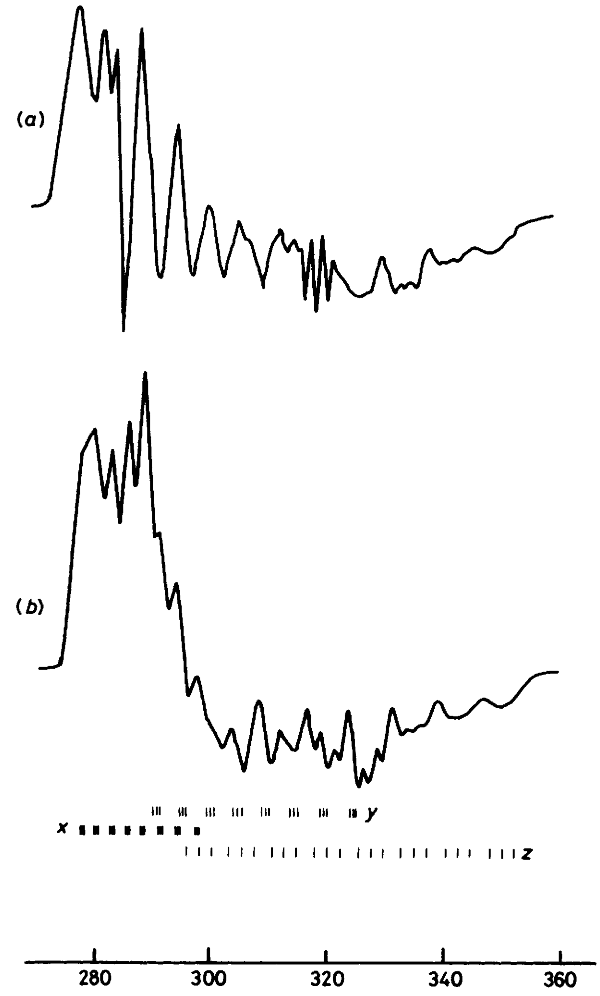

Figure 5. (*a*) E.s.r. spectrum due to frozen (−140 °C) 5% dmf–H_2O (v/v) solution of $[Co(tmtppa)]^{4+}$ (1.0 × 10^{-4} mol dm^{-3}) containing 4-methylpyridine (2.0 × 10^{-3} mol dm^{-3}). Microwave frequency 9.147 GHz. (*b*) Computer simulation based on parameters in Table 4

Table 4. Magnetic parameters of low-spin five- and six-co-ordinate cobalt(II) tetra-2,3-pyridinoporphyrazinate complexes *

		$g_\perp$			$10^4 A_\perp^{Co}/cm^{-1}$		$10^4 A_\parallel^{Co}/cm^{-1}$	$10^4 A_\perp^{N}/cm^{-1}$		$10^4 A_\parallel^{N}/cm^{-1}$
Type	Base	g_x	g_y	$g_\parallel (g_z)$	A_x^{Co}	A_y^{Co}	A_z^{Co}	A_x^{N}	A_y^{N}	A_z^{N}
I	3-Methylpyridine	2.238	2.195	2.012	25	12	85	1	1	15
	Isoquinoline	2.238	2.194	2.009	28	14	87	1	1	
	Pyridine	2.234	2.195	2.012	24	12	85	1	1	15
	4-Methylpyridine	2.270	2.124	2.0157	30	48	70	1	1	15
II	4-Methylpyridine	2.169	2.156	2.017	65	72	68	11	15	15
	Pyridine	2.172	2.162	2.017	65	74	68	11	11	15
	3-Methylpyridine	2.168	2.153	2.005	65	68	68	11	15	15

* Re-fitting errors: see Table 1 and text.

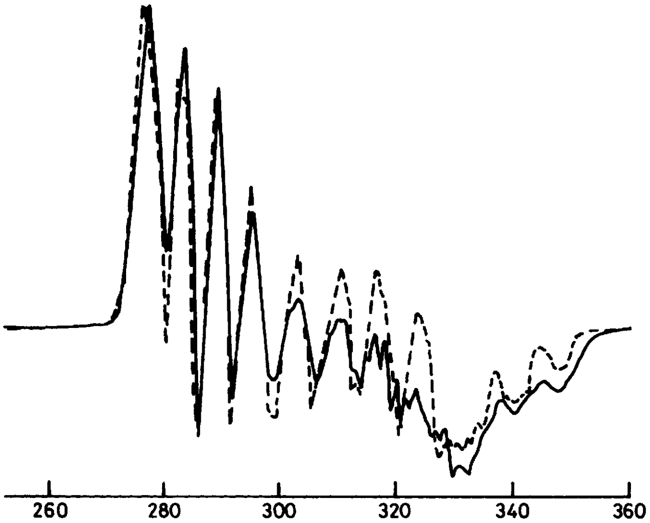

Figure 6. E.s.r. spectrum due to frozen (−140 °C) 5% dmf–H_2O (v/v) solution of $[Co(tmtppa)]^{4+}$ (1.0×10^{-4} mol dm^{-3}) containing 4-methylpyridine (1.0×10^{-2} mol dm^{-3}). Microwave frequency 9.147 GHz. The dashed line represents computer simulation of the spectrum using the magnetic parameters outlined in Table 4

change to that assigned to a six-co-ordinate (Type II) form of the cobalt(II) chelate.

An analogous spectral change upon the addition of excess base was observed by Walker[36] for [Co(tpp)] (tpp = 5,10,15,20-tetraphenylporphyrinate) who attributed the transition from Type I ⟶ Type II spectra as the result of further base co-ordination to the five-co-ordinate chelate (Type I) to give the bis-adduct, $[Co(tpp)L_2]$ where L = base. The parameters of the $[Co(tmtppa)]^{4+}$ (Type II) spectra are listed in Table 4. Similar spectra of the six-co-ordinate complex have also previously been noted for $[Co(tspc)(NH_3)_2]^{4-}$,[43] the magnetic parameters obtained being listed in Table 4 for comparison.

Although the e.s.r. parameters differ slightly depending on the base, the e.s.r. spectra due to the cobalt complex of tmtppa in nitrogenous bases are quite similar. In contrast, the e.s.r. spectra obtained from an aqueous solution of $[Co(tmtppa)]^{4+}$ prepared under nitrogen and containing imidazole or *N*-methylimidazole show strikingly different features. The e.s.r. spectrum is shown in Figure 7. Passing oxygen through the solution did not alter the e.s.r. spectrum, neither did lowering the temperature to 4 K. The resolution of the $g_\parallel$ (low-field component) shows splitting originating from the interaction of the cobalt(II) ion with two nitrogen atoms which would give a 1 : 2 : 3 : 2 : 1 pattern if the two interactions were identical. The attempts to obtain satisfactory simulations of the e.s.r. spectrum were made very difficult as a result of the small $A_\perp$ value for cobalt. Under these circumstances, the perturbation theory expressions used in the simulation program may not have been as reliable as one would like near the ' perpendicular ' part of the spectrum at *ca.* 330 mT. Furthermore, small values of *A* can very easily lead to ' angular anomalies ' at the high-field end of the spectrum which are not resolved in the experimental data. The

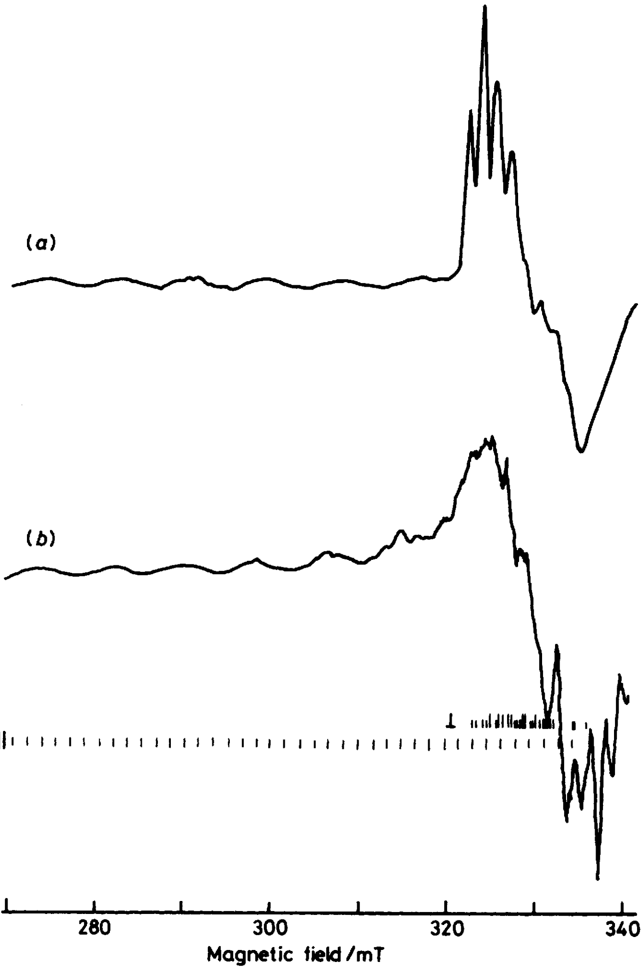

Figure 7. (*a*) E.s.r. spectrum due to frozen (−140 °C) 5% dmf–H_2O (v/v) solution of $[Co(tmtppa)]^{4+}$ (1.0×10^{-4} mol dm^{-3}) containing *N*-methylimidazole (5.0×10^{-4} mol dm^{-3}). Microwave frequency 9.147 GHz. (*b*) Computer simulation using parameters in text

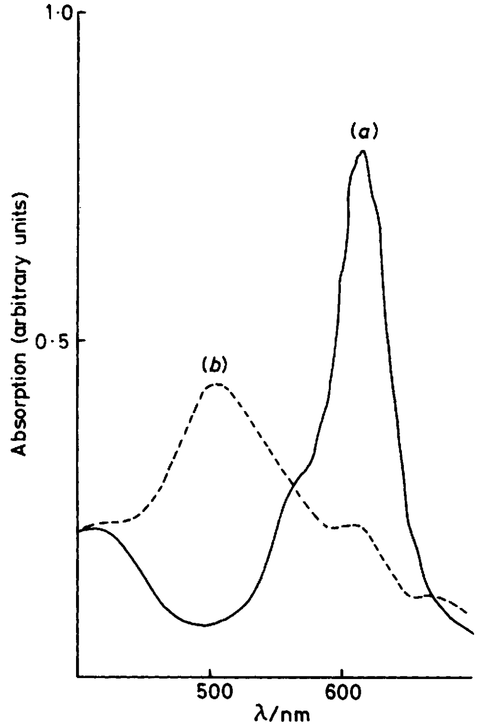

Figure 8. Absorption spectra in the visible region of an aqueous solution of (*a*) [Co(tmtppa)]$^{4+}$ (2.0 × 10^{-5} mol dm^{-3}) and (*b*) after addition of ascorbic acid to make the solution 1.0 × 10^{-4} mol dm^{-3} with respect to this reagent. 1-cm Glass cell

resolved lines at *ca.* 325 mT are, in fact, due to the seventh ' parallel ' groups of lines, the splitting being due to nitrogen superhyperfine splitting (s.h.f.s.). Some allowance was made for either linear or quadratic dependence of ' parallel ' linewidth upon m_l values but not for both effects simultaneously. There is clearly some dependence of linewidth on m_l and we have been unable, with the present programs, to match all of the fine detail. In order to test whether some of the difficulties encountered in the computer simulations could be traced to inaccuracies in the perturbation theory program, a spectrum was run on a VAX III computer using the program QPOW, kindly supplied by Professor R. L. Belford of the University of Illinois. With the parameters listed later in this paragraph, except for putting $A_{\perp} = 8 \times 10^{-4}$ cm^{-1}, only very slight differences were found. Nevertheless, the identification of the reverse *g* values is quite clear. As an alternative strategy we also considered the possibility of including a cobalt quadrupole interaction. This only worsened the simulated spectrum in the ' perpendicular ' region. Computer simulation of the e.s.r. spectrum, using Lorentzian lineshapes, shown by Figure 7 yielded the following values of the magnetic parameters: $g_{\parallel} = 2.160$, $g_{\perp} = 1.984$, $A_{\parallel}^{Co} = 82 \times 10^{-4}$, $A_{\perp}^{Co} = 7 \times 10^{-4}$, $A_{\parallel}^{N}$ 16×10^{-4}, and $A_{\perp}^{N} = 14 \times 10^{-4}$ cm^{-1}. In particular acceptable $A_{\perp}^{Co}$ values range from 3×10^{-4} to 8×10^{-4} cm^{-1}.

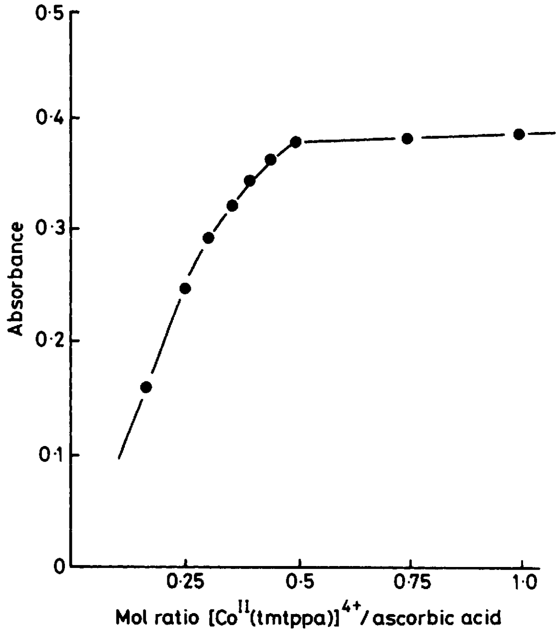

Figure 9. Spectrophotometric titration of an aqueous solution of [Co(tmtppa)]$^{4+}$ (2 × 10^{-5} mol dm^{-3}) monitored at 505 nm under nitrogen with ascorbic acid (7.5 × 10^{-3} mol dm^{-3})

Reduction of [Co(tmtppa)]$^{4+}$ *by Ascorbic Acid.*—The complex [Co(tmtppa)]$^{4+}$ is stable in acidic to neutral pH's in aqueous solution but shows signs of decomposition in slightly alkaline solution. Addition of ascorbic acid to aqueous [Co(tmtppa)]$^{4+}$ results in an immediate colour change from blue to violet as shown in Figure 8. A spectrophotometric titration under nitrogen of an aqueous solution of [Co(tmtppa)]$^{4+}$ with one containing ascorbic acid as illustrated by Figure 9 shows that when the mol ratio of cobalt chelate to ascorbic acid reached 1 : 0.5 the colour change of blue to violet is complete. Exposure of the violet solution ($\lambda_{max.}$ 505 nm) to molecular oxygen results in a rapid colour change to blue ($\lambda_{max.}$ 616 nm) due to formation of [Co(tmtppa)]$^{4+}$. Similar spectrophotometric titration and autoxidation results were obtained for the copper(II) and nickel(II) chelates.

The formation of the violet solution which takes place as a result of the addition of ascorbic acid to the aqueous solution under nitrogen of [Co(tmppa)]$^{4+}$ results in a change of the e.s.r. spectrum due to the cobalt(II) chelate. The intensity of the e.s.r. signal is progressively diminished as a result of successive additions of ascorbic acid until the mol ratio of chelate to ascorbic acid reaches 1 : 0.5 when the e.s.r. signal due to the frozen solution of the reaction mixture is barely detectable. The e.s.r. spectral results and spectrophotometric titrations point to the one-electron reduction of [Co(tmtppa)]$^{4+}$ by ascorbic acid to form the violet coloured corresponding cobalt(I) complex.

D.C. Polarography of the Adducts.—Aqueous solutions of the cobalt(II), copper(II), or nickel(II) complexes of tmtppa, 0.1 mol dm^{-3} with respect to potassium chloride give rise to two d.c. polarographic waves, a typical result being shown by Figure 10. The common features of the polarograms are the presence of a wave in the region $E_{\frac{1}{2}}$ −0.55 V *versus* s.c.e. (saturated calomel electrode) and a larger wave in the voltage region −1.20 V. Comparison of these wave heights with those from the polarograms due to cadmium sulphate of the same concentration and solution conditions indicated that the waves at −0.55 V could be due to a one-electron reduction while the wave at −1.20 V represented possibly a four-electron reduction. The usual plot of $\log_{10} i/(i_d - i)$ against voltage in the case of the polarographic wave due to cadmium ion gave the value of *n*, the number of electrons transferred to the metal ion, as 2.03 which is close to the theoretical value and indicative of a reversible electroreduction at the dropping mercury electrode. However, as summarized by Table 5, both polarographic waves give values of *n* well below those expected

Table 5. Polarographic characteristics of metal tmppa chelates (1.0 × 10^{-3} mol dm^{-3}; 0.1 mol dm^{-3} KCl, 20 °C) compared with those of Cd^{2+} (1.0 × 10^{-3} mol dm^{-3}, 0.1 mol dm^3 KCl); $E_{\frac{1}{2}}$ *vs.* s.c.e.

Metal compound	i_d/μA	$E_{\frac{1}{2}}$/V	n	i_d/μA	$E_{\frac{1}{2}}$/V	n
Cd^{2+}	4.8	−0.61	2.03			
$[Cu(tmtppa)]^{4+}$	1.9	−0.49	0.65	9.2	−1.32	0.59
$[Ni(tmtppa)]^{4+}$	1.9	−0.52	0.52	7.2	−1.10	0.56
$[Co(tmtppa)]^{4+}$	1.9	−0.64	0.49	7.4	−1.05	0.75

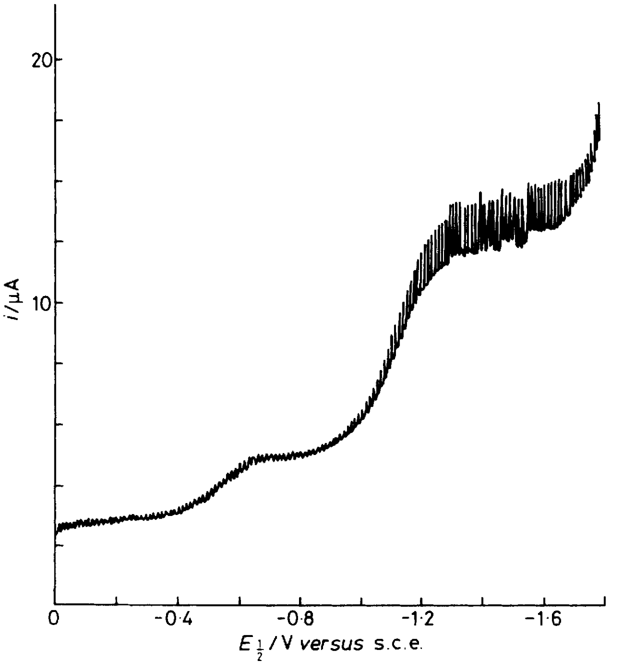

Figure 10. D.c. polarogram of $[Ni(tmtppa)]^{4+}$ (1.0 × 10^{-3} mol dm^{-3}), 0.1 mol dm^{-3} KCl, 20 °C

for a one- or multi-electron change, although linear plots of $\log_{10}i/(i_d - i)$ *vs.* voltage were obtained in each case. The results indicate that the electrode reactions are polarographically irreversible. In order to establish the nature of the electron-transfer reactions at the dropping mercury electrode, aqueous solutions of the metal tmtppa chelates were treated with ascorbic acid. In the case of aqueous solutions containing the copper(II) and nickel(II) chelates at the concentration levels used for polarographic measurements purple flocculant precipitates formed immediately upon addition of ascorbic acid, cysteine, sodium dithionite, hydroxylamine or mercaptoethanol. Fortunately, addition of ascorbic acid to $[Co^{II}(tmtppa)]^{4+}$ results in the formation of the cobalt(I) complex which does not form a precipitate on standing for some hours. The polarogram of an aqueous solution of $[Co^{II}(tmtppa)]^{4+}$ (1.0 × 10^{-3} mol dm^{-3}, 0.1 mol dm^{-3} KCl) to which ascorbic had been added under nitrogen consisted of a single wave ($E_{\frac{1}{2}}$ −1.05 V, i_d 7.4 μA) indicating that the polarographic wave $E_{\frac{1}{2}}$ at −0.64 V observed in the absence of the reducing agent could be ascribed to a one-electron addition to the cobalt(II) chelate and presumably to the copper(II) and nickel(II) chelates. Controlled potential reduction of the aqueous solution containing the cobalt(II) complex of tmtppa, 0.1 mol dm^{-3} with respect to potassium chloride, at the mercury pool resulted in formation of a violet solution which again possessed a polarograph response of a single wave, $E_{\frac{1}{2}}$ −1.05 V.

Discussion

The e.s.r. spectral results indicate that the electronic environment within the tetrapyridinoporphyrazine macrocycle is comparable to that of the phthalocyanine ring system. The axial interaction of the cobalt(II) centre within the porphyrazine macrocycle with certain heterocyclic bases is sufficiently strong to extend the otherwise limited solubility of the cobalt(II) chelate in organic solvents. Five- and six-co-ordination of the cobalt(II) occurs in these circumstances and the electronic and e.s.r. spectral information shows that the water-soluble tetramethyl tetracationic forms of the copper(II) and cobalt(II) tetrapyridinoporphyrazine chelates as the methyl sulphate salts are stable in acidic solution, but decompose in alkaline solution and are only partially recovered from slightly alkaline conditions.

Previous e.s.r.[34,37,39,44] paramagnetic anisotropy studies[45] and molecular orbital and crystal-field calculations[46] of cobalt(II) phthalocyanine show that the odd electron occupies an $A_{1g}(d_{z^2})$ orbital but there is also some contribution from the d_{xz} and d_{yz} orbitals.[39]

In the presence of heterocyclic bases two spectral patterns are observed, designated Type I for the mono-base adduct and Type II for the bis-base adduct. In the case of the five-co-ordinate complexes, the cobalt high-field $g_{\parallel}$ (g_z) hyperfine lines were split into three superhyperfine lines owing to the magnetic interaction between the $3d_{z^2}$ odd electron and an extra out-of-plane nitrogen of the co-ordinating base. Under ideal circumstances the intensities of the superhyperfine lines show the ratio 1 : 1 : 1 with coupling constant in the range 15 × 10^{-4}—17 × 10^{-4} cm^{-1}.

The addition of excess co-ordinating base to an aqueous solution of $[Co(tmtppa)]^{4+}$ results in a transition from a Type I spectrum to the spectrum designated Type II. Five lines for two interacting nitrogen atoms are obscured in the broad $g_{\parallel}$ hyperfine lines and by the perpendicular branch of the spectrum at low field.[36] The Type II spectrum reported here is markedly different from those reported for cobalt(II) phthalocyanine in various amines.[31]

Walker[36] found that e.s.r. parameters of [Co(tpp)L] and $[Co(tpp)L_2]$ were not significantly dependent on the basicity of the amine although the formation of the bis-adduct is easily attained with stronger bases and that this ability may involve a balance between the σ-donating and π-accepting ability of the amine.

The e.s.r. spectra of $[Co(tmtppa)]^{4+}$ observed in the presence of imidazole or *N*-methylimidazole at 77 or 4 K have not previously been reported. The spectra are unusual in respect that $g_{\parallel} > g_{\perp}$ whereas in the previous cases $g_{\parallel} < g_{\perp}$. The occurrence of ' reverse ' *g* values is well documented for copper complexes.[47-49]

For six-co-ordinate copper complexes with $g_{\parallel} < g_{\perp}$ in the solid state, a Jahn–Teller induced tetragonal distortion is expected to result in a compression of the octahedron leading to a d_{z^2} ground state. The normal $d_{x^2-y^2}$ ground state comes about from an elongation along the *z* axis and has $g_{\parallel} > g_{\perp}$. Nishida *et al.*[50] have described the e.s.r. spectra of seven-co-ordinate pentagonal bipyramidal copper(II) complexes. In

EtOH–H_2O, these complexes show e.s.r. spectra where $g_{\parallel} < g_{\perp}$ ($g_{\parallel}$ *ca.* 1.99 and $g_{\perp}$ *ca.* 2.35) and have been attributed to a d_{z^2} ground state configuration of the copper(II) centre.

In the case of the e.s.r. spectra observed for $[Co(tmtppa)]^{4+}$ in the presence of imidazole or *N*-methylimidazole, a plausible explanation at this stage would be that as a result of strong imidazole co-ordination the electronic configuration of the complex is altered such that $g_{\parallel} > g_{\perp}$. The reversal of g values may possibly result from the raising of the energy of the d_{z^2} orbital above that of $d_{x^2-y^2}$, such that a $(d_{x^2-y^2})^1$ ground state configuration is established. It must be borne in mind that this way of discussing low-spin cobalt(II) in terms of single *d* orbitals is but a convenient simplification of the true situation which involves a seven electron or alternatively three ' hole ' configuration. Analysis of the spectra at the low-field end reveals superhyperfine splitting with a coupling constant in accordance with nitrogen, 15×10^{-4} cm^{-1}. Furthermore, the splitting into five resolvable peaks with an intensity ratio of 1 : 2 : 3 : 2 : 1 indicates a magnetic interaction of the Co^{II} centre with two nitrogen atoms ($I = 1$). Cobalt(II) with a $d_{x^2-y^2}$ ground state would not be sensitive to out-of-plane interactions but rather to an in-plane interaction with the four pyrrolic nitrogens as is seen in the case of $[Co(tmtppa)]^{4+}$.

Previous studies on Co^{II} corrin model complexes of vitamin B_{12} have shown the possibility of an unusual $d_{x^2-y^2}$ ground state for cobalt(II).[51] The presence of three principal *g*-tensor components in the spectra of the cobalt(II) corrole anion indicates that the complex has rhombic or lower symmetry. Three possible ground state configurations were considered: (*i*) d_{xy}, (*ii*) d_{z^2}, and (*iii*) $d_{x^2-y^2}$ for the cobalt(II) corrole anion. The first, d_{xy}, was dismissed since this orbital is directed towards the ligating pyrrole nitrogen and should be highest in energy. A theoretical calculation based on the expressions derived by Maki *et al.*[52] showed that the experimental parameters obtained are consistent with a $(d_{x^2-y^2})^1$ ground state where $P = 69 \times 10^{-1}$ cm^{-1} and $K = 1.04$. The small value of the hyperfine parameter, P, *ca.* 30% of its free-ion value, and the large value of K, which measured the *s*-electron (core polarization) contribution to cobalt h.f.s., suggests the model is inadequate. Furthermore, the location of the unpaired electron in an in-plane orbital would explain why the complex shows little or no tendency towards axial co-ordination of ligands such as pyridine. The spin-Hamiltonian parameters obtained by Hush and Woolsey [51] may, however, be correlated with a $(d_{z^2})^1$ state on the basis of the calculated plots relating g and hyperfine values as a function of the energy separation of the d_{yz} and d_{z^2} as derived by Hitchman.[40] In the present complex, the parameters do not fall into the pattern of either a d_{yz} or d_{z^2} state. It has been suggested [40] that the *g* values of planar cobalt(II) complexes having C_{2v} or D_{2h} symmetry may be drastically affected by the mixing of the $d_{x^2-y^2}$ and d_{z^2} orbitals, as suggested by McGarvey [53,54] if the ground state is $^2A_1$ in unusual circumstances.

A $d_{x^2-y^2}$ state for $[Co(tmtppa)]^{4+}$ is unusual from the point that one would not expect a ground state of $d_{x^2-y^2}$, but also that the change from $(d_{z^2})^1$ to $(d_{x^2-y^2})^1$ occurs only in the presence of an imidazole functional group. Previous investigation on the interactions of histidine and other imidazole derivatives with transition-metal ions in chemical and biological systems have been recently reviewed.[55] A number of transition-metal macrocyclic complexes form bis-base adducts, where the stability order generally follows $CN^- > NH_3 \approx$ imidazole > pyridine. In some instances imidazole > NH_3 and this is attributed to the greater π-acceptor properties of imidazole although neither σ-donor or π-acceptor strength alone dominates the nature of the interaction with a cobalt(II) centre which may suggest a combination of factors. In the present complex the formation of imidazole complexes of $[Co(tmtppa)]^{4+}$ occurs when as little as a two-fold excess of base is present whereas in the case of pyridine the mono-base adduct could be formed in a 5—10 fold excess of base. The unique observation of a possible $d_{x^2-y^2}$ ground state for cobalt(II) in these concentrations is intriguing. In passing, it may be mentioned that an e.s.r. spectrum quite similar to that shown by Figure 10 was obtained when $[Co(tmtppa)]^{4+}$ was inserted into apomyoglobin using the experimental procedures described previously.[56] Presumably in this case the cobalt(II) e.s.r. spectral response is influenced by the axial interaction with the histidine groups within the protein structures.[57]

Experimental

The e.s.r. spectra, recorded as the first derivatives of absorption, were obtained using a Varian E-12 spectrometer with an E-101 microwave bridge at *X*-Band (*ca.* 9.15 GHz) and a home built *S*-Band microwave bridge operating at *ca.* 2.9 GHz.[58] Low temperatures were achieved by means of an Oxford Instruments helium flow cryostat (*ca.* 4 K), a Varian E-257 variable temperature accessory (above *ca.* 100 K) or at liquid nitrogen temperature using narrow tail quartz dewars. Magnetic fields were calibrated against proton n.m.r. frequencies measured using a Hewlett Packard HP 5254L frequency counter. Microwave frequencies were measured above 3 GHz using a Hewlett Packard HP 540B microwave mixer and the counter while below 3 GHz they were obtained with the aid of a 0.2—3 GHz 5254B plug-in unit on the counter.

Computer simulations were carried out by means of a simulation program described previously [30] using a Burroughs B6700 Computer at the Monash Computer Centre or an LSI 11/23 laboratory-based computer coupled to a digital plotter.

Air-free samples were prepared from degassed solutions which were transferred to e.s.r. cells fitted with quick-fit joints and valves suitable for evacuation by a freeze-thawing process on a vacuum line.

Measurements of pH were made using a Radiometer-22 pH meter employing a combination glass-calomel electrode, calibrated at 20 °C using 0.05 mol dm^{-3} potassium hydrogenphthalate [$KH(C_8O_4H_4)$, pH = 4.00], 0.025 mol dm^{-3} potassium dihydrogen phosphate (KH_2PO_4–Na_2HPO_4, pH = 6.88), 0.05 mol dm^{-3} potassium tetraoxalate [$KH_3(C_2O_4)_2 \cdot 2H_2O$, pH = 1.67], and saturated calcium hydroxide (pH = 12.63) buffer solutions.

Visible absorption spectra were recorded on a Varian 635 ultraviolet–visible spectrometer at room temperature using 1-cm glass and silica cells.

D.c. polarographic measurements were made on a Shimadzu Seisakasho type R22 polarograph using a water jacketed H-type cell, one arm of which was served as the s.c.e., the temperature being maintained at 20 ± 0.1 °C with nitrogen being used to remove dissolved oxygen from the sample solutions.

Microanalyses were carried out by the C.S.I.R.O. Microanalytical Service, Melbourne.

Tetra-2,3-pyridinoporphyrazinatocopper(II).—This complex was prepared by the method described by Yokote *et al.*[14] Urea (6.5 g), ammonium molybdate (0.046 g), 2,3-pyridinedicarboxylic acid (Aldrich Chemicals, 1.0 g), and anhydrous copper(II) chloride (0.2 g) were ground together until homogeneous. The mixture was placed in the steel bomb, sealed and heated at 210 °C for 4—5 h, and allowed to cool to room temperature over a 24 h period. The crude blue-violet product

Table 6. Analytical data for the tetra-2,3-pyridinoporphyrazine chelates and their cationic *NN'N''N'''*-tetramethyl forms

	Calculated (%)			Found (%)		
Compound	C	H	N	C	H	N
[Cu(tppa)]·$2H_2O$	54.60	2.60	27.30	54.45	2.70	27.25
[Co(tppa)]·$2H_2O$	55.00	2.65	27.50	54.95	2.70	27.30
[Ni(tppa)]·$2H_2O$	55.00	2.65	27.50	54.95	2.70	27.60
$[Cu^{II}(tmtppa)]^{4+}[SO_3(OCH_3)]_4^{-}\cdot H_2O$	39.20	3.45	15.40	39.20	3.45	15.25
$[Co^{II}(tmtppa)]^{4+}[SO_3(OCH_3)]_4^{-}\cdot 2H_2O$	38.75	3.60	15.05	38.85	3.70	15.00
$[Ni^{II}(tmtppa)]^{4+}[SO_3(OCH_3)]_4^{-}\cdot 2H_2O$	38.75	3.60	15.10	38.70	3.65	15.20

(5.45 g) was crushed and washed successively with warm water, warm sodium hydroxide solution (5% w/v), warm water, warm dilute hydrochloric acid (2.5% v/v), and finally with warm water. The product was dried at 80 °C. The deep violet-blue product was purified by dissolving in concentrated sulphuric acid and pouring the solution on to ice. The precipitated product was collected by centrifugation (*ca.* 200 r.p.m./10 min) and transferred to a fine glass sinter funnel where the mass was thoroughly washed with hot water, warm aqueous sodium carbonate solution and again with warm water. The product was dried at 80 °C over phosphorus pentoxide (yield 52%).

Elemental analyses of the product showed a high sulphur content which was consistent with the presence of four molecules of sulphuric acid, presumably as a result of the quaternization of the pyridine nitrogens. A better sublimable product could be obtained by using concentrated hydrochloric acid instead of sulphuric acid and pouring the solution into excess aqueous sodium hydroxide. When dried the product had a lustrous finish with a high purple reflectivity [Found (using sulphuric acid): C, 33.30; H, 2.60; N, 16.65; S, 12.70. $C_{28}H_{12}CuN_{12}\cdot 2H_2O\cdot 4H_2SO_4$ requires C, 33.35; H, 2.40; N, 14.40; S, 12.70. Found (using hydrochloric acid): C, 54.55; H, 2.70; N, 27.25. $C_{28}H_{12}CuN_{12}\cdot 2H_2O$ requires C, 54.60; H, 2.60; N, 27.30%].

Quaternized Copper(II) *Tetra*-2,3-*pyridinoporphyrazinate.*— This complex was prepared according to the method previously reported by Scott.[11] The copper chelate was heated to 120 °C in freshly distilled dmf and a ten-fold excess of dimethyl sulphate, also distilled immediately prior to use, was added dropwise using a sealed pressure equalising dropping funnel. The mixture was heated, with stirring, for 30 min during which time the copper chelate first began to dissolve then precipitate upon cooling to room temperature. Most of the dmf was removed by distillation at diminished pressure and the resulting slurry poured into acetone. The porphyrazine immediately precipitated and the resulting product was collected by centrifugation and washed successively with acetone, ethanol, diethyl ether, and dried at 80 °C over phosphorus pentoxide. The recovery of porphyrazine chelate in the quaternized form was 82%. Residual small amounts of non-quaternized copper porphyrazine could be removed by dissolving the product in water, filtering, and reprecipitating in acetone as previously described.

Tetra-2,3-*pyridinoporphyrazinatocobalt*(II).—This complex was similarly prepared.[14] Urea (3.2 g), ammonium molybdate (0.126 g), and 2,3-pyridinecarboxylic (1.0 g) were ground together until homogeneous. The mixture was stirred in 1,2,4-trichlorobenzene (40 cm³) for 1 h at 156—160 °C. A ground mixture of cobalt(II) oxalate [$Co(C_2O_4)\cdot 2H_2O$, 1.1 g] and urea (2.5 g) was slowly added under nitrogen. The temperature was maintained at 205—210 °C for 3.5 h. At completion, excess 1,2,4-trichlorobenzene was removed by distillation under reduced pressure. The crude product was washed with benzene (100 cm³), crushed and washed successively with ethanol, warm water, warm aqueous sodium hydroxide solution (5% w/v), warm water, warm dilute hydrochloric acid (2.5% v/v), warm water and dried at 80 °C to give 0.882 g of product (45% yield). The product was further purified by dissolving in concentrated hydrochloric acid and pouring into an excess of aqueous sodium hydroxide solution. The precipitate was collected by centrifugation and dried at 80 °C *in vacuo* over phosphorus pentoxide.

Quaternized nickel(II) and cobalt(II) complexes of tetra-2,3-pyridinoporphyrazine were prepared by the method previously described for the copper derivative although the reaction was carried out under nitrogen for the cobalt(II) chelate.

The analytical results for the various chelates are summarised by Table 6.

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