An Electron Spin Resonance Study* of the Dioxygen Adduct of Bis[2-(2′-pyridylmethylenehydrazonomethyl)phenolato]cobalt(II) and Related Materials

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The cobalt(II) chelates of 2-(2′-pyridylmethylenehydrazonomethyl)phenol and 2-(pyrrol-2′-ylmethylenehydrazonomethyl)phenol have low-spin forms in dimethylformamide and dimethylformamide containing pyridine. In these solvents the cobalt(II) chelates form reversible adducts with molecular oxygen. Spin-Hamiltonian parameters and linewidth terms have been evaluated from the e.s.r. spectral data of the low-spin forms of the cobalt(II) chelates and their adducts with molecular oxygen.

An earlier study of the copper(II) chelate of 2-(2′-pyridylmethylenehydrazonomethyl)phenol (HL^1) showed that the resolution of the e.s.r. spectral superhyperfine structure, due to the interaction of the electron of the copper(II) centre with the in-plane N_4 donor set provided by two ligand anions, was dependent on the axial interaction of the copper(II) centre with a heterocyclic nitrogenous base.[1] It was found that the loss of resolution of the superhyperfine structure could be quantified by consideration of the e.s.r. spectral linewidth terms. As part of a further study aimed at correlating the magnitude of the linewidth terms with structural features of transition-metal ion co-ordination, the characteristic e.s.r. spectra due to the dioxygen adduct of the cobalt(II) chelates of HL^1 and 2-(pyrrol-2′-ylmethylenehydrazonomethyl)phenol (HL^2) formed in the presence of various axial bases were studied. The formation and properties of molecular oxygen adducts by a wide variety of cobalt(II) compounds and related materials have been outlined.[2] The cobalt(II) compounds which form reversible molecular oxygen adducts at room temperature and which are characterized by well resolved e.s.r. spectra are particularly suitable for study. The cobalt(II) chelates described here possess both of these attributes.

Results

The cobalt(II) chelate of HL^1, isolated as its dihydrate, is soluble in *N,N*-dimethylformamide (dmf). The electronic spectrum (in the region of visible light) of the yellow solution of $Co(L^1)_2 \cdot 2H_2O$ in dmf containing pyridine (5%, v/v) under an atmosphere of dinitrogen is shown by Figure 1 which also shows the deepening of the colour which occurs when the solution is exposed to a stream of dioxygen. The original colour is restored by further passage of dinitrogen through the solution for some minutes. This cycle may be repeated several times without any loss of spectral intensity.

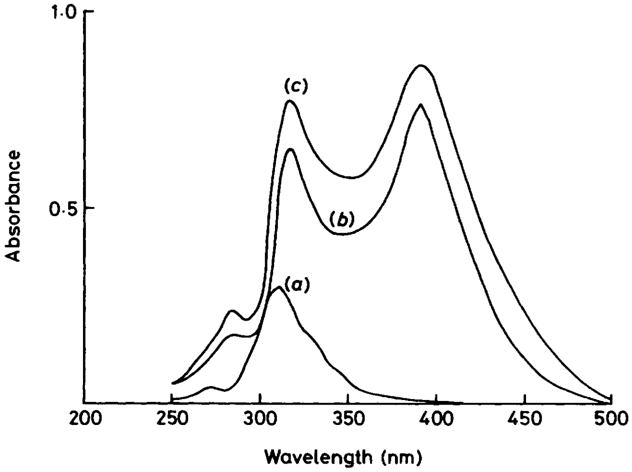

Figure 1. U.v.–visible absorption spectra using 1-cm pathlength quartz cells, of dmf solutions of (*a*) HL^1 (2.0×10^{-4} mol dm^{-3}), (*b*) $Co(L^1)_2 \cdot 2H_2O$ (2.0×10^{-4} mol dm^{-3}) containing pyridine (5%, v/v) under a dinitrogen atmosphere, and (*c*) $Co(L^1)_2 \cdot 2H_2O$ (2.0×10^{-4} mol dm^{-3}) containing pyridine (5%, v/v) exposed to a molecular oxygen atmosphere

The e.s.r. spectrum due to a frozen (77 K) solution of $Co(L^1)_2 \cdot 2H_2O$ in chloroform–dmf (1 : 1, v/v) is shown by Figure 2 and is typically that due to cobalt(II) ($3d^7$) in a low-spin state. The addition of pyridine (5%, v/v) to the solution prior to freezing brings about changes to the e.s.r. spectrum, due to the cobalt(II) chelate, shown by Figure 3. An important feature of this e.s.r. spectrum is the appearance of superhyperfine lines arising from interaction of the unpaired electron of the low-spin cobalt(II) centre with one nitrogen nucleus of an axially bound pyridine molecule. In contrast, the e.s.r. spectrum due to $Co(L^1)_2 \cdot 2H_2O$ doped (1%, w/w) into $Zn(L^1)_2 \cdot 2H_2O$, where axial base interactions are absent save possibly from the water molecules, is shown by Figure 4. The e.s.r. spectrum due to a frozen (77 K) solution of $Co(L^1)_2 \cdot 2H_2O$ in chloroform is shown by Figure 5. The complexity of this spectrum could arise from the existence of the chelate in at least two isomeric forms. Closely similar results were obtained using the cobalt(II) chelate of HL^2.

The e.s.r. spectrum due to a frozen solution of $Co(L^1)_2 \cdot 2H_2O$ in dimethyl sulphoxide (dmso) which, prior to freezing, was exposed to a stream of oxygen is illustrated by Figure 6, and shows that complete conversion to the dioxygen adduct form of the chelate takes place. As shown by Figure 7 the resolution of the high-field lines (Z, z_g) is greatly improved as a result of the oxygenation of $Co(L^1)_2 \cdot 2H_2O$ in dmf solution. On the other hand the intensity of low-field lines (Y, y_g) is enhanced as a result of the addition of pyridine (5%, v/v) to the dmf solution of the cobalt(II) chelate followed by exposure to molecular oxygen,

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* *Non-S.I. unit employed:* G = 10^{-4} T.

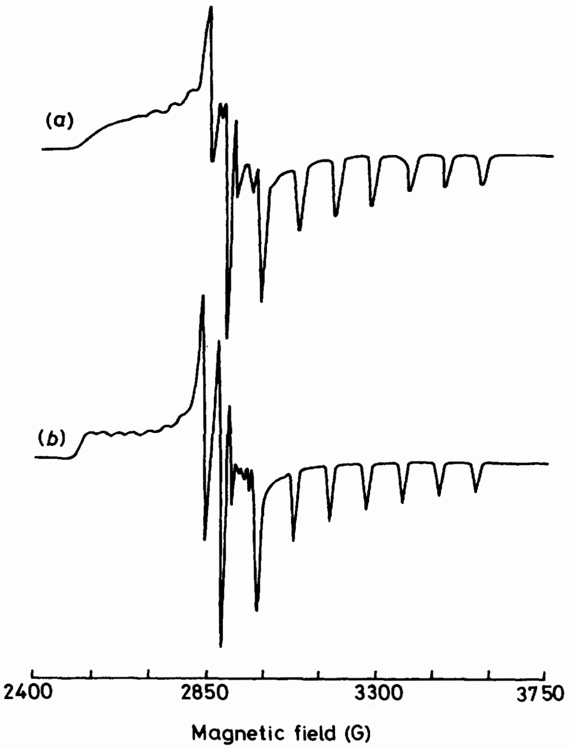

Figure 2. First-derivative X-band e.s.r. spectrum of a frozen (77 K) dmf solution due to $Co(L^1)_2{\cdot}2H_2O$ (3.0×10^{-3} mol dm^{-3}) containing chloroform (50% *v*/*v*). Microwave frequency 9.135 GHz. (*a*) Experimental spectrum. (*b*) Computer simulation using the spin-Hamiltonian parameters in Table 2(*a*) and linewidth terms in Table 2(*b*)

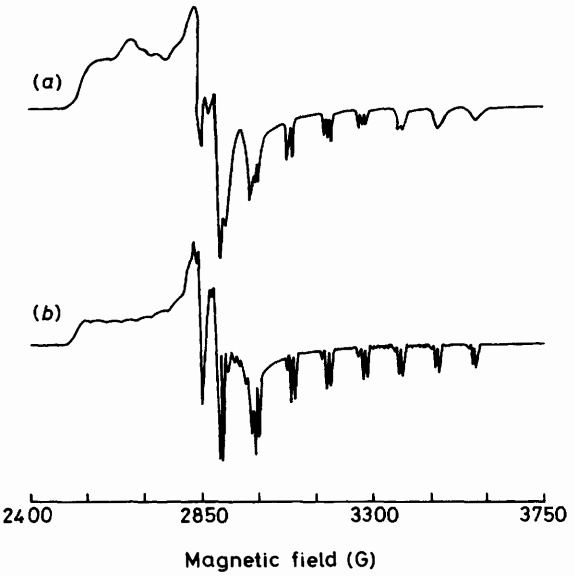

Figure 3. First-derivative X-band e.s.r. spectrum of a frozen (77 K) dmf solution due to $Co(L^1)_2{\cdot}2H_2O$ (3.0×10^{-3} mol dm^{-3}) containing pyridine (5%, v/v) under a dinitrogen atmosphere. Microwave frequency 9.135 GHz. (*a*) Experimental spectrum. (*b*) Computer simulation using the spin-Hamiltonian parameters in Table 2(*a*) and linewidth terms in Table 2(*b*)

as illustrated by Figure 8. Largely similar e.s.r. spectral results showing the same trends were obtained as a result of the oxygenation of solutions containing the cobalt(II) chelate of HL^2.

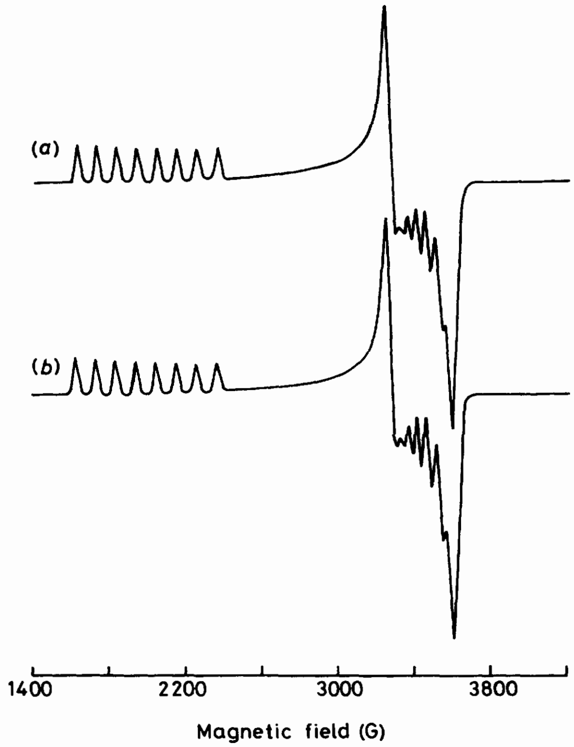

Figure 4. First-derivative X-band e.s.r. spectrum of $Co(L^1)_2{\cdot}2H_2O$ (1%, w/w) doped in $Zn(L^1)_2{\cdot}2H_2O$ at 77 K. Microwave frequency 9.135 GHz. (*a*) Experimental spectrum. (*b*) Computer simulation using the spin-Hamiltonian parameters in Table 2(*a*) and linewidth terms in Table 2(*b*)

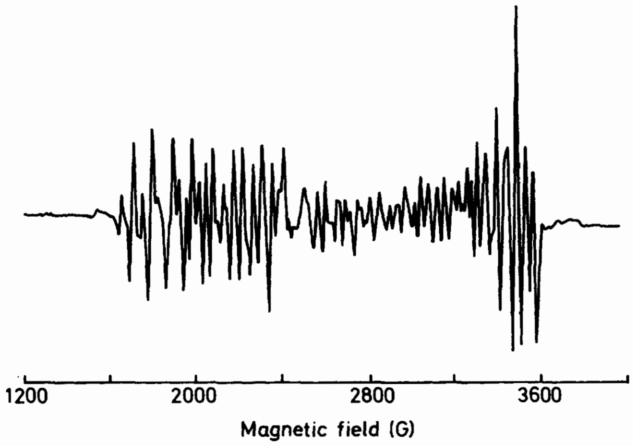

Figure 5. First-derivative X-band e.s.r. spectrum of a frozen (77 K) chloroform solution due to $Co(L^1)_2{\cdot}2H_2O$ (3.0×10^{-3} mol dm^{-3}). Microwave frequency 9.135 GHz

Interpretation of E.S.R. Spectra.—E.s.r. spectra due to low-spin forms of the cobalt(II) *chelates.* The e.s.r. spectra due to the low-spin forms of the cobalt(II) chelates of HL^1 and HL^2 are described by the following spin Hamiltonian[3–5] [equation (1)],

$$\mathscr{H} = g_{\parallel}\beta B_z S_z + g_{\perp}\beta(B_x S_x + B_y S_y) + A_{\parallel}S_z I_z + A_{\perp}(S_x I_x + S_y I_y) + P[I_z - \tfrac{1}{3}I(I+1)] - g_N\beta_N B\cdot I \quad (1)$$

where $g_{\parallel}$ and $g_{\perp}$ are the g values measured along the molecular symmetry axis (z) and in the molecular plane, respectively; $A_{\parallel}$ and $A_{\perp}$ are the corresponding hyperfine constants.

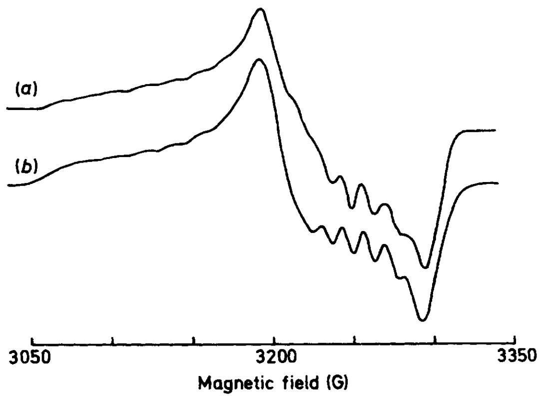

Figure 6. First-derivative *X*-band e.s.r. spectrum of a frozen (77 K) dmso solution due to the molecular oxygen adduct of $Co(L^1)_2 \cdot 2H_2O$ (3.0×10^{-3} mol dm^{-3}) exposed to a molecular oxygen atmosphere. Microwave frequency 9.135 GHz. (*a*) Experimental spectrum. (*b*) Computer simulation using the spin-Hamiltonian parameters in Table 3(*a*) and linewidth terms in Table 3(*b*)

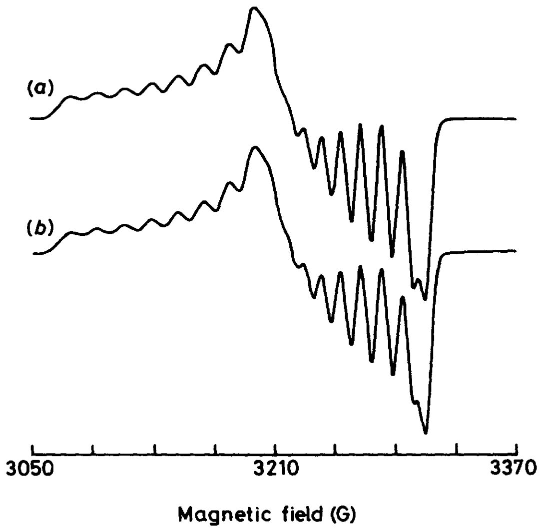

Figure 7. First-derivative *X*-band e.s.r. spectrum of a frozen (77 K) dmf solution due to the molecular oxygen adduct of $Co(L^1)_2 \cdot 2H_2O$ (3.0×10^{-3} mol dm^{-3}) exposed to a molecular oxygen atmosphere. Microwave frequency 9.135 GHz. (*a*) Experimental spectrum. (*b*) Computer simulation using the spin-Hamiltonian parameters of Table 3(*a*) and linewidth terms in Table 3(*b*)

In some cases supplementation by the ligand hyperfine term due to interactions with a ligand nuclei is necessary and accounted for as given by equation (2).

$$\mathcal{H} = \sum_{i=1}^{n} [A_{\parallel}^{N}(S_zI_{iz}) + A_{\perp}^{N}(S_xI_{iy} + S_yI_{iy}) \qquad (2)$$

In equations (1) and (2) all the terms have their usual meaning and for the cobalt(II) ion ($3d^7$), $S = \frac{1}{2}$ and $I = \frac{7}{2}$.

To simulate the spectra the procedures described previously were employed[6] with particular attention being paid to the linewidth terms σ_R, C_{1i}, and C_{2i} which have been described.[5] It was found that the computer simulations of the experimental e.s.r. spectra did not require the inclusion of quadrupole terms or the nuclear Zeeman term. The spin-Hamiltonian parameters and linewidth terms derived from computer simulation of the e.s.r. spectrum due to $Co(L^1)_2 \cdot 2H_2O$ doped into the corresponding zinc(II) chelate are shown in Table 1 and for $Co(L^1)_2 \cdot 2H_2O$ in dmf and dmf containing pyridine (5%, v/v) in Table 2.

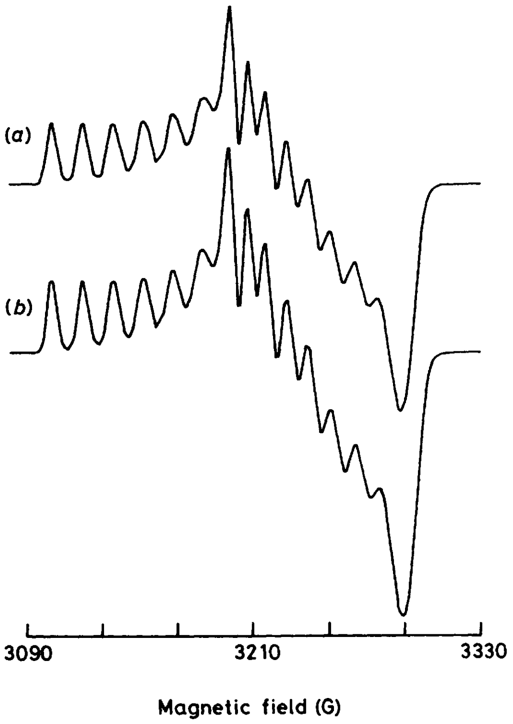

Figure 8. First-derivative *X*-band e.s.r. spectrum of a frozen (77 K) dmf solution due to the molecular oxygen adduct of $Co(L^1)_2 \cdot 2H_2O$ (3.0×10^{-3} mol dm^{-3}) containing pyridine (5%, v/v) exposed to a molecular oxygen atmosphere. Microwave frequency 9.135 GHz. (*a*) Experimental spectrum. (*b*) Computer simulation using the spin-Hamiltonian parameters in Table 3(*a*) and linewidth terms in Table 3(*b*)

E.s.r. spectra due to the dioxygen adducts of the cobalt(II) *chelates.* A molecular model of the cobalt oxygen adducts showing C_s local symmetry which takes into account the spatial disposition of the dioxygen molecule with respect to the cobalt centre, as well as the symmetry properties of the *g* and *A* tensors has been described.[2,7–10] The spin-Hamiltonian appropriate to this model is given by equation (3), where *S* is the effective

$$\mathcal{H} = \beta \sum_{i=x_g,y_g,z_g} g_iB_iS_i + \sum_{j=X,Y,Z} A_jS_jI_j \qquad (3)$$

electron spin ($\frac{1}{2}$) and $I = \frac{7}{2}$ for the electron nuclear hyperfine interaction involving cobalt. Here x_g, y_g and z_g are used to denote the *g* principal directions whereas *X*, *Y*, and *Z* are used for the hyperfine co-ordinates on the cobalt centre. Computer simulations were carried out as described[9] with the inclusion of the linewidth terms as outlined previously.[5] The numerical values of the spin-Hamiltonian parameters and linewidth terms obtained by computer simulation of the e.s.r. spectra due to the dioxygen adducts of the cobalt(II) chelates are shown in Table 3. The spin-polarization terms ($f + h$) and ($g + h$), calculated from the hyperfine values given in Table 3(*a*) as described previously,[9,10] are outlined in Table 3(*c*).

Discussion

The cobalt(II) chelates of HL^1 and HL^2 are isolated in the high-spin form as dihydrates. In frozen (77 K) chloroform the e.s.r. spectra indicate that the chelates exist in at least two low-spin isomeric forms, of which one predominates. Though

Table 1. Spin-Hamiltonian parameters (*a*) and linewidth terms (*b*) for $Co(L^1)_2 \cdot 2H_2O$ doped in $Zn(L^1)_2 \cdot 2H_2O$

(*a*)*						(*b*)†								
g_x	g_y	g_z	10^4A_x	10^4A_y	10^4A_z	σ_{Rx}	σ_{Ry}	σ_{Rz}	C_{1x}	C_{1y}	C_{1z}	C_{2x}	C_{2y}	C_{2z}
				cm^{-1}			MHz						MHz	
3.264	1.899	1.875	160	35	40	11	23	22	0.0069	0.0040	0.0040	6.0	6.0	6.0

* Error values: $g = \pm 0.001$; $A_x = \pm 2$; A_y and $A_z = \pm 1$. † Error values: $\sigma_x = \pm 2$; $\sigma_y, \sigma_z = \pm 1$; $C_1 = \pm 0.0001$; $C_2 = \pm 0.2$.

Table 2. Spin-Hamiltonian parameters (*a*) and linewidth terms (*b*) for the chelate $Co(L^1)_2 \cdot 2H_2O$; (*i*) in dmf under an N_2 atmosphere and (*ii*) in dmf containing pyridine (5%, v/v) under an N_2 atmosphere

	(*a*)[a]								
	g_x	g_y	g_z	10^4A_x	10^4A_y	10^4A_z	$10^{4N}A_x$	$10^{4N}A_y$	$10^{4N}A_z$
						cm^{-1}			
(*i*)	2.432	2.222	2.022	46	11	90			
(*ii*)	2.443	2.233	2.017	47	12	92	12	12	15

	(*b*)[b]								
	σ_{Rx}	σ_{Ry}	σ_{Rz}	C_{1x}	C_{1y}	C_{1z}	C_{2x}	C_{2y}	C_{2z}
		MHz						MHz	
(*i*)	53	12	9	0.0009	0.0009	0.0015	1.3	1.0	1.2
(*ii*)	60	14	8	0.0010	0.0007	0.0005	1.0	0.9	0.5

[a] Error values: $g = \pm 0.001$; A_x and $A_y = \pm 1$; $A_z = \pm 2$; ${}^NA = \pm 1$. [b] Error values: $\sigma_x = \pm 2$; σ_y and $\sigma_z = \pm 1$; $C_1 = \pm 0.0001$; $C_2 = \pm 0.2$.

Table 3. Spin-Hamiltonian parameters (*a*) and linewidth terms (*b*) for the molecular oxygen adducts of the cobalt(II) chelates (at *X*-band), and spin-polarization terms (*c*) deduced from hyperfine values in (*a*)

		(*a*)[a,b]						
Compound[c]		g_x	g_y	g_z	10^4A_x	10^4A_y	10^4A_z	α/°
						cm^{-1}		
$Co(L^1)_2 \cdot 2H_2O$	(*i*)	2.007	2.080	1.999	7	19	12	30
	(*ii*)	2.007	2.080	1.998	7	19	12	30
	(*iii*)	2.016	2.065	1.997	7	17	9	31
$Co(L^2)_2 \cdot 2H_2O$	(*i*)	2.007	2.078	1.998	8	18	12	30
	(*ii*)	2.008	2.080	1.999	7	19	12	30
	(*iii*)	2.008	2.078	1.996	8	19	10	30

		(*b*)[d]								
		σ_{Rx}	σ_{Ry}	σ_{Rz}	C_{1x}	C_{1y}	C_{1z}	C_{2x}	C_{2y}	C_{2z}
			MHz						MHz	
$Co(L^1)_2 \cdot 2H_2O$	(*i*)	6	15	10	−0.0008	−0.0008	−0.0014	1.4	2.1	1.4
	(*ii*)	9	3	9	−0.0005	−0.0018	−0.0030	1.0	1.0	6.6
	(*iii*)	4	5	10	−0.0010	−0.0010	−0.0015	1.3	1.0	−1.3
$Co(L^2)_2 \cdot 2H_2O$	(*i*)	14	21	17	−0.0003	−0.0004	−0.0004	3.3	5.0	4.9
	(*ii*)	4	14	5	−0.0008	−0.0008	−0.0012	1.4	2.0	1.3
	(*iii*)	4	4	12	0.0010	0.0012	0.0030	1.3	1.0	1.2

		(*c*)	
		$10^4(f + h)$	$10^4(g + h)$
		cm^{-1}	
$Co(L^1)_2 \cdot 2H_2O$	(*i*)	7.6	14.0
	(*ii*)	7.6	14.0
	(*iii*)	4.1	11.7
$Co(L^2)_2 \cdot 2H_2O$	(*i*)	6.4	11.7
	(*ii*)	7.6	14.0
	(*iii*)	4.1	12.9

[a] Error values: $g = \pm 0.001$; $A = \pm 1$; $\alpha = \pm 1$. [b] To convert hyperfine constants to MHz multiply values in table by 3, *i.e.* 19 × 3 = 57 MHz. [c] (*i*) In dmso; (*ii*) in dmf; (*iii*) in dmf containing pyridine (5%, v/v). [d] Error values: $\sigma_R = \pm 1$; $C_1 = \pm 0.0001$; $C_2 = \pm 0.2$.

Table 4. Analytical* and magnetic susceptibility data for the ligands and their cobalt(II) chelates

Compound	C	H	N	$\mu_{eff.}$
HL^1	69.45 (69.35)	4.85 (4.90)	18.55 (18.65)	
HL^2	67.80 (67.60)	5.25 (5.15)	19.85 (19.70)	
$Co(L^1)_2 \cdot 2H_2O$	57.40 (57.90)	4.60 (4.55)	15.30 (15.45)	4.38
$Co(L^2)_2 \cdot 2H_2O$	55.35 (55.50)	4.55 (4.65)	16.30 (16.20)	4.46

* Calculated values are given in parentheses.

complicated by the existence of more than one form, each is typical of four-co-ordinate chelates which take a single form when the cobalt(II) chelate is doped into the corresponding zinc(II) chelate. The values of the spin-Hamiltonian parameters are in the region of those due to cobalt(II) Schiff-base chelates which, as discussed previously, arise from a d_{yz} ground state.[7] In the co-ordinating solvent conditions presented by frozen dmf the cobalt(II) chelates exist in a single low-spin form which allows axial interaction of a single pyridine molecule and where the cobalt(II) centre is six co-ordinated. In these circumstances the linewidth term C_{2z} falls to a value which allows observation of the e.s.r. spectral superhyperfine lines arising from co-ordination of the pyridine. It is of interest to note that the presence of pyridine in the axial position does not greatly influence the magnitude of the spin-Hamiltonian parameters although the value of C_{2z} is sensitive to replacement of dmf by pyridine in the axial position.

The values of the spin-Hamiltonian parameters are not sensitive to changes in the structure of the aldazine ligand although the basicity of the pyridyl group is much greater than that of the pyrrole moiety. However in experimental terms the presence of pyridine greatly influences the resolution of the hyperfine lines particularly in the g_y region. This enhanced resolution is evident in the spin-polarization term ($f + h$) and in the linewidth terms. Qualitatively this may arise from a greater structural rigidity being imposed on the co-ordinated dioxygen molecule by the presence of pyridine in the axial position.

Experimental

The u.v.–visible, i.r., magnetic susceptibility, and e.s.r. spectral data were collected as outlined earlier.[1]

The aldazines HL^1 and HL^2 were prepared as described previously by reacting salicylaldehyde hydrazone with pyridine-2-carbaldehyde or pyrrole-2-carbaldehyde respectively.[1]

Preparation of Bis[2-(2′-*pyridylmethylenehydrazonomethyl*)-*phenolato*]*cobalt*(II) *Dihydrate*.—A dmf (50 cm^3) solution of cobalt(II) chloride hexahydrate (2.4 g) was added to a dmf solution (20 cm^3) of 2-(2′-pyridylmethylenehydrazonomethyl)-phenol (4.5 g) and the reaction mixture refluxed for 30 min. Most of the solvent was removed by distillation at reduced pressure [10 mmHg (136 × 9.8 Pa)] and the chelate isolated after addition of water (100 cm^3). The product was washed with several portions (20 cm^3) of warm (50 °C) methanol and air dried. Yield: 4.5 g, 83%

The zinc(II) chelate was prepared in a similar manner[1] as was the cobalt(II) chelate of HL^2. The elemental analyses of all the compounds and their magnetic susceptibilities are summarized in Table 4.

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