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Cobalt-mediated selective C–H bond activation. Direct aromatic hydroxylation in the complexes [Co^{III}{o-OC$_6$H$_3$(R)N=NC$_5$H$_4$N}$_2$]ClO$_4$·H$_2$O (R = H, *o*-Me/Cl, *m*-Me/Cl or *p*-Me/Cl). Synthesis, spectroscopic and redox properties

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The reactions of low-spin complexes [Co^{II}L$_3$][ClO$_4$]$_2$·H$_2$O **1** [L = 2-(arylazo)pyridine, (R)C$_6$H$_4$N=NC$_5$H$_4$N (R = H, *o*-Me/Cl, *m*-Me/Cl or *p*-Me/Cl] with *m*-chloroperbenzoic acid (*m*-ClC$_6$H$_4$CO$_3$H) in acetonitrile solvent at room temperature resulted in low-spin [Co^{III}L′$_2$]ClO$_4$·H$_2$O **2** [L′ = *o*-OC$_6$H$_3$(R)N=NC$_5$H$_4$N]. In complexes **2** the *o*-carbon–hydrogen bond of the pendant phenyl ring of both parent ligands L has been selectively and spontaneously hydroxylated. During the transformation of **1** to **2** the metal ion is oxidised from the starting Co^{II} to Co^{III}. The meridional configuration (*cis*-*trans*-*cis* with respect to the oxygen, azo and pyridine nitrogens respectively) of complexes **2** has been established by ^{1}H and ^{13}C NMR spectroscopy. When one methyl or chloro group was present at the *meta* position of the pendant phenyl ring of L the reaction resulted in two isomeric complexes due to free rotation of the singly bonded *meta*-substituted phenyl ring with respect to the azo group. In acetonitrile solvent, complexes **2** systematically display one d–d transition ($^1A_{1g} \longrightarrow {}^1T_{1g}$) near 850 nm, two metal to ligand charge-transfer transitions in the visible region and intraligand transitions in the UV region. In acetonitrile solution all complexes **2** exhibit irreversible $Co^{III} \longrightarrow Co^{IV}$ oxidation near 2 V and reversible $Co^{III} \rightleftharpoons Co^{II}$ reduction near 0.0 V *versus* Ag–AgCl. The ligand-based expected four azo (N=N) reductions are observed sequentially for all the complexes at the negative side of the reference Ag–AgCl. Complexes **2** can be quantitatively and stereoretentively reduced to the low-spin cobalt(II) congeners, [Co^{II}L′$_2$] **2**$^-$ electrochemically as well as chemically by using hydrazine hydrate. These complexes display eight-line EPR spectra in acetonitrile solution at 77 K. Complex **2a**$^-$ exhibits a ligand to metal charge-transfer transition at 534 nm and intraligand transition at 345 nm. Two possible d–d transitions, $^2E \longrightarrow {}^2T_1$ and $^2E \longrightarrow {}^2T_2$ are observed at 700 and 800 nm respectively.

Metal ion-mediated activation of carbon–hydrogen bonds of organic molecules is a fundamentally important chemical process as this may lead to the formation of various interesting products which are otherwise difficult or even impossible to synthesize by the conventional synthetic routes.[1] In this process the presence of metal ion helps to create a suitable chemical platform for the interacting molecules which in turn facilitates the desired reactions. In this article we report one such reaction where the *ortho*-carbon–hydrogen bond of the pendant phenyl ring of a 2-(arylazo)pyridine ligand (R)C$_6$H$_4$N=NC$_5$H$_4$N (L) in the cobalt complexes [Co^{II}L$_3$]$^{2+}$ **1** has been selectively and spontaneously hydroxylated in the presence of *m*-chloroperbenzoic acid at ambient temperature.

The hydroxylation of an aromatic ring is known to be an important chemical process in chemistry and biology.[2] Herein we describe the cobalt ion-mediated aromatic hydroxylation reaction in a group of seven complexes, spectroscopic characterisation of the final hydroxylated products **2**, metal- and ligand-centred electroactivities and solution characterisation of very rare low-spin cobalt(II) octahedral complexes having Co^{II}-N$_4$O$_2$ chromophores.

Results and Discussion

Synthesis

Seven 2-(arylazo)pyridine ligands used for the present study are abbreviated as L^1–L^7. The reactions of the meridional tris complexes [Co^{II}L$_3$][ClO$_4$]$_2$·H$_2$O **1** with *m*-ClC$_6$H$_4$CO$_3$H in a ratio of 1 : 4 in acetonitrile solvent at room temperature result in a bluish green solution immediately. Although the red-brown starting complexes **1** turn to bluish green immediately, stirring is continued to get the maximum yield. Chromatographic purifications of the crude green solutions on a silica gel column using chloroform–acetonitrile (2 : 1) as eluent followed by removal of solvents under reduced pressure afford pure bluish green compounds in the solid state having the composition [Co^{III}{*o*-OC$_6$H$_3$(R)N=NC$_5$H$_4$N}$_2$]ClO$_4$·H$_2$O **2** (Scheme 1). All the starting complexes **1a**–**1g** behave similarly in the presence of perbenzoic acid.

In the course of the reaction (Scheme 1) one ligand L is liberated from the co-ordination sphere of the starting tris complexes **1** and the *o*-carbon atom of the pendant phenyl ring of each of the remaining two ligands L is selectively and directly hydroxylated. The liberated ligand L has been recovered quantitatively by column chromatography. In view of the selective hydroxylation of the phenyl ring, the usual bidentate (N,N) parent ligand L has been transformed into a tridentate (O,N,N) ligand L′ and two such ligands are bound to the metal ion in a meridional fashion. During this carbon–hydrogen bond activation process the cobalt ion is oxidised from its starting bivalent state in **1** to the trivalent state in **2**. Since the reactions take place particularly under atmospheric conditions, the oxygen in air may therefore be responsible for the oxidation of the metal ion (see later).

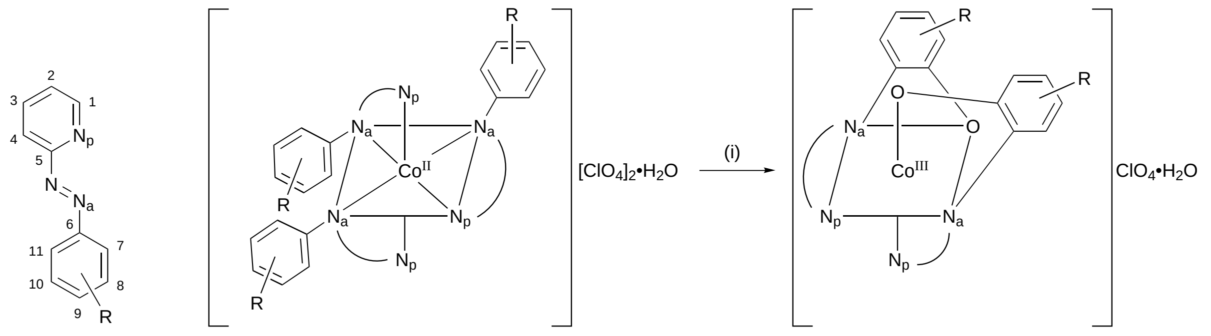
In the case of starting complexes **1d** and **1e** where one methyl group and chloride group respectively are present at the *meta* position of the active phenyl ring of each ligand, free rotation along the N_{azo}–C_{phenyl} bond may lead to the formation of three possible isomers **3**–**5**. However, an intimate mixture of isomers **3** and **4** has been detected in solution for both cases. All attempts to separate the individual isomers **3** and **4** by chromatography have failed.

Since in the absence of hydroxylating agent (perbenzoic acid)

Table 1 Microanalytical,[a] conductivity[b] and electronic spectral[b] data

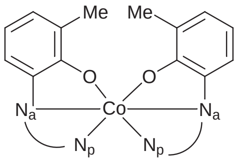
Compound	Analysis (%) C	H	N	Λ_M/Ω^{-1} cm^2 mol^{-1}	λ/nm (ε/dm^3 mol^{-1} cm^{-1})	IR/cm^{-1} ν(N=N)	ν(ClO_4^-)
2a	46.26 (46.12)	3.30 (3.14)	14.54 (14.68)	162	858 (170), 667[c] (6610), 612 (9330), 367 (24 130), 315 (8710)	1400	1140, 624
2b	47.86 (47.96)	3.62 (3.66)	14.10 (13.99)	156	846 (81), 673[c] (2600), 620 (3410), 350 (12 530), 305 (6460)	1397	1074, 627
2c	41.02 (41.16)	2.62 (2.49)	12.97 (13.09)	154	875 (30), 673[c] (2860), 614 (3860), 350 (14 520), 315 (4860)	1381	1141, 623
2d	48.13 (47.96)	3.59 (3.66)	13.85 (13.99)	160	875 (300), 686[c] (4680), 631 (6350), 392 (17 300), 301 (12 940)	1391	1095, 627
2e	41.28 (41.16)	2.59 (2.49)	12.88 (13.09)	166	878 (40), 670[c] (3370), 619 (4650), 387 (11 730), 299 (8840)	1401	1091, 630
2f	48.17 (47.96)	3.69 (3.66)	13.83 (13.99)	168	862 (350), 656[c] (6350), 603 (8340), 396 (21 840), 314 (10 930)	1380	1086, 620
2g	41.02 (41.16)	2.55 (2.49)	13.26 (13.09)	162	858 (30), 615[c] (6350), 593 (8960), 396 (24 600), 314 (7730)	1400	1090, 621

[a] Calculated values in parentheses. [b] In acetonitrile solution at 298 K. [c] Shoulder.



L[1]	R = H	**1a**	**2a**
L[2]	R = 7-Me	**1b**	**2b**
L[3]	R = 7-Cl	**1c**	**2c**
L[4]	R = 8-Me	**1d**	**2d**
L[5]	R = 8-Cl	**1e**	**2e**
L[6]	R = 9-Me	**1f**	**2f**
L[7]	R = 9-Cl	**1g**	**2g**

Scheme 1 (i) *m*-$ClC_6H_4CO_3H$, MeCN, stirring



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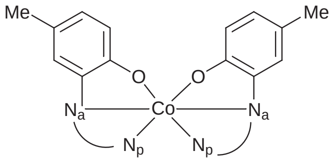

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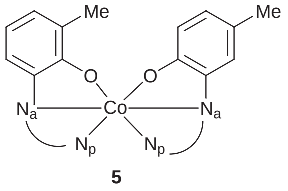

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the starting complexes **1** remain unchanged in acetonitrile medium, the possibility of the formation of any solvent-dependent reactive intermediate prior to the activation process may be ruled out. Under identical reaction conditions but in the absence of starting complexes **1** the free L fail to undergo the transformation $NC_5H_4N{=}NC_6H_4(R)H_4 \longrightarrow NC_5H_4N{=}NC_6H_3(R)OH$ which indicates the direct involvement of the metal ion in the activation process.

The microanalytical data of the products **2** (Table 1) are in good agreement with the calculated values and thus confirm the composition. Solid state magnetic moment measurements at 298 K establish that the complexes are uniformly diamagnetic (low-spin Co^{III}, t_{2g}^6, $S = 0$). In acetonitrile the complexes show 1 : 1 conductivity (Table 1). All the complexes **2** are highly soluble in polar solvents such as acetonitrile, dimethylformamide, dimethyl sulfoxide and moderately soluble in non-polar solvents like chloroform, dichloromethane, tetrahydrofuran and benzene.

Infrared spectra

The Fourier transform IR spectra of the complexes **2** were recorded as KBr discs in the region 4000–400 cm^{-1}. Selected frequencies are listed in Table 1. Two strong bands near 1580 and 1590 cm^{-1} are assigned to ν(C=C) and ν(C=N) stretching frequencies respectively and the ν(N=N) stretching frequency of the ligands is observed in between 1400 and 1380 cm^{-1}. The ν(N=N) of free L appears near 1425 cm^{-1}; this lowering in azo frequency in complexes **2** is attributed to the presence of $d_\pi(Co^{III}) \longrightarrow \pi^*(L')$ back bonding where $\pi^*(L')$ is primarily dominated by the azo function.[3] A strong and broad vibration near 1100 cm^{-1} and a strong and sharp band near 620 cm^{-1} are observed for all the complexes due to the presence of ionic perchlorate. A broad band due to water of crystallisation occurs at 3400 cm^{-1}.

Table 2 Proton and ^{13}C NMR spectral data

	^{1}H, δ(J/Hz)[a]							
Compound	H(1)	H(2)	H(3)	H(4)	H(8)	H(9)	H(10)	H(11)
2a	8.16 (5.9)[b]	6.90 (8.1, 7.8)[c]	8.10 (6.7, 7.3)[c]	8.07 (8.1)[b]	6.76 (8.9)[b]	7.38 (6.5, 7.2)[c]	7.40 (5.7, 6.4)[c]	7.61 (5.9)[b]
2b	8.14 (6.8)[b]	7.18 (7.4, 7.6)[c]	8.06 (7.4, 7.7)[c]	7.62 (6.0)[b]	6.63 (7.4)[b]	7.38 (6.5, 5.9)[c]	6.60 (10.1)[b]	2.88 (Me)
2c	8.22 (6.5)[b]	7.22 (8.3, 9.6)[c]	8.17 (8.1, 7.7)[c]	7.72 (7.2)[b]	6.70 (8.8)[b]	7.53 (6.1, 5.7)[c]	6.91 (7.38)[b]	— —
2f	8.20 (6.3)[b]	7.35 (6.7, 6.3)[c]	8.06 (6.7, 6.1)[c]	8.02 (6.9)[b]	6.55[d] —	2.25 (Me)	6.74 (9.2)[b]	7.56 (5.8)[b]
2g	8.18 (9.3)[b]	7.40 (6.2, 6.7)[c]	8.13 (9.3, 9.8)[c]	8.05 (8.3)[b]	6.80[d] —	— —	6.94 (7.7)[b]	7.54 (9.3)[b]

	^{13}C, δ(J/Hz)[e]										
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	C(11)
2a	150.54 (730)[b]	120.79 (600)[b]	144.38 (690)[b]	141.89 (630)[b]	142.28[d] —	180.88[d] —	168.36[d] —	118.43 (660)[b]	122.99 (660)[b]	125.27 (670)[b]	129.05 (690)[b]

[a] Tetramethylsilane as internal standard. [b] Doublet. [c] Triplet. [d] Singlet. [e] In $(CD_3)_2SO$.

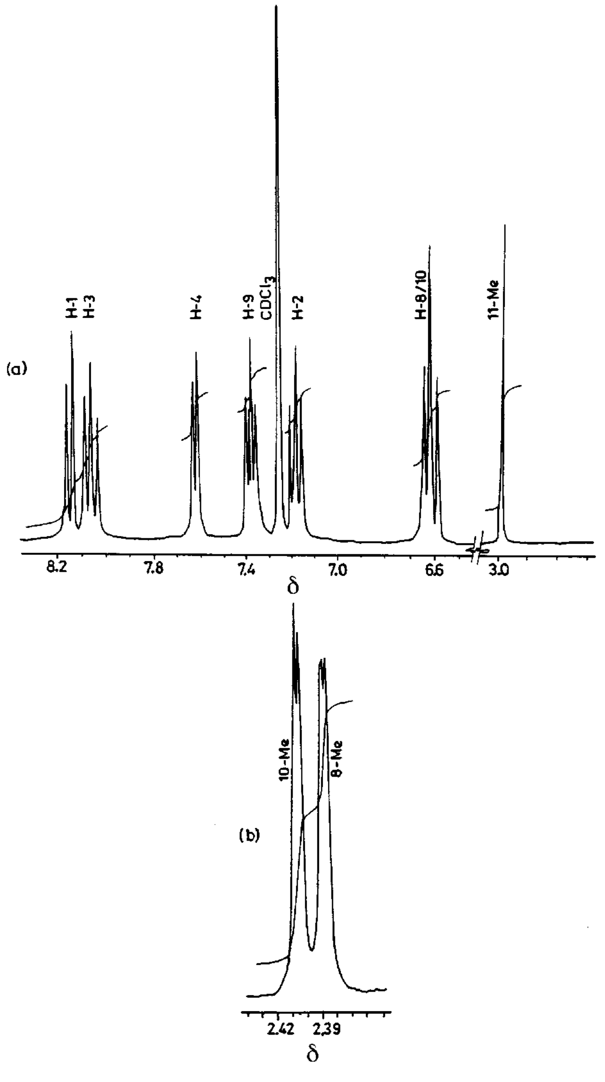


Fig. 1 Proton NMR spectra in $CDCl_3$ of (a) [Co^{III}{o-OC_6H_3(Me-o)-N=NC_5H_4N}$_2$]ClO_4·H_2O **2b** and (b) methyl peaks for [Co^{III}{o-OC_6H_3(Me-m)N=NC_5H_4N}$_2$]ClO_4·H_2O **2d**

^{1}H NMR spectra

The complexes **2a**–**2c**, **2f** and **2g** display well resolved ^{1}H NMR spectra in $CDCl_3$ solvent. Chemical shift and spin–spin splitting (among nearest neighbouring protons) values are depicted in Table 2. A representative spectrum is shown in Fig. 1(a). The individual proton resonances are assigned (Table 2) on the basis of their relative intensities, spin–spin structure and substituent induced change in splitting pattern.[4] The complex **2a** displays four doublets and four triplets having equal intensities. A direct comparison of the spectrum of complex **2a** with that of free L^1 reveals the absence of a H(7) signal for the transformed ligand $L^{1\prime}$ present in **2a**. Similarly the NMR spectra for each of the other substituted complexes (**2b**,**2c** and **2f**,**2g**) display seven signals having equal intensities indicating the absence of H(7). This absence therefore unambiguously supports the cobalt-mediated activation of the *ortho* C–H(7) bond of the pendant phenyl ring of ligand L′ in **2**.

Since the ^{1}H NMR spectra of complex **2a** and the other substituted complexes (**2b**, **2c**, **2f**, **2g**) display eight and seven proton signals respectively corresponding to one hydroxylated ligand L′ present in the complexes **2**, it can therefore be inferred that each half of the molecule **2** is equivalent due to localised mirror symmetry around the cobalt centre. Thus ^{1}H NMR spectral data imply a meridional geometry for **2** having a *cis-trans-cis* configuration with respect to oxygen, azo and pyridine nitrogens respectively (Scheme 1).

One methyl peak has been observed for each of the complexes **2b** and **2f** at δ 2.88 and 2.25 respectively as imposed symmetry makes the two ligands in **2** equivalent.

In the case of complex **2d** the aromatic region of the spectrum is complicated due to the presence of two isomers **3** and **4** in solution, however the well resolved upfield methyl signals and direct comparison of the individual methyl intensities with those of the respective aromatic protons enabled us to reach reasonable conclusions. From the symmetry point of view one methyl signal is expected for each of the isomers **3** and **4** and two equally intense peaks for isomer **5**. As the spectrum of **2d** exhibits two unequally intense methyl peaks at δ 2.39 and 2.41 respectively [Fig. 1(b)] having intensity ratio 3:4, isomers **3** and **4** are therefore predominant in solution. The downfield portion of the spectrum is overcrowded due to the partial overlapping of the aromatic protons of isomers **3** and **4** (not shown) which has precluded unequivocal assignment of the signals.

In the case of complex **2e**, the aromatic region of the spectrum is also complicated, like the spectrum of **2d**, due to the presence of a mixture of isomers. Since there is no isolated upfield signal (methyl of **2d**) in case of **2e**, it is difficult to make any conclusive statement about the nature of the isomeric mixture present. However, the aromatic proton counts match well with those of complex **2d**. In view of this we assume that in solution similar isomers **3** and **4** are also present in **2e**.

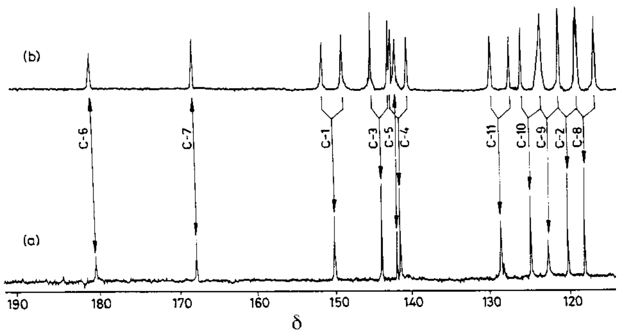


Fig. 2 Carbon-13 NMR spectra of complex $[Co^{III}(o\text{-}OC_6H_4N{=}NC_5H_4N)_2]ClO_4{\cdot}H_2O$ **2a**: (a) decoupled, (b) coupled

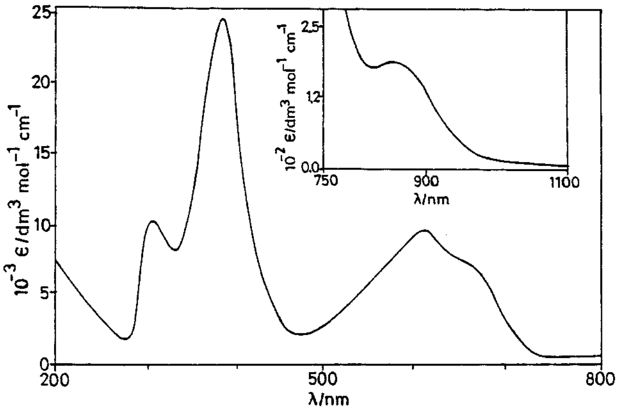


Fig. 3 Electronic spectrum of complex **2a** in acetonitrile solvent. The inset shows the low-energy d–d transition

^{13}C NMR spectra

The ^{13}C NMR spectrum of one representative complex (**2a**) was recorded in $(CD_3)_2SO$ solvent. Both the decoupled and coupled spectra are shown in Fig. 2. The chemical shift and coupling constant values are listed in Table 2. The decoupled spectrum [Fig. 2(a)] displays eleven distinct peaks corresponding to one ligand ($L^{1\prime}$) which provides further support in favour of the presence of mirror symmetry in the complex. The corresponding coupled spectrum [Fig. 2(b)] exhibits three singlets and eight doublets. The parent azopyridine ligand L^1 should exhibit two singlets [C(5) and C(6)] and nine doublets. Thus on going from ligand L^1 in the starting complex **1a** to ligand $L^{1\prime}$ in the final transformed complex **2a** one doublet [C(7)] has been changed to a singlet. This change in pattern of the C(7) signal further unequivocally establishes the activation of the C(7)–H bond of the phenyl ring. The individual carbon resonances were assigned on the basis of their electronic environments, like the proton resonances.

FAB Mass spectrum

The FAB mass spectrum of one representative complex (**2a**) was recorded. The maximum peak is observed at *m/z* 455 which corresponds to the molecular ion $[Co^{III}(NC_5H_4N{=}NC_6H_4O)_2]^+$ (calculated molecular weight 455).

Thus the FAB mass, ^1H and ^{13}C NMR spectroscopic results along with the microanalytical, conductivity, magnetic moment and IR data collectively establish the composition and stereochemistry of the complexes **2**.

Electronic spectra

Electronic spectra of the complexes **2** were recorded in acetonitrile solvent in the region 1100–200 nm. The spectral data are listed in Table 1 and a representative spectrum is shown in Fig. 3. In the visible region the complexes exhibit one intense band near 600 nm with a shoulder to lower energy near 670 nm (Table 1). On the basis of their high intensities the two bands are believed to be charge transfer in nature. Since Co^{III} in the complexes is in the low-spin t_{2g}^6 configuration, the bands near 600 and 670 nm may be due to $d_\pi(Co^{III})$ to ligand LUMO and LUMO + 1 metal to ligand charge-transfer transitions respectively, where LUMO and LUMO + 1 (LUMO = lowest unoccupied molecular orbital) are believed to be primarily dominated by the azo function and the pyridine part of the ligand respectively.[5] The other two bands in the UV region (Table 1) are presumably due to intraligand $\pi \longrightarrow \pi^*$ and $n \longrightarrow \pi^*$ transitions respectively. Here the transitions are sensitive to the nature of the substituents present in the ligand framework[6] (Table 1).

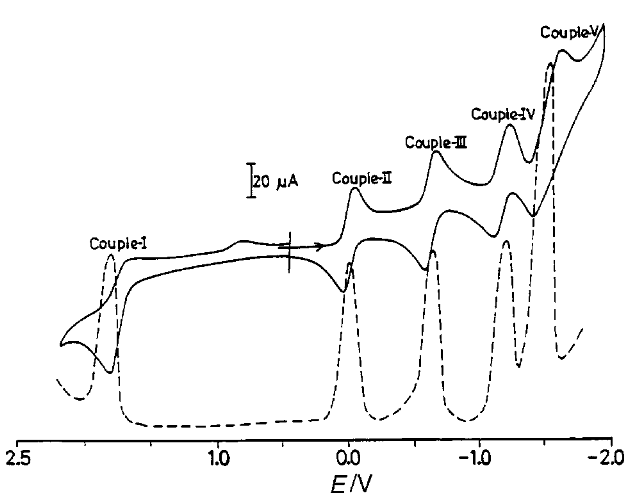


Fig. 4 Cyclic voltammogram (——) and differential pulse voltammogram (– – –) (scan rate 50 mV s^{-1}) of ≈10^{-3} mol dm^{-3} solutions of complex **2a** in acetonitrile

In the lower energy part of the visible region (≈850 nm) all the complexes systematically display one weak transition (Table 1). Based on the low intensity of this lower energy band it is considered to be due to one of the possible d–d transitions.[7] Low-spin cobalt(III) complexes are expected to exhibit two spin-allowed transitions at relatively lower energies, $^1A_{1g} \longrightarrow {}^1T_{1g}$ and $^1A_{1g} \longrightarrow {}^1T_{2g}$. The observed band near 850 nm is therefore assigned to the $^1A_{1g} \longrightarrow {}^1T_{1g}$ transition. The other higher energy transition, $^1A_{1g} \longrightarrow {}^1T_{2g}$, has not been detected and is possibly masked by the nearby intense charge-transfer transitions.

Electron-transfer properties

The electron-transfer properties of the complexes **2** have been studied in acetonitrile solution by cyclic voltammetry (CV) using a platinum working electrode. The complexes are electroactive with respect to the metal as well as ligand centres and display five redox processes in the potential range ±2.5 V *versus* Ag–AgCl electrode (tetraethylammonium perchlorate as electrolyte at 298 K). The reduction potentials are listed in Table 3 and representative voltammograms are shown in Fig. 4. The assignments of the responses to the specific couples I–V in Table 3 are made on the basis of the following considerations.

Cobalt(III)–cobalt(II) couple. In acetonitrile solvent the complexes display one reversible reduction couple (Fig. 4, couple II), E°_{298} in the region −0.1 to 0.1 V *versus* Ag–AgCl reference electrode with characteristic cathodic (E_{pc}) and anodic (E_{pa}) peak potentials. This reversible reduction process is assigned to the cobalt(III)–cobalt(II) couple, equation (1). The one-electron nature of the couple is confirmed by constant-potential coulometry (see later). The presence of the bivalent paramagnetic low-spin cobalt(II) congener ($\mathbf{2}^-$) in the reduced solution

$$[Co^{III}L'_2]^+ + e^- \rightleftharpoons [Co^{II}L'_2] \qquad (1)$$

Table 3 Electrochemical data for complexes **2** and EPR data for $\mathbf{2}^-$

	Electrochemical data[a]						
	Co^{III}–Co^{IV} Couple I	Co^{III}–Co^{II} Couple II	Ligand reductions, $E°_{298}$/V(ΔE_p/mV)			EPR data[b]	
Compound	E_{pa}[c]/V	$E°_{298}$/V(ΔE_p/mV)	Couple III	Couple IV	Couple V	g	A/G
2a	1.82	−0.005 (80)	−0.62 (80)	−1.18 (90)	−1.42 (120)	1.910	40
2b	1.75	−0.130 (80)	−0.65 (80)	−1.31 (90)	−1.49 (110)	2.006	30
2c	1.97	0.050 (90)	−0.48 (80)	−1.05 (100)	−1.20 (120)	2.005	29
2d	1.78	−0.090 (90)	−0.66 (90)	−1.26 (90)	−1.46 (130)	2.005	31
2e	1.95	0.120 (80)	−0.49 (70)	−0.96 (90)	−1.34 (120)	2.004	26
2f	1.80	−0.050 (80)	−0.63 (70)	−1.21 (90)	−1.45 (110)	1.996	25
2g	1.93	0.080 (90)	−0.52 (80)	−1.02 (100)	−1.36 (120)	2.020	24

[a] Conditions: solvent, acetonitrile; supporting electrolyte, $[NEt_4][ClO_4]$; reference electrode, Ag–AgCl; solute concentration, 10^{-3} mol dm^{-3}; working electrode, platinum. Cyclic voltammetric data: scan rate, 50 mV s^{-1}; $E°_{298} = 0.5\,(E_{pc} + E_{pa})$ where E_{pc} and E_{pa} are the cathodic and anodic peak potentials respectively. [b] In acetonitrile solution at 77 K (liquid nitrogen). [c] E_{pa} is considered due to the irreversible nature of the voltammogram.

is confirmed by an EPR study (see later). The formal potential of the couple [equation (1)] varies depending on the R group present in the ligand as expected (Table 3). Under identical experimental conditions the cobalt(III)–cobalt(II) potential for the starting complexes **1** appears in the region 0.9–1.2 V *versus* Ag–AgCl.[8] Thus on moving from the complexes **1** to **2** the Co^{III}–Co^{II} potential decreases by ≈1 V. The azopyridine ligand L is known to stabilise low-valent metal complexes (+2 in the case of Co) due to its strong π-acidic nature, and this is always reflected in high M^{II}–M^{III} oxidation potentials.[9] Hence the substantial lowering of the cobalt(III)–cobalt(II) reduction potential (≈1 V) in **2** as compared to the starting complexes **1** is primarily due to the combined effects of (i) insertion of a σ-donating phenolato oxygen atom in the selective *ortho* position of the pendant phenyl ring of L′ and (ii) removal of one strong π-acidic ligand L from the starting complexes **1**.

Ligand reduction. All the complexes **2** display three successive reversible reductions (couples III–V, Fig. 4) other than the cobalt(III)–cobalt(II) reduction (couple II). The one-electron stoichiometry of couples III and IV and the two-electron stoichiometry of couple V are established by comparison with the Co^{III}–Co^{II} reduction (couple II) with the help of the cyclic voltammetric current height as well as differential pulse voltammetry (Fig. 4). Azopyridine ligand L is known to accept two electrons in the electrochemically accessible LUMO which is predominantly azo in character.[3,6,10] Since two such electroactive azo groups are present in complexes **2**, four successive one-electron azo reductions equations (2)–(5) are expected for

$$[Co^{II}L'_2] + e^- \rightleftharpoons [Co^{II}L'(L'^{\bullet -})]^- \quad (2)$$

$$[Co^{II}L'(L'^{\bullet -})]^- + e^- \rightleftharpoons [Co^{II}(L'^{\bullet -})_2]^{2-} \quad (3)$$

$$[Co^{II}(L'^{\bullet -})_2]^{2-} + e^- \rightleftharpoons [Co^{II}(L'^{\bullet -})(L'^{2\bullet -})]^{3-} \quad (4)$$

$$[Co^{II}(L'^{\bullet -})(L'^{2\bullet -})]^{3-} + e^- \rightleftharpoons [Co^{II}(L'^{2\bullet -})_2]^{4-} \quad (5)$$

each complex. However, in practice two one-electron reductions corresponding to equations (2) and (3) appeared distinctly (couples III and IV) the other two reductions [equations (4) and (5)] being overlapped (couple V). The electrochemically generated reduced species are too unstable to isolate.

Oxidation process. Complexes **2** display an irreversible oxidation process in the region 1.8–2.0 V *versus* Ag–AgCl (Fig. 4, couple I). Although the current height of the oxidation process (i_{pa}) is ≈1.5 times more than the previously observed other reversible processes (couples II–V), the one-electron nature of couple I is determined by direct comparison of its differential pulse voltammogram peak height with those of the previous one-electron processes (Fig. 4). This irreversible oxidation process could be either due to cobalt(III)–cobalt(IV) oxidation or oxidation of the co-ordinated ligand. The former assignment seems to be more reasonable as free L does not exhibit any oxidation process within the experimental potential limit (+2.5 V). However, the possibility of the oxidation of co-ordinated L′ cannot be ruled out.

Electrochemical and chemical reductions of complexes 2

Coulometric reductions of the complexes **2** (couple II) at −0.3 V *versus* Ag–AgCl in acetonitrile solvent using a platinum-gauze working electrode under a dinitrogen atmosphere afforded a violet solution. The observed Coulomb count corresponds to one-electron transfer for all the complexes (‘n’ = 1.05, **2a**; 1.09, **2b**; 0.97, **2c**; 1.07, **2d**; 1.09, **2e**; 0.96, **2f**; 1.11, **2g**; $n = Q/Q'$, where Q' is the calculated Coulomb count for a one-electron transfer and Q is that after exhaustive electrolysis). The resulting violet reduced solutions ($\mathbf{2}^-$) display voltammograms which are superposable on those of the corresponding parent complexes **2** which suggests the stereoretentive nature of the reduction process. The electrochemical reoxidations of the reduced violet solutions regenerate the corresponding bivalent complexes **2** quantitatively. Although the reduced cobalt(II) complexes can be generated by bulk electrolysis under a dinitrogen atmosphere, the reduced species $\mathbf{2}^-$ are unstable at room temperature under atmospheric conditions which has precluded their further isolation in the solid state.

In order to confirm that the violet reduced solutions consist of cobalt(II) species as opposed to the reduced ligand, the X-band EPR spectra of the fresh solutions (produced coulometrically in acetonitrile solvent followed by quick freezing in liquid nitrogen at 77 K) of all the complexes were recorded. The spectra exhibit eight lines characteristic of hyperfine splitting by the ^{59}Co nucleus (100% natural abundance, $I = \frac{7}{2}$).[8,11]

The acetonitrile solutions of complexes **2** can also be reduced chemically to the same violet cobalt(II) complexes by hydrazine hydrate. The reduced complexes $\mathbf{2}^-$ are unstable, however we have succeeded in recording their EPR spectra by freezing the reduced solutions immediately in liquid N_2. The reduced cobalt(II) complexes $\mathbf{2}^-$ obtained either by electrochemical or chemical means exhibit identical EPR spectra. A representative spectrum is shown in Fig. 5. The centre field g values and the average hyperfine splitting (A) are given in Table 3.

Although the reduced complexes $\mathbf{2}^-$ are unstable, we have managed to record the UV/VIS spectrum of one complex ($\mathbf{2a}^-$) generated by electrochemical means. The qualitative spectrum is shown in Fig. 6. It exhibits two intense bands at 534 and 345 nm. The UV band at 345 nm is associated with a shoulder at lower energy, 420 nm. Since Co^{II} in $\mathbf{2a}^-$ is in the low-spin $t_{2g}^6e_g^1$ configuration the band at 534 nm may be due to a ligand to metal charge-transfer transition.[8] The higher energy bands at 420 and 345 nm are presumably due to intraligand n–π* and

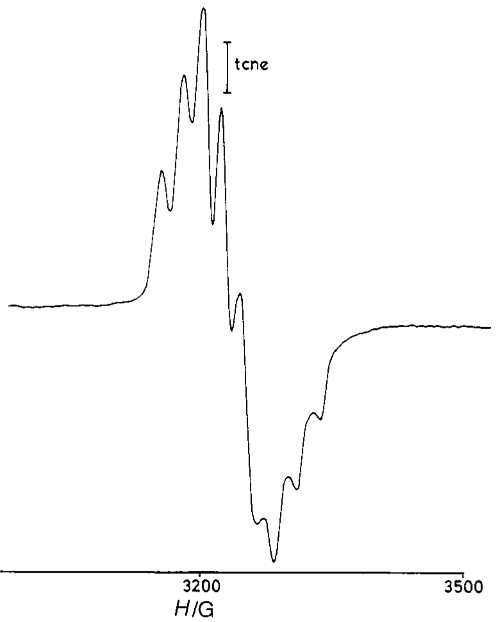


Fig. 5 X-Band EPR spectrum of chemically reduced complex **2c** in acetonitrile solution at 77 K (G = 10^{-4} T; tcne = tetracyanoethylene)

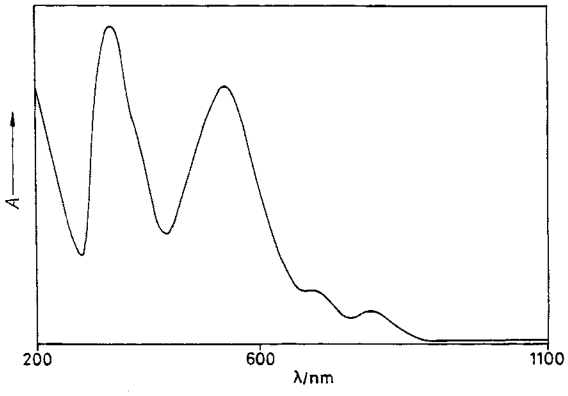
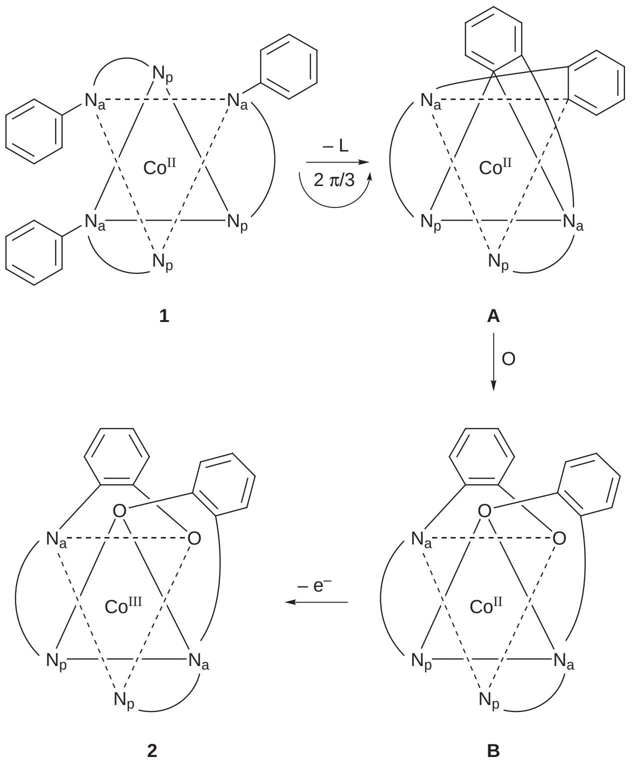


Fig. 6 Electronic spectrum of complex **2a**$^-$ in acetonitrile solvent



Scheme 2

π–π* transitions.[8] In the lower energy part of the visible region the complex displays two weak transitions at 700 and 800 nm (Fig. 6). These are believed to be possible d–d transitions, $^2E \longrightarrow {}^2T_1$ and $^2E \longrightarrow {}^2T_2$ respectively.[12]

We would like to note here that the cobalt(II) ion in an octahedral environment prefers a high-spin configuration and as a consequence low-spin octahedral cobalt(II) species are rare.[8,13] Thus the complexes **2**$^-$ provide a rare example of the low-spin cobalt(II) octahedral system and to the best of our knowledge this demonstrates the first example of low-spin cobalt(II) complexes of CoN_4O_2 chromophoric class in the solution state.

We were unable to grow suitable single crystals for X-ray characterisation, however the spectral results match well with those of structurally characterised similar ruthenium thiolated complexes.[14] This provides additional strong support particularly in favour of the proposed stereochemistry of complexes **2**.

The mechanism of the conversion of complexes **1** into **2** in the presence of perbenzoic acid is not clearly understood. The conversion involves three primary simultaneously operating steps such as (i) removal of one molecule of ligand L from the starting complex **1**, (ii) formation of a new selective C–O centre followed by metallation and (iii) oxidation of the cobalt(II) ion to cobalt(III). Since all the above steps (substitution, insertion and electron transfer) proceed rapidly without any detectable intermediate, it is difficult to draw any conclusions regarding the mechanism. However, on the basis of the available knowledge of the chemistry of associated moieties the following tentative mechanism may be proposed. Since orthometallations from the pendant phenyl ring of L[15] and related ligands such as azobenzene (PhN=NPh),[16] azophenol [$PhN{=}NC_6H_4(OH)$],[17] dihydroxyazobenzene [$(OH)C_6H_4N{=}NC_6H_4(OH)$],[17] azobenzene thioether [$(RS)C_6H_4N{=}NPh$][18] and phenolic Schiff bases [$(HO)C_6H_4N{=}C(H)Ph$,[19] $PhCH_2N{=}C(H)C_6H_4(OH)$[20]] and the labile nature of one of the ligands L of **1** are known, we assume that complex **1** may be transformed initially into a four-membered reactive intermediate (**A**, Scheme 2) as a first step of the C–H bond activation process. The insertion of oxygen, generated from the perbenzoic acid, into the four-membered reactive M–C σ bond (**A**) (if it exists) would eventually lead to the formation of **B**. Insertion of oxygen atoms (generated from perbenzoic acid) into M–C σ bonds in palladium and platinum systems has been documented.[21] The inaccessibility of the orthometallated intermediate **A** might be due to its extreme reactivity which has possibly originated from the thermodynamically unfavourable four-membered orthometallated ring. During the transformation of **1** to **2** the metal ion has been oxidised from its bivalent state in the starting complexes **1** to the trivalent state in the hydroxylated complexes **2**. The low Co^{II}–Co^{III} oxidation potential (≈0.0 V) in complexes **2** indicates the possibility of the existence of the cobalt(II) congener **B** as a reactive intermediate, which may be spontaneously oxidised by the air to the stable cobalt(III) state as in **2**. This assumption gets strong support from the experimentally observed fact that the chemically or electrochemically generated **B** is unstable under atmospheric conditions and spontaneously oxidised to the stable trivalent complexes **2**.

Further work is in progress in related cobalt systems to understand the mechanism.

Conclusion

We have observed cobalt ion-prompted direct and selective activation of the C–H bond of the pendant phenyl ring of L. This activation process in turn develops a facile aromatic hydroxylation reaction under ambient conditions. The hydroxylated complexes **2** can act as precursors for the chemical as well as electrochemical synthesis of very rare octahedral low-spin cobalt(II) complexes 2^-. They have shown a complete set of sequential electron-transfer processes which are not often observable.[22]

Experimental

Materials

Cobalt carbonate (J. T. Baker, Colorado, USA) was converted into cobalt perchlorate by the standard method. The complexes $[Co^{II}L_3][ClO_4]_2\cdot H_2O$ were prepared according to the reported procedures.[8] *m*-Chloroperbenzoic acid was obtained from Aldrich, USA. Other chemicals and solvents were reagent grade and used as received. Silica gel (60–120 mesh) used for chromatography was of BDH quality. For spectroscopic/electrochemical studies HPLC-grade solvents were used. Commercial tetraethylammonium bromide was converted into pure tetraethylammonium perchlorate by an available procedure.[22]

Physical measurements

Solution electrical conductivity was checked using a Systronic conductivity bridge-305. Electronic spectra (1100–200 nm) were recorded using a Shimadzu UV-160A spectrophotometer, Fourier-transform IR spectra on a Nicolet spectrophotometer with samples prepared as KBr pellets. Magnetic susceptibility was measured with a PAR vibrating sample magnetometer. The ^1H and ^{13}C NMR spectra were obtained with a 300 MHz Varian Fourier-transform spectrometer. Cyclic voltammetric measurements were carried out using a PAR model 273A potentiostat and galvanostat with a platinum working electrode, platinum-wire auxiliary electrode and Ag–AgCl reference electrode in a three-electrode configuration. A PAR model 273A coulometer was used for coulometry. The supporting electrolyte was NEt_4ClO_4 and the solute concentration $\approx 10^{-3}$ and $\approx 10^{-2}$ mol dm^{-3} for the cyclic voltammetric and coulometric experiments respectively. The half-wave potential $E°_{298}$ was set equal to $0.5\,(E_{pc} + E_{pa})$, where E_{pc} and E_{pa} are the cathodic and anodic cyclic voltammetric peak potentials respectively. The scan rate used was 50 mV s^{-1}. A platinum-wire gauze electrode was used for coulometry. All the experiments were carried out under a dinitrogen atmosphere. Electrochemical data were collected at 298 K and are uncorrected for the junction potential. The EPR spectra were recorded with a Varian model 109C E-line X-band spectrometer fitted with a quartz Dewar for measurements at 77 K (liquid nitrogen), and calibrated by using tetracyanoethylene (tcne, $g = 2.0023$). The elemental analyses (C,H,N) were carried out with a Carlo Erba (Italy) elemental analyser. The FAB mass spectrum at 298 K was recorded on a JEOL SX 102/DA-6000 mass spectrometer.

Preparation of complexes 2

The hydroxylated complexes **2a**–**2g** were prepared by following a general method. Details are given for complex **2a**.

Complex **1a** (100 mg, 0.12 mmol) and *m*-chloroperbenzoic acid (82.8 mg, 0.48 mmol) were dissolved separately in acetonitrile (10 cm^3). The perbenzoic acid solution was added dropwise to **1a** over a period of 15 min with stirring. The progress of the reaction was monitored by TLC. The stirring was continued for 24 h. After completion of reaction the solvent was removed under reduced pressure. The solid product thus obtained was purified by column chromatography on a silica gel column (60–120 mesh) in benzene. The excess of ligand L^1 was eluted first with chloroform–acetonitrile (5 : 1) and rejected. The pure bluish green product (**2a**) was eluted with chloroform–acetonitrile (2 : 1). Evaporation of the solvents under reduced pressure afforded pure solid **2a**. Finally the product was recrystallised from dichloromethane–hexane (1 : 4). Yields varied in the range 55–60%.

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