Electron Spin Resonance Study of the Copper(II) and Cobalt(II) Chelates of 2,3;7,8;12,13;17,18-Tetrakis-(9,10-dihydroanthracene-9,10-diyl)porphyrazine

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The X-band e.s.r. spectra due to the benzene soluble copper(II) (1a) chelate of 2,3; 7,8; 12,13; 17,18-tetrakis-(9,10-dihydroanthracene-9,10-diyl)porphyrazine and the corresponding cobalt(II) chelate (1b) in the absence and presence of axially coordinating heterocyclic bases have been recorded. Spin Hamiltonian parameters have been determined by computer simulation of the various e.s.r. spectra and, in the case of the copper(II) chelate, compared with those obtained from the copper(II) chelates of certain phthalocyanines. The e.s.r. spectral properties of the cobalt(II) chelate (1b) porphyrazine in benzene solution were found to be remarkably dependent on the water hydration which accompanies the chelate in its isolation, requiring drying of the solution by molecular sieves. Axial coordination of the cobalt(II) centre of the chelate by pyridine, tetrahydrofuran or thiophene results in a large shift in the g_{\perp} region of the spectrum, observed in the absence of axial coordination, to higher fields while causing a dramatic fall in the numerical values of ${}^{Co}A_{\parallel}$ and ${}^{Co}A_{\perp}$. The e.s.r. spectra due to frozen benzene solutions of the cobalt chelate (1b) containing various amounts of N-methylimidazole show that axial coordination of the cobalt(II) chelate centre by one heterocyclic base occurs at low concentrations of N-methylimidazole. At higher concentrations, two modes of binding of the N-methylimidazole may be clearly discerned, one characterized by an e.s.r. spectral component typical of low spin cobalt(II) $(g_{\parallel} < g_{\perp})$ and a very unusual spectrum where the g-values are ca. 1.98.

The thermal stability of metallo phthalocyanines¹ and dodecahedrane² is a consequence of their molecular structure. Organic substituents have been used to increase the solubility of the phthalocyanines. Such hydrocarbon substituent groups include trimethylsilyl and t-butyl radicals³⁻⁵ while phthalocyanines containing rather more complicated hydrocarbon substituent groups such as tetra(1-phenyl)-2,3-naphthocyanine⁶ and 2,3;7,8;12,13;17,18-tetrakis-(9,10-dihydroanthracene-9,10-diyl)porphyrazine⁷ have been described. In addition, the syntheses of 2,3;7,8;12,13;17,18-tetrakis-(9,10-dihydroanthracene-9,10-diyl)porphyrazine (TDAP) and its metallo derivatives which are soluble in a number of organic solvents have been reported.⁸

Solubility in organic solvents provides circumstances for the measurement of the e.s.r. spectral features of the organic solvent-soluble phthalocyanines and related macrocyclic compounds and, in the case of the cobalt(II) chelates, allows study of their interaction with molecular oxygen. The present work is devoted to such measurements on the copper(II) and cobalt(II) chelates (1a, b).



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) while spectra at S-band (*ca.* 2.3 GHz) were obtained using a home-built 1–4 GHz microwave bridge in place of the E-101 bridge. Samples were placed in a Varian multipurpose cavity at X-band or in a loop-gap resonator at S-band. The microwave frequency was measured directly using an EIP 548A frequency counter while magnetic fields were calibrated against proton resonance using a Hewlett Packard HP5254L counter.

Spectra collected early in the project were digitized using an x-y recorder while later spectra were directly accumulated on a LSI 11/23 laboratory computer, and data transferred to a VAX 11/780 computer at the Monash Computer Centre for subsequent analysis and plotting.

Absorption spectra of the coloured solutions were recorded on a Varian 635 spectrophotometer at room temperature using 1 cm glass cells. Microanalyses were carried out by the Australian Mineral Development Laboratories, Melbourne.

The preparation of the chelates (1a, b) involved three stages, namely the synthesis of 11,12-dicyano-9,10-dihydroethenoanthracene, the use of the dicyano compound to make the magnesium chelate (1c), and finally conversion of the magnesium chelate into ones containing copper(II) and cobalt(II), isolated as their dihydrates.

A convenient method for the preparation of 11,12-dicyano-9,10-dihydro-9,10ethenoanthracene⁹ is one which starts with the Diels-Alder addition of the dimethyl acetylenedicarboxylate to anthracene^{10,11} to give dimethyl 2,3-(9,10-dihydroanthracene-9,10-diyl)maleate followed by conversion of the diester product to the diamide by treatment with ammonia and final conversion to the dicyano form by reaction of the diamide with thionyl chloride in dimethylformamide. Thus, to prepare 9,10-dihydro-9,10-ethenoanthracene-11,12-diamide finely powdered dimethyl 2,3-(9,10-dihydro-

anthracene-9,10-diyl)maleate (11.0 g) was added to a solvent mixture consisting of dioxane (25% v/v) methanol (25% v/v) and concentrated aqueous ammonia (50% v/v; d = 0.880). Liquid ammonia (70 cm³) was added cautiously to the reaction mixture with stirring of the slurry for two days at room temperature. The solid product which contained 9,10-dihydro-9,10-ethenoanthracene-11,12-diamide was collected by filtration and the diamide recrystallized from a solvent mixture of acetonitrile (50% v/v) and water (6.7 g, 65%), m.p. 295 °C (decomp.), m/z 290 (M^+ , 12%), 272 (22), 254 (12), 247 (65), 230 (38), 218 (38), 202 (100) and 178 (60). To prepare 11,12-dicyano-9,10-dihydro-9,10-ethenoanthracene a chilled $(-15 \,^{\circ}\text{C})$ slurry of 9,10-dihydro-9,10-ethenoanthracene-11,12-diamide (6.7 g) in dimethylformamide (50 cm³) was added slowly to a cold (-15 °C) solution of thionyl chloride (5.5 g) in dimethylformamide (50 cm³) keeping the temperature below -10 °C. The reaction mixture was allowed to rise slowly to room temperature with constant stirring. After a further 2 h, the product was isolated by pouring the reaction mixture on to ice and filtering the suspension. The solid product was recrystallized from acetonitrile (5.3 g, 85%), m.p. 267-268 °C (Found: C, 85.38; H, 4.20; N, 10.72%. Calc. for $C_{18}H_{10}N_2$: C, 85.02; H, 3.96; N, 11.02%); m/z 254 $(M^+, 100\%), 227$ (38), 203 (12) and 178 (38); $\delta_{\rm H}$ 7.57 (4 H), 7.17 (4 H) and 6.03 (2 H). The magnesium chelate (1c) was prepared from 11,12-dicyano-9,10-ethenoanthracene by the method outlined in the literature⁸ (yield 5%, $\log \varepsilon$ 4.95 at 602 nm).

The cobalt(II) chelate (1b) was prepared by a modification of the method described in the literature.⁸ Glacial acetic acid (0.1 cm^3) was added to a refluxing solution of the magnesium(II) chelate (1c) (100 mg) in benzene (50 cm³) and heating was continued for 10 min. The cooled benzene solution was washed well with dilute aqueous ammonia (2 mol dm^{-3}) , then with water. At this stage, electronic spectrum of the product was characteristic of the demetallated porphyrazine which was isolated by removal of the benzene under reduced pressure. The solid was dissolved in hot dimethylformamide (20 cm³, 120 °C) and the solution was treated with a warm (50 °C) solution of anhydrous cobalt(II) chloride (0.2 g) in dimethylformamide (15 cm^3). The reaction mixture was then heated to 150 °C for 15 min. During this time the characteristic spectrum of the porphyrazine in free base form changed completely to that of the metallated product which was isolated by pouring the reaction mixture onto ice, and centrifugation of the thawed material (yield 70 mg). The product, isolated as its dihydrate⁸ was purified chromatographically on a silica column eluting with benzene (λ_{max} 576 nm; log ε 4.53). The copper(II) chelate of the porphyrazine was prepared in the same way as that outlined for the synthesis of the cobalt(II) chelate but using a dimethylformamide solution of anhydrous copper(II) chloride as the starting material. The copper(II) and nickel(II) chelate of 2,9,16,23-tetra(3-pyridyloxy)phthalocyanine (TOPPC) were prepared from the free ligand which was obtained by the procedure described previously.¹² 3,10,17,24-Tetranitrophthalocyanine was prepared from the reaction of lithium butoxide with 4-nitrophthalonitrile in hot butanol¹³ and was converted into the copper(II) chelate by reaction with copper(II) chloride in dimethylformamide.

Results

The copper(II) chelate of (1a) is soluble in benzene. Its X-band e.s.r. spectrum in frozen benzene solution is illustrated in fig. 1 which shows the superhyperfine lines on the g_{\perp} and g_{\parallel} components of the spectrum typical of that when the unpaired electron of the central copper(II) ion (I = 3/2) interacts with the nuclei of four equivalent bonding nitrogen atoms (I = 1) of the ligand.

The major influence on the bonding of the metal ion centre in the conjugated macrocyclic chelates is the N_4 -donor set which is an integral part of the macrocyclic structure. To gain some idea of the smaller influence exerted by the outer ring structure, the e.s.r. spectra due to copper(II) phthalocyanines with very different substituent groups



Fig. 1. (a) X-Band e.s.r. spectrum due to a frozen (120 K) benzene solution of (1a) $(1.0 \times 10^{-3} \text{ mol} \text{ dm}^{-3})$. Microwave frequency 9.148 GHz. (b) Computer simulation using the parameters outlined in tables 1(a) and 1(b). Stick spectra correspond to parallel (||), perpendicular (\perp) and angular anomaly at low field (a).

were recorded. The copper(II) chelate of TOPPC is soluble in a number of organic solvents where, however, u.v.-visible and e.s.r. spectral measurements show that the chelate is entirely in aggregated form which persists when adsorbed from dimethyl-formamide on to a Y-type zeolite. An e.s.r. spectrum due to the monomeric form of copper(II) TOPPC which resembles closely that shown in fig. 1 was obtained by doping (1%) into nickel(II) TOPPC. The copper(II) chelate of 3,10,17,24-tetranitrophthalocyanine (TNPC) is insoluble in organic solvents but may be recovered unchanged from concentrated sulphuric acid which was used to dope the chelate (1%) into the free base. The e.s.r. spectrum due to copper(II) TNPC in these circumstances is quite similar to that shown in fig. 1.

Since a wide variety of cobalt(II) chelates, particularly in the presence of coordinated bases, form molecular oxygen adducts or undergo oxidation in the presence of dioxygen, the e.s.r. spectra due to (1b) in benzene solution alone or containing various bases were recorded on samples free of dioxygen and maintained in an atmosphere of dinitrogen. The e.s.r. spectrum of (1b) in frozen benzene solution is shown in fig. 2(a) and is seen to possess well defined g_{\perp} and g_{\parallel} regions arising from the nuclear hyperfine interactions of the central cobalt(II) ion (I = 7/2). This result was achieved by using carefully dried benzene and storing the (1b)-benzene solution over a drying agent (molcular sieves). When the cobalt (II) chelate (1b), which is prepared as its dihydrate, is dissolved in benzene which has not been subjected to a drying procedure, the e.s.r. spectrum shown in fig. 2(b)is obtained. The presence of a small amount of water reduces markedly the intensity of the lines on the g_{\parallel} region while new lines appear in the g_{\parallel} region which are accompanied by broader lines attributable to the corresponding g_{\perp} region. The e.s.r. spectral result depicted by fig. 2(b) is a composite of the spectrum of (1b) and (1b) with axial ligation by water. Closer inspection of fig. 2(a) shows that it too has a small contribution from the 'wet' spectrum. The spectra of the 'dry' and 'wet' components were obtained by a judicious set of spectral subtractions by computer. First the spectrum in fig. 2(a) was



subtracted from that of fig. 2(b) in such proportions as to remove the outermost peaks in the spectrum associated with the 'dry' species. The resulting 'wet' spectrum, and associated simulation, is shown in fig. 2(c). Then a small proportion of the spectrum in fig. 2(c) was subtracted from the original spectrum [(fig. 2(a)] to provide a better representation of the 'dry' spectrum. This is shown in fig. 2(d) along with a computer simulation. All subsequent experiments were carried out using solutions of (1b) that had been dried over molecular sieves.

Addition of pyridine to a benzene solution of cobalt(II) TDAP has a profound effect on the X-band e.s.r. spectrum of (1b) as illustrated by fig. 3(a) which shows hyperfine with superhyperfine lines arising from axial ligation of cobalt(II) centre by two pyridine

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Fig. 2. (a) X-Band e.s.r. spectrum due to a frozen (120 K) benzene solution of (1b) $(1.0 \times 10^{-3} \text{ mol dm}^{-3})$ dried over molecular sieves for some hours, under dried dinitrogen atmosphere. (b) X-Band e.s.r. spectrum due to a frozen (120 K) benzene solution of (1b) cobalt(II) dihydrate $(1.0 \times 10^{-3} \text{ mol dm}^{-3})$ under dried dinitrogen atmosphere. (c) Spectrum of fig. 2(b) corrected by subtraction of spectrum in fig. 2(a) so as to yield 'wet' spectrum. Lower curve is computer-simulation based on parameters in tables 2(a) and 2(b). (d) Spectrum of fig. 2(a) corrected by subtraction of 'wet' spectrum of fig. 2(c) so as to yield 'dry' spectrum. Lower curve is computer simulation 4 based on parameters in tables 2(a) and 2(b). Stick spectra as in fig. 1(b).

molecules in the *trans* position with respect to the macrocyclic ring system. Fig. 3(c) shows the corresponding S-band spectrum. Fig. 3(b) and (d) are the respective computer simulations.

The e.s.r. spectra of (1b) in pure tetrahydrofuran or thiophene are typically due to 6coordination of the cobalt(II) centre. Both spectra possess well resolved g_{\parallel} regions while the g_{\perp} region is well resolved in the case of axial ligation by tetrahydrofuran. The addition of pyrrole to a benzene solution containing (1b) leads to the observation of an e.s.r. spectrum which has superhyperfine structure in the g_{\parallel} region appropriate to the axial interaction of one pyrrole molecule with the cobalt(II) centre. As shown by fig. 4(*a*), the e.s.r. spectrum obtained from a benzene solution of (1b) and N-methylimidazole is due to two species, one having a distinctive axial interaction with two imidazole nitrogen atoms covering the entire spectral range of fig. 4(*a*). Subtracting the simulated spectrum [fig. 4(*d*)] of that species from fig. 4(*a*) leaves an anisotropic spectrum in the range 320-340 mT [fig. 4(*e*)] whose simulation is given in fig. 4(*f*). This is confirmed by the addition of the simulated spectra shown in fig. 4(*a*) and 4(*f*) to yield the computed spectrum fig. 4(*b*) to be compared with fig. 4(*a*). The net result of these subtractions and simulations is that the second species is found to be quite unusual for low-spin cobalt(II).

If the amount of N-methylimidazole present in the benzene solution of (1b) is greatly reduced from that used previously to 0.1%, the e.s.r. spectrum obtained in this circumstance is quite similar to that obtained from a frozen benzene solution of the cobalt(II) chelate containing pyrrole and where the superhyperfine lines in the g_{\parallel} region of the spectrum point to axial coordination of one N-methylimidazole molecule to the cobalt(II) centre. If the amounts of N-methylimidazole present in the benzene solution



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Fig. 3. (a) X-Band e.s.r. spectrum (at 9.115 GHz) due to a frozen (120 K) benzene solution of (1b) $(1.0 \times 10^{-3} \text{ mol dm}^{-3})$ containing pyridine (10% v/v) under dried dinitrogen atmosphere. (b) Computer simulation using the parameters outlined in tables 2(a) and 2(b). Stick spectra as in fig. 1(b). (c) S-Band e.s.r. spectrum (at 2.341 GHz) [see fig. 3(a) caption]. (d) Computer simulation of S-band e.s.r. spectrum based on parameters outlined in tables 2(a) and 2(b). Stick spectra as in fig. 1(b).



Fig. 4(a) and (b). For legend see p. 1484.

of cobalt(II) chelate are increased to 1%, the e.s.r. spectrum contains one component, namely the axial Co(II) TDAP potion of fig. 4(a) and shown by the simulation fig. 4(d). Increasing the amount of N-methylimidazole to 5% gives rise to the progressive emergence of a portion of the spectrum shown by the simulation in fig. 4(f).

The exposure of a benzene solution containing (1b) and N-methylimidazole to dioxygen followed by freezing of the solution to record the e.s.r. spectrum results in the spectral result shown in fig. 5. A similar result was obtained by exposure of a benzene solution containing (1b) and pyridine to molecular oxygen, though the resolution of the peaks was rather poorer. However, in each case the spectral result provides evidence of the formation of molecular oxygen adduct of the cobalt(II) chelate in frozen solution.

Interpretation of the E.S.R. Spectra due to the Copper(11) and Cobalt(11) Macrocyclic Chelates

The e.s.r. spectra (1a) and the low-spin cobalt(II) chelates (1b) depicted here can be described by the following spin Hamiltonian

$$\mathscr{H} = g_{\parallel}\beta B_z + g_{\perp}\beta [B_x S_x + B_y S_y] + A_{\parallel} S_z I_z + A_{\parallel} (S_x I_x + S_y I_y).$$
(1)





Fig. 4(c) and (d). For legend see p. 1484.

Eqn (1) is supplemented by the ligand hyperfine term due to N-ligands in the axial position in the case of cobalt(II) or as a result of nitrogen atoms of the macrocyclic ligand in the equatorial plane in the case of copper(II) as follows

$$\mathscr{H}_{\rm L} = \sum_{i=1}^{n} \left[A_{\parallel}^{\rm N}(S_z I_{iz}^{\rm N}) + A_{\perp}^{\rm N}(S_x I_{ix}^{\rm N} + S_y I_{iy}^{\rm N}) \right].$$
(2)

In eqn (1) and (2) all the terms have their usual meaning.¹⁴ For copper(II), S = 1/2 and I = 3/2 for both copper isotopes ⁶³Cu and ⁶⁵Cu. These are present in approximately natural abundances (0.69 and 0.31). Hyperfine values are given for ⁶³Cu. For cobalt(II) S = 1/2 and I = 7/2.

A comment about the use of eqn (2) is necessary. It is assumed that the four nitrogens from the macrocycle which are coordinated to copper(II) are equivalent. Since the nitrogen hyperfine structure is nearly isotropic one can, to a good approximation, allow for a little anisotropy within and normal to the molecular plane. In the case of two axial nitrogens coordinated to cobalt(II), one might have to consider two different pictures in which the two pyridines are either parallel or orthogonal to each other. It is doubtful whether these effects could effectively be discriminated from e.s.r. data. To



Fig. 4. (a) X-Band e.s.r. spectrum due to a frozen (120 K) benzene solution of (**1b**) $(1.0 \times 10^{-3} \text{ mol} \text{ dm}^{-3})$ containing N-methylimidazole (5% v/v) under dried dinitrogen atmosphere (C). (b) Resultant simulation due to two components [see fig. 7(c)-(f)]. (c) Subtraction of simulation [fig. 4(d)] from fig. 4(a) to yield normal low-spin cobalt species similar to that in fig. 3(a). Sharp peaks at ca. 325 mT result of imperfect simulation [see fig. 4(d)]. (d) Computer simulation of spectrum in fig. 4(c) [see tables 2(a) and 2(b)]. Stick spectra as in fig. 1(b). (e) Subtraction of fig. 4(c) from fig. 4(a) to yield second species. Note remnant of low-spin cobalt species which is due to imperfect subtraction. (f) Computer simulation of spectrum in fig. 4(e) restricted to region around 325 mT. Stick spectra as in fig. 1(b).

simulate the spectra the procedures described previously were used using the expressions for the magnetic fields at which transitions occur and the transition probabilities using second order perturbation theory.^{15,16}

The spin Hamiltonian parameters and linewidth terms $\sigma_{\rm R}$, C_{1i} and C_{2i} were determined by computer simulation of the experimental e.s.r. spectra as outlined previously.¹⁷⁻¹⁹ The actual linewidth in frequency units is

$$\sigma_i = \{\sigma_{\rm Ri}^2 + [C_{1i}v_0(B) - C_{2i}m_1]^2\}^{1/2}$$
(3)

where i = || and \perp , or, in general, x, y and z. The $\sigma_{\rm R}$ terms are residual linewidths due to dipolar broadening and/or unresolved ligand hyperfine interactions while the C_1 and

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Fig. 5. (a) X-Band e.s.r. spectrum due to an oxygenated frozen (120 K) benzene solution of (1b) $(1.0 \times 10^{-3} \text{ mol dm}^{-3})$ containing N-methylimidazole. (b) Computer simulation based on parameters in text. Stick spectra are labelled z for the common z-axis of the for g- and A-values, x (g-value), X (A-value), y (g-value), Y (A-value) and a (angular anomaly in low field). Here g and A are rotated by angle α in the xy plane [see ref. (22) for more detail about the Co–O₂ model. Stick spectra are defined as follows: z for the common g_z and A_z axes; x for the g_x axis; y for the g_y axis; X for the A_x axis; Y for the A_y axis. Here g and A principal axes make an angle of 30° above the common z axis [see ref. (22)].

 C_2 terms represent strain-induced distribution of g-values and A-values,²⁰ while $v_0(B)$ is the frequency difference between the energy levels as a function of magnetic field. Here, for both || and \perp spectra, three parameters are used to control widths of four copper transitions or eight cobalt transitions. It is assumed that the orientational dependence of the resultant linewidth is as follows

$$\sigma_{\nu}^{2} = \sigma_{\parallel}^{2} \cos^{2}\theta + \sigma_{\perp}^{2} \sin^{2}\theta \tag{4}$$

where θ is the angle between the molecular symmetry axis and the d.c. magnetic field. σ_v and $v_0(B)$ occur in the expression for the lineshape at a constant microwave frequency, v_c^{17-19}

$$S(v_{c}, B) = C \sum_{i=1}^{2} \sum_{M_{1}} \sum_{M_{N}} \sum_{\theta=0}^{\pi/2} a(i) b(M_{N}) \overline{g_{1}^{2}} f[v_{c} - v_{0}(B), \sigma_{v}] \Delta \cos \theta$$
(5)

where the a(i) terms represent isotopic abundances of copper isotopes (for cobalt that simulation is not required). The $b(M_N)$ are the binomial coefficients for equivalent nitrogens viz. 1:4:10:16:19:16:10:4:1 for four nitrogens (copper case) or 1:2:3:2:1 for two nitrogens (cobalt case).

The fundamental reason for using eqn (5) is given elsewhere.²¹

In all but one case [fig. 2(c)], spectral fits were refined using an automatic least-squares fitting routine. In that case, in contrast to all the other results considered here, three g- and A-values as well as three sets of linewidth parameters were required for the fit.

The numerical values for the spin Hamiltonian parameters for the copper(Π) chelates (1a) are listed in tables 1(a) and 1(b) where they may be compared with those obtained

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			$^{ m Cu}A_{\perp}$	$^{ m Cu}A_{\perp}$	A_{\perp}^{N}	$A_{\parallel}^{\mathrm{N}}$
	g_{\perp} g_{\parallel} $10^{-4} \mathrm{cm}^{-1}$					
(a) (1a) in benzene	2.050	2.153	27.8	215.5	16.4	16.4
(b) (1b) adsorbed on alumina	2.053	2.162	24.6	211		
copper TOPPC	2.044	2.145	17.0	220.0	17	17
copper TNPC	2.045	2.145	15.0	220.0	15.0	17.0

Table 1(a). Spin Hamiltonian parameters for (1a) and related compounds

Error values: $g \equiv \pm 0.001$; ${}^{c_u}A_{\perp} \equiv \pm 1$; ${}^{c_u}A_{\parallel} \equiv \pm 2$; A_{\perp}^{N} and $A_{\parallel}^{N} = \pm 1$.

Table 1(b). Linewidth terms for (1a) and related compounds

	$\sigma_{ m R}$ / MHz	$\sigma_{ m R\parallel} / m MHz$	<i>C</i> ₁₁	$C_{1\parallel}$	$C_{2\perp}/MHz$	$C_{2\parallel}/{ m MHz}$
(a) (1a) in benzene	11.3	7.6	0.00017	0.0	1.45	0.0064
(b) (1a) adsorbed on alumina	15.7	19.6	0.00002	0.0043	0.45	0.36
copper TOPPC	12.0	7.6	0.00002	0.0004	1.45	0.0064
copper TNPC	4.0	8.0	0.0002	0.0	1.45	0.0064

Error values: $\sigma_{R\perp}$ and $\sigma_{R\parallel} \equiv \pm 2 \text{ MHz}$; $C_{1\perp}$ and $C_{1\parallel} \equiv \pm 0.0001$; $C_{2\perp}$ and $C_{2\parallel} \equiv \pm 0.01 \text{ MHz}$.

from the copper(II) chelates of the phthalocyanines. The numerical values of the spin Hamiltonian parameters and linewidth terms for the cobalt(II) chelate (1b) in the absence and presence of various coordinating bases are presented in tables 2(a) and 2(b).

The e.s.r. spectrum due to the dioxygen adduct of cobalt(II) tdbp formed in frozen benzene solution containing N-methylimidazole may be accounted for by a molecular model of the cobalt-dioxygen group showing C_s symmetry and which accounts for the symmetry properties of the g and A matrices.²¹⁻²⁶ The spin Hamiltonian appropriate to this model is as follows

$$\mathscr{H}_{s} = \beta \sum_{i=x, y, z} g_{i} B_{i} S_{i} + \sum_{i=x, y, z} A_{j}, S_{j}, I_{j}$$
(6)

where S is the effective electron spin (1/2) and I = 7/2 for the electron nuclear spin hyperfine interaction of the cobalt centre. Here x, y and z are used to denote principal directions of the g matrix while X, Y and Z are the hyperfine coordinates on the cobalt centre. In this model it is assumed that both z and Z axes are both parallel to the molecular plane of the cobalt complexes but that the x and X axes make an angle α where the value of α is to be determined from the computer simulation.

Computer simulations were carried out as described²⁴ with the inclusion of the linewidth terms as outlined previously.¹⁸ A reasonable fit of the experimental e.s.r. spectrum due to the dioxygen adduct of the cobalt(II) chelate (**1b**) formed in frozen benzene solution containing *N*-methylimidazole was achieved using the following values of the spin Hamiltonian parameters and linewidth terms: $g_x = 2.001$; $g_y = 2.062$; $g_z = 2.005$; $A_z(X) = 5.1 \times 10^{-4} \text{ cm}^{-1}$; $A_y(Y) = 12.7 \times 10^{-4} \text{ cm}^{-1}$; $A_x(Z) = 10.4 \times 10^{-4} \text{ cm}^{-1}$; $\alpha = 30^\circ$; $\sigma_{Rx} = 13.1 \text{ MHz}$; $\sigma_{Ry} = 20 \text{ MHz}$; $\sigma_{Rz} = 8.017 \text{ Hz}$; $C_{1x} = 0.0010$; $C_{1y} = 0.0008$; $C_{1z} = 0.014$; $C_{2x} = 1.3$; $C_{2y} = 5.8$; $C_{2z} = 1.3 \text{ MHz}$.

Discussion

The e.s.r. spectral properties shown by the copper(Π) chelate (1a) are quite similar to those obtained from the various copper(Π) phthalocyanine chelates. During a study of

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			${}^{\mathrm{Co}}A_{\perp}$		$A^{ m N}_{\perp}$	$A^{\mathrm{N}}_{\parallel}$		
base	g_{\perp}	${oldsymbol{g}}_{{}_{\parallel}}$	$10^{-4} \mathrm{cm}^{-1}$					
base absent								
('dry')	2.849	1.917	25.0	150				
('wet')	2.507,	1.986	24.6	113				
· · ·	2.200							
pyridine								
(X-band)	2.179	1.994	47.8	77.5	11.5	14.9		
(S-band)	2.182	1.972	45.3	75.6	11.5	14.9		
tetrahydrofuran	2.282	1.987	24.4	108.2				
thiophene	2.253	1.995	13.3	101.5				
N-methylimidazole								
spectrum 1	2.151	1.986	55.9	73.4	11.5	14.9		
spectrum 2	1.988	1.979	3.0	17.1	3.4	5.9		
pyrrole	2.267	1.994	9.0	91.4	10.7	18.2		

Table 2(a). Spin Hamiltonian parameters for (1b) in the presence of various bases

Error values: $g \equiv \pm 0.001$; ${}^{\text{co}}A_{\perp} \equiv \pm 2$; ${}^{\text{co}}A_{\parallel} \equiv \pm 2$; ${}^{\text{N}}A_{\perp}$ and ${}^{\text{N}}A_{\parallel} \equiv \pm 1$.

base	$\sigma_{R\perp}$ /MHz	$\sigma_{R\parallel}/MHz$	$C_{1\perp}$	$C_{1\parallel}$	$C_{2\perp}$	$C_{2\parallel}$
base absent						
('dry')	10.0	57	-0.0096	-0.0008	2.0	1.6
('wet')	36.0,	38.0	-0.0053,	-0.0005	36.0,	17.0
. ,	29.0		-0.0065		4.0	
pyridine (X-band)	10.0	8.5	0.0034	0.00036	16.6	5.8
tetrahydrofuran	25.0	22.0	-0.0058	-0.00135	17.6	12.0
thiophene	17.9	13.0	-0.00057	-0.00030	21.2	9.5
N-methylimidazole						
spectrum 1	15.0	8.55	0.0034	0.00036	16.5	5.7
spectrum 2	14.8	12.2	-0.0020	-0.0017	-3.4	-2.7
pyrrole	16.4	11.4	-0.0027	-0.00035	15.2	7.0

Table 2(b). Linewidth terms for (1b) in the presence of various bases

Error values: $\sigma_{R\perp}$ and $\sigma_{R\parallel} \equiv \pm 2 \text{ MHz}$; $C_{1\perp}$ and $C_{1\parallel} \equiv \pm 0.0001$; $C_{2\perp}$ and $C_{2\parallel} \equiv \pm 0.1 \text{ MHz}$.

the chromatographic behaviour of (1a) it was noticed that (1a) is adsorbed by γ -alumina from benzene solution. After separation of the solvent, if the γ -alumina is allowed to air dry at room temperature for *ca*. 1 h, the e.s.r. spectrum recorded at *ca*. 110 K is closely similar to that observed in frozen benzene solution. When the γ -alumina is heated (322 K) for *ca*. 1 h to drive off remaining benzene, the e.s.r. spectrum due to the absorbed copper(II) chelate is completely free of superhyperfine lines in the g_{\parallel} and g_{\perp} regions of the e.s.r. spectrum. When the dried γ -alumina is further exposed to benzene the superhyperfine lines are once more observed. These results point to the role of benzene in the packing of (1a) on the surface of γ -alumina such that the presence of solvent molecules serves to keep molecules of the copper(II) chelate well separated. Removal of the solvent may result in closer packing of the copper(II) chelate molecules on the surface such that weak-magnetic dipolar interactions cause broadening which increase the residual linewidth terms as outlined in table 1 (*b*) such that the superhyperfine lines are no longer observed. The spin Hamiltonian parameters outlined in table 1 (*a*) are

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closely similar for the environments provided by the porphyrazine and phthalocyanine macrocycles while the very different peripheral substituents in the phthalocyanine system result in small changes in the parameters.

Ionically charged peripheral substituents on the porphyrazine and phthalocyanine conjugated macrocyclic ring system have a greater influence on the g-values associated with the copper(II) centre since in the copper(II) chelate of 4,11,18,25-tetramethyl-4,11,18,25-tetra-azaphthalocyanine²⁷ $g_{\parallel} = 2.189$, $g_{\perp} = 2.074$ while for the copper(II) chelate of 3,11,17,24-tetrasulphophthalocyanine²⁸ $g_{\parallel} = 2.189$, $g_{\perp} = 2.056$ with the values of the remaining spin Hamiltonian parameters being similar to those observed in the present work.

The e.s.r. spectra of low-spin cobalt(II) conjugated macrocyclic chelates may be obtained by doping the chelate into a suitable diamagnetic host lattice such as the free ligand or the corresponding nickel(II) chelate which both serve to prevent axial interactions with the cobalt(II) centre. The ligand 2,3;7,8;12,13;17,18-tetrakis-(9,10dihydroanthracene-9,10-diyl)porphyrazine though allowing the positioning of other axially bound ligands to the cobalt(II) centre provides a unique opportunity to record the e.s.r. spectrum in a non-coordinating solvent where no other axial interactions occur. In these circumstances the X-band e.s.r. spectra are characterized by high numerical values of g_{\perp} , A_{\perp} and A_{\parallel} . Upon axial ligation the predominantly d_{z^2} ground state is preserved as seen by the axial or nearly axial symmetry of the spin Hamiltonian even though the value of g_{\perp} and A_{\perp} and A_{\parallel} are all considerably reduced. Such effects are due to electron transfer and covalent overlap between the metal ion and the nitrogen ligands. The present work shows that the cobalt(II) centre of (1b) is remarkably sensitive to the water of hydration introduced during the isolation of the chelate as a dihydrate. Its axial electronic contribution is uniquely observed and qualitatively seen to change the g_{\perp} and g_{\parallel} regions of the e.s.r. spectrum due to the cobalt(II) chelate. With respect to axial coordination by pyridine the occurrence of well resolved nitrogen superhyperfine structure in part of the perpendicular spectrum, towards low field, results from the subtle interplay between $\sigma_{R\perp}$, $C_{1\perp}$ and $C_{2\perp}$. The e.s.r. spectra due to the tetrahydrofuran and thiophene solvates of (1b) require

pure solvents for their observation so that the solvation of the chelate by these solvents contrasts with the much stronger retention of water by the cobalt(II) centre. In addition, axial ligation by tetrahydrofuran and thiophene have a smaller influence on the fall in the value of A_{\parallel} observed in the absence of axial ligation though the value of A_{\parallel} is below that observed when pyridine is present in the axial position.

Axial ligation of the cobalt(II) centre in (1b) by N-methylimidazole is remarkable in giving rise to three distinct interactions which depend on the amount of reagent present. The comparison of the spin Hamiltonian parameters due to (1a) with those derived from the computer simulation of the e.s.r. spectra due to copper(II) phthalocyanines leaves the impression that the TDAP ligand properties closely resemble those of certain phthalocyanines. However, it has been suggested previously that the e.s.r. spectrum due to the N-methylimidazole complex of the cobalt(II) chelate of 4,11,18,25-tetramethyl-4,11,18,25-tetra-azaphthalocyanine, formed at quite low concentrations of the heterocyclic base, is one which involves $g_{\parallel} > g_{\perp}$ arising from an unusual ground state of cobalt(II).14 A re-evaluation of that result along the lines described here in relation to the network of spectral subtractions and simulation in fig. 7(a)-(f) led to the identification of two spectra, one due to typical low-spin cobalt(II) species and the other due to the unusual species [see fig. 7(d)] where $g_{\parallel} \approx g_{\perp} \approx 1.98$.

In the present circumstances this type of e.s.r. spectrum is observed only when, relatively, much larger amounts of N-methylimidazole are used and, while showing the porphyrazine lineage of the ligand, the e.s.r. spectrum observed at lower concentrations of N-methylimidazole is closer to that which may be expected from the cobalt(II) chelate of a phthalocyanine. The implication is that the peripheral ethenoanthracene groups in

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TDAP make a contribution to the electronic conjugation of the macrocyclic ligand similar to that of the benzenoid groups in a phthalocyanine while preserving sufficiently different electronic properties to give rise to concentration-dependent behaviour in the axial binding of N-methylimidazole to the cobalt(II) centre.

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