DALTON

Cobalt-mediated direct and selective aromatic thiolation in the complex $[Co^{III}(o\text{-}SC_6H_4N{=}NC_5H_4N)_2]ClO_4$. Synthesis, spectroscopic characterisation and electron-transfer properties

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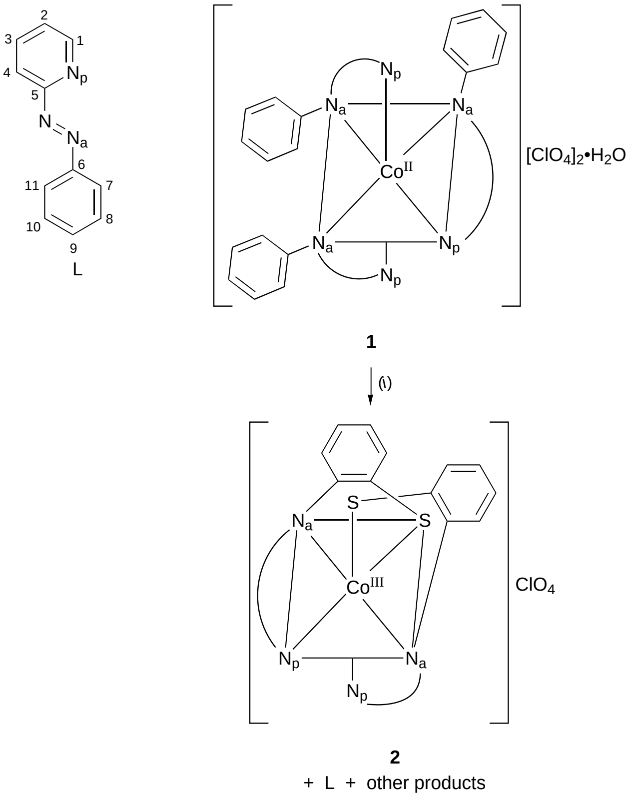
The reaction of K[SC(S)OR] (R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^i or CH_2Ph) with the complex $[Co^{II}L_3][ClO_4]_2\cdot H_2O$ **1** [L = phenyl(2-pyridyl)diazene, $C_6H_5N{=}NC_5H_4N$] in boiling dimethylformamide resulted in $[Co^{III}L'_2]ClO_4$ **2** ($L' = o\text{-}SC_6H_4N{=}NC_5H_4N$). In complex **2** the *o*-carbon–hydrogen bond of the pendant phenyl ring of both the parent ligands L has been selectively and directly thiolated *via* carbon–sulfur bond cleavage of the dithiocarbonate. During the thiolation the metal ion is oxidised from the starting Co^{II} in **1** to Co^{III} in the final product **2**. The reaction is highly sensitive to the nature of the solvent used, taking place only in those having high boiling points and relative permittivities. Its rate is dependent on the nature of the R group present in the thiolating agent, following the order Me ≈ Et > Pr^n > Bu^n > Pr^i > Bu^i ⩾ benzyl. A meridional configuration (*cis-trans-cis* with respect to the sulfur, azo and pyridine nitrogens respectively) has been established by ^{1}H and ^{13}C NMR spectroscopy. The complex exhibits reversible $Co^{III} \rightleftharpoons Co^{II}$ reduction at −0.135 V and four ligand-based azo (N=N) reductions at −0.51 (one electron) and at −1.175 V (simultaneous three-electron reduction) respectively *versus* saturated calomel electrode. The oxidation of the co-ordinated thiol group occurs at 0.90 V.

Metal-ion-mediated transformation of organic molecules is known to be an important fundamental chemical reaction.[1] One example of such processes is the metal-assisted activation of the carbon–hydrogen bond of the co-ordinated organic molecules.[2] In this process the metal ion acts as a pivot; in its presence various kinds of fascinating chemical reactions can take place which are otherwise difficult or even impossible by other available synthetic routes.[3] In this article we report one such reaction where the *o*-carbon–hydrogen bond of the pendant phenyl ring of phenyl(2-pyridyl)diazene L in the cobalt complex **1** has been selectively and directly thiolated by cleavage of the carbon–sulfur bond of an *O*-alkyl/aryl dithiocarbonate molecule.

Although aromatic thiols constitute an important class of organic compounds, the conversion of $C_6H_5{-}H$ into $C_6H_5{-}S^-$ by conventional methods involves a multistep process.[4] To the best of our knowledge this work demonstrates the first example of a first-row transition-metal-mediated direct and regiospecific thiolation of the phenyl ring. Herein we describe a detailed synthetic account of this cobalt-mediated activation of the C−H bond of the co-ordinated ligand L, spectroscopic characterisation of the final thiolated product **2**, metal- and ligand-centred electroactivities and solution EPR characterisation of the unstable reduced cobalt(II) congener.

Transition-metal-assisted carbon–sulfur bond cleavage in organic molecules and concomitant formation of a new carbon–sulfur centre are important in synthetic organic chemistry,[5] biological processes[6] as well as in industry.[7]



Scheme 1 (*i*) K[SC(S)OR] (R = Me, Et, Pr^n, Pr^i, Bu^n or CH_2Ph), dmf, heat; Np is the pyridine nitrogen and Na is the diaza one

Results and Discussion

Synthesis

The reaction of the meridional complex $[Co^{II}L_3][ClO_4]_2\cdot H_2O$ **1** with an excess of the potassium salt of *O*-ethyl dithiocarbonate in boiling dimethylformamide (dmf) solvent for 4 h results in a greenish solution. Chromatographic purification of the above crude product on a silica gel column using chloroform–acetonitrile (8 : 1) as eluent followed by removal of solvents under reduced pressure affords a pure green compound in the solid state having the composition $[Co^{III}(o\text{-}SC_6H_4N{=}NC_5H_4N)_2]ClO_4$ **2** (Scheme 1). In the course of this reaction one L is liberated from the co-ordination sphere of the starting complex **1** and the *o*-carbon atom of the pendant phenyl ring of each of the remaining two ligands L is selectively and directly thiolated *via* carbon–sulfur bond cleavage of the dithiocarbonate molecule. The liberated L has been recovered quantitatively by column chromatography. As a result of the selective thiolation of the phenyl ring the usual bidentate (N,N) parent

Table 1 Proton and ^{13}C NMR spectral data for compound **2**

	^{1}H, δ (*J*/Hz)[a]							
Solvent	H(1)	H(2)	H(3)	H(4)	H(8)	H(9)	H(10)	H(11)
$CDCl_3$	8.42 (8.4)[b]	7.19 (7.9, 8.4)[c]	8.11 (7.9, 8.4)[c]	8.20 (9.0)[b]	7.28 (8.5)[b]	7.36 (8.0, 6.8)[c]	7.46 (6.6, 7.2)[c]	7.89 (5.8)[b]
CD_2Cl_2	8.42 (7.6)[b]	7.21 (8.1, 7.5)[c]	8.15 (7.6, 8.1)[c]	8.20 (8.6)[b]	7.30 (8.1)[b]	7.41[d]	7.41[d]	7.85 (6.1)[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)
149.07 (750)[b]	120.55 (675)[b]	136.57 (645)[b]	143.12 (687)[b]	148.69[f]	165.72[f]	161.93[f]	125.38 (666)[b]	127.78 (708)[b]	128.75 (675)[b]	129.19 (660)[b]

[a] Tetramethylsilane as internal standard. [b] Doublet. [c] Triplet. [d] Complex multiplet pattern due to overlap of H(9) and H(10) resonances, centred at δ 7.41. [e] In $(CD_3)_2SO$. [f] Singlet.

ligand L has been directly transformed into the tridentate (S,N,N) ligand L′. During this activation process the cobalt is oxidised from its starting bivalent state in **1** to the trivalent state in **2**. Since the reaction takes place particularly under atmospheric conditions the oxygen in air may be responsible for the metal oxidation (see later).

To hasten the reaction a 1 : 5 ratio of complex **1** and the dithiocarbonate is used. The reaction is very sensitive to the nature of the solvent used. It does not take place in common organic solvents such as chloroform, dichloromethane, benzene, acetonitrile, methanol, ethanol, 2-methoxyethanol, ethyl benzoate, tetrahydrofuran, 2-methyltetrahydrofuran and water, whereas in high-boiling and high relative permittivity solvents like dimethylformamide, dimethyl sulfoxide, $P(NMe_2)_3O$, 1-methylpyrrolidin-2-one and *N*-methylformamide it occurs with varying degree of efficiency. Dimethylformamide was found to be the best one from a practical point of view, *i.e.* to get the maximum yield in the minimum time.

In the absence of thiolating agent, the starting complex **1** is found to be unchanged in the above-mentioned polar solvents even under reflux. Thus the formation of any solvent-dependent reactive intermediate prior to the activation process may be ruled out.

The reaction rate is dependent on the nature of the R group present in the thiolating agent. The reaction was monitored spectrophotometrically as well as on a TLC plate periodically using different dithiocarbonates K[SC(S)OR] under identical experimental conditions. The reactivity order was: Me ≈ Et > Pr^n > Bu^n > Pr^i > Bu^i ≫ benzyl, indicating a distinct role of R group.

In order to find out other suitable agents for this thiolation, the reaction (Scheme 1) was tested with benzenethiol, carbon disulfide (the precursor of the dithiocarbonate), S_8, thiirane, dithiocarbamate, $Na[S_2P(OEt)_2]$ and $Na[S_2PPh_2]$ instead of the dithiocarbonate but the desired product **2** was not formed.

Microanalytical data for complex **2** (Experimental section) confirm its composition. The complex is highly soluble in polar solvents such as acetonitrile, dimethylformamide, dimethyl sulfoxide and moderately soluble in non-polar solvents like chloroform, dichloromethane, tetrahydrofuran and benzene. In acetonitrile the complex behaves as a 1 : 1 electrolyte (conductivity value, Λ_M 155 Ω^{-1} cm^2 mol^{-1}). Solid-state magnetic moment measurement at 298 K established that the complex is diamagnetic, *i.e.* it has the low-spin t_{2g}^6 configuration.

Infrared spectrum

The Fourier-transform IR spectrum of complex **2** was recorded as a KBr disc. It exhibits several bands with variable intensities. A very strong and broad vibration at 1098 cm^{-1} and a strong and sharp band at 617 cm^{-1} are observed due to the presence of ionic perchlorate. The ν(N=N) stretching frequency appears at 1380 cm^{-1} as a strong and sharp band. Free L exhibits ν(N=N) at 1425 cm^{-1}.[8] Thus upon complexation ν(N=N) decreases which indicates the presence of $d_\pi(Co^{III}) \longrightarrow \pi^*(L')$ back bonding, where π*(L′) is primarily dominated by the azo function.

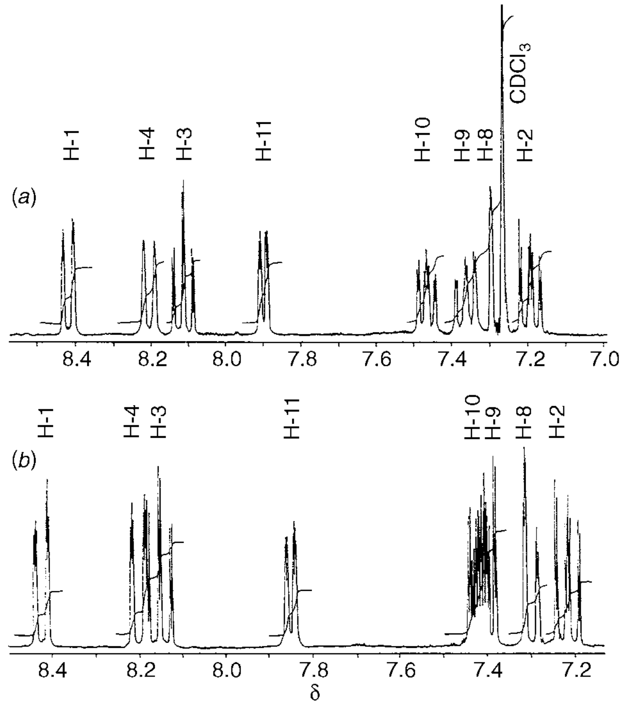


Fig. 1 Proton NMR spectra of $[Co^{III}(o\text{-}SC_6H_4N{=}NC_5H_4N)_2]ClO_4$ **2** in (*a*) $CDCl_3$ and (*b*) CD_2Cl_2

Proton NMR spectra

The ^1H NMR spectra of complex **2** were recorded in $CDCl_3$ and CD_2Cl_2 solvents. The chemical shifts and coupling constants are listed in Table 1 and the spectra are shown in Fig. 1(*a*) and 1(*b*). In both solvents the complex displays four doublets and four triplets having equal intensities. The patterns of the signal distributions in the two solvents are identical (Fig. 1). The individual proton resonances are assigned on the basis of their relative intensity, spin–spin structure and also with the help of reported proton NMR spectra of ruthenium and osmium complexes of ligand L.[9]

A direct comparison of the spectrum of complex **2** with that of free L reveals the absence of an H(7) signal for the phenyl ring in ligand L′ which is present in complex **2**. Thus the newly formed L′ ligand in **2** exhibits two doublets [H(1) and H(4)] and two triplets [H(2) and H(3)] from the pyridine ring and two doublets [H(8) and H(11)] and two triplets [H(9) and H(10)] from the phenyl ring which account for the observed eight pro-

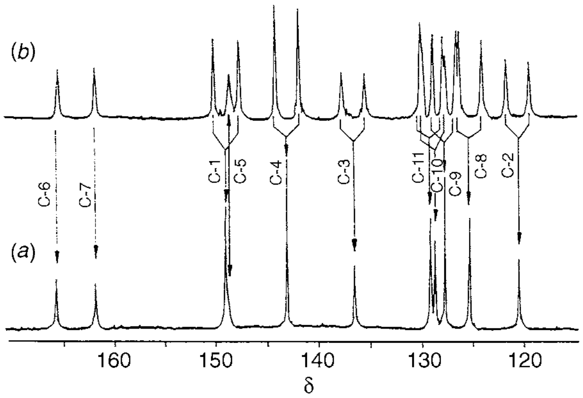


Fig. 2 Carbon-13 NMR spectra of complex **2** in $(CD_3)_2SO$: (*a*) decoupled, (*b*) coupled

tons having equal intensities. The absence of proton H(7) is therefore unambiguous support for cobalt-mediated activation of the *o*-carbon–hydrogen [C–H(7)] bond of the pendant phenyl ring of ligand L′ in **2**. The signals due to H(10), H(9) and H(2) [Fig. 1(*a*)] display multiple lines because of splitting due to coupling with the *m*-protons which are in different chemical environments.

The spectrum of the complex in $CDCl_3$ shows three distinct doublets [H(1), H(4), H(11)] and four triplets [H(3), H(10), H(9), H(2)] [Fig. 1(*a*)]. The fourth doublet [H(8)] merges partially with the $CDCl_3$ peak at δ 7.26. In order to get rid of this problem the spectrum was also recorded in CD_2Cl_2 where that particular area is transparent. The spectrum in CD_2Cl_2 displays four distinct doublets [including the H(8) doublet] and two triplets. The other two triplets due to H(9) and H(10) protons overlap each other which can be clearly understood from the relative integration values [Fig. 1(*b*)]. The chemical shifts and coupling constants of the peaks in $CDCl_3$ and CD_2Cl_2 are slightly different (see Table 1).

Since the ^1H NMR spectra in both solvents show only eight signals corresponding to one thiolated ligand L′, it can be inferred that they basically represent half of the molecule. This is possible if the molecule possesses localised mirror symmetry. Thus the ^1H NMR spectra suggest the meridional form of the complex where the co-ordinating atoms are in *cis-trans-cis* configuration with respect to the sulfur, azo and pyridine nitrogens respectively (Scheme 1).

Carbon-13 NMR spectra

The ^{13}C NMR spectrum of the complex was recorded in $(CD_3)_2SO$ as solvent. Both the decoupled and coupled spectra are shown in Fig. 2. The chemical shifts and the coupling constants are listed in Table 1. The decoupled spectrum [Fig. 2(*a*)] exhibits ten distinct and one partially overlapping peak. The eleven carbon signals correspond to one L′ ligand again indicating the presence of mirror symmetry. The corresponding coupled spectrum [Fig. 2(*b*)] shows three singlets {that corresponding to C(5) merges with the C(1) signal in the decoupled spectrum [Fig. 2(*a*)] but clearly appears in the coupled spectrum} and eight doublets. Free L should have two singlets [C(5) and C(6)] and nine doublets. Thus the change of one doublet [C(7)] to the corresponding singlet while going from ligand L in the starting complex **1** to L′ in the final complex **2** further unequivocally establishes the activation of the C(7)–H bond of the phenyl ring of L′ in **2**. The individual carbon resonances were assigned on the basis of their electronic environments, like the proton resonances.

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

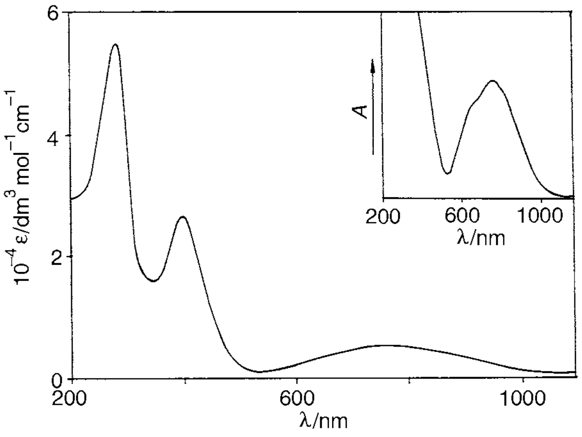


Fig. 3 Electronic spectrum of complex **2** in acetonitrile solvent. The inset shows an expansion of the lowest-energy (metal-to-ligand charge-transfer, m.l.c.t.) band

Electronic spectrum

The electronic spectrum of complex **2** was recorded in MeCN solvent (Fig. 3 and Experimental section). In the visible region the complex displays one moderately intense broad band at 786 nm with a shoulder at 664 nm and a sharp intense band at 404 nm. On the basis of their high intensities these two bands are assigned as charge transfer in nature. Since Co^{III} in complex **2** is in the low-spin t_{2g}^6 configuration, the bands at 786 and 404 nm may be due to $d_\pi(Co^{III})$ to ligand LUMO and LUMO +1 m.l.c.t. transitions respectively, where LUMO and LUMO +1 (LUMO = lowest unoccupied molecular orbital) are believed to be primarily dominated by the sulfur and the azo group and the pyridine part of the ligand respectively.[3,10]

In the UV region the complex shows one very intense transition at 280 nm which is presumably due to intraligand π–π* and/or n–π* transition involving energy levels higher than those of the ligand LUMO.

Electron-transfer properties

The electron-transfer properties of complex **2** have been studied in acetonitrile solution by cyclic voltammetry (CV) using a platinum working electrode. The complex is electroactive with respect to the metal as well as ligand centres and exhibits four redox processes in the potential range ±1.5 V *versus* saturated calomel electrode (SCE) (tetraethylammonium perchlorate as electrolyte, at 298 K). Voltammograms are shown in Fig. 4, reduction potentials in Table 2. The assignments of the responses to the specific couples I–IV in Table 2 were made on the basis of the following considerations.

The cobalt(III)–cobalt(II) couple. Complex **2** displays one reversible reductive couple (Fig. 4, couple II) with characteristic cathodic (E_{pc}) and anodic (E_{pa}) peak potentials at −0.17 and −0.10 V respectively. The cathodic and anodic peak heights (i_{pc} and i_{pa}) are equal and vary as the root square of the scan rate; E_{pc} and E_{pa} are virtually independent of the scan rate. This reversible reduction process is assigned to reduction of the trivalent cobalt(III) species to the bivalent cobalt(II) congener, equation (1).

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

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 in the reduced solution as opposed to the reduced ligand is confirmed by the characteristic eight-line EPR spectrum (Fig. 5). Under identical experimental conditions the formal potential of the

Table 2 Electrochemical data for compound **2** in acetonitrile solvent at 298 K

E°_{298}/V (ΔE_p/mV)

Ligand oxidation Couple I	Metal reduction Couple II	Ligand reduction Couple III	 Couple IV
0.90 (100)	−0.135 (70)	−0.51 (80)	−1.175 (150)

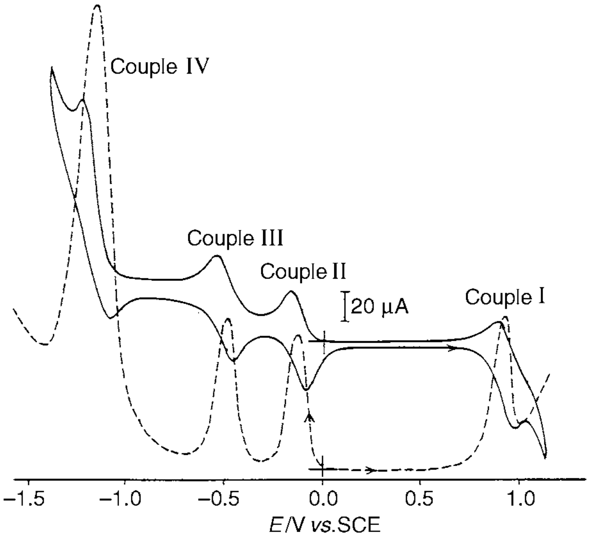


Fig. 4 Cyclic voltammograms and differential pulse voltammograms (scan rate 50 mV s^{-1}) of a ≈10^{-3} mol dm^{-3} solution of complex **2** in acetonitrile

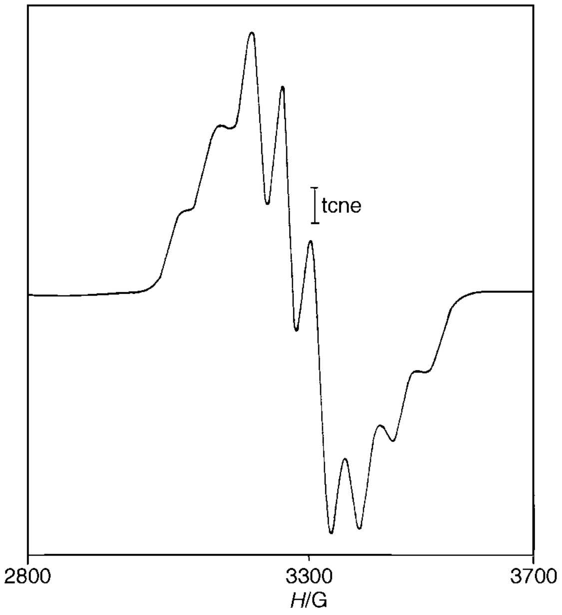


Fig. 5 X-Band EPR spectrum of chemically reduced complex **2** in acetonitrile solution at 77 K (G = 10^{-4} T; tcne = tetracyanoethylene)

cobalt(III)–cobalt(II) couple of the starting complex **1** appears at 1.1 V *versus* SCE.[11] Thus while moving from **1** to the thiolated complex **2** the formal potential of this couple decreases by 1.235 V. The parent ligand L is known to stabilise low-valent metal complexes because of its strong π-acidic character, which is always reflected in a high metal(III)–metal(II) reduction potential.[12] Therefore the more than 1 V lowering of the cobalt(III)–cobalt(II) reduction potential in **2** as compared to the starting complex **1** is primarily due to the insertion of the σ-donor thiol group in the *ortho* position of the phenyl ring of the parent ligands and also due to the removal of one strong π-acidic ligand L from **1**.

The low (<0 V *versus* SCE) cobalt(II)–cobalt(III) oxidation potential of complex **2** can account for its stabilisation in the trivalent rather than the bivalent state.

Ligand oxidation. Complex **2** exhibits a second quasi-reversible oxidation process at 0.90 V *versus* SCE (Fig. 4, couple I). Coulometric oxidation of the couple I at 1.0 V *versus* SCE at room temperature shows continuous Coulomb counts. This implies that the oxidised species rapidly decomposes on the coulometric time-scale. Although the current height of this oxidation process (i_{pa} or i_{pc}) is ≈1.5 times more than the previously observed cobalt(III)–cobalt(II) couple, the one-electron nature of couple I is confirmed by direct comparison of the differential pulse voltammogram peak height of couple I with that of the experimentally established previous couple II (Fig. 4). This oxidation process could be either due to cobalt(III)–cobalt(IV) oxidation or oxidation of the co-ordinated thiol group. The assignment to oxidation of the co-ordinated thiol group seems to be more reasonable as oxidation of thiol groups is known to be a very facile process.

Ligand reduction. The ligand L is known to act as a potential electron-transfer centre. Each ligand can accept two electrons in the electrochemically accessible LUMO which is predominantly azo in character.[8,12,13] Complex **2** contains two L′ ligands having one azo group in each, therefore four one-electron ligand-based reductions are expected, equations (2)–(5). Cyclic voltammograms of the complex exhibited two reductions (couples III and IV, Fig. 4) other than the cobalt(III)–cobalt(II) reduction (couple II), at −0.51 and −1.175 V respectively. The one- and three-electron stoichiometries of couples III and IV respectively are identified by comparison with the cobalt(III)–cobalt(II) reduction (couple I) with the help of the cyclic voltammetric current height as well as differential pulse voltammetry (Fig. 4). Thus all the expected four ligand-based reductions are observed experimentally. Instead of observing all the four ligand-based reductions separately, only the first [equation (2)] appears distinctly (couple III), the other three [equations (3)–(5)] being overlapped at −1.175 V (Fig. 4, couple IV).

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

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

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

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

Electrochemical and chemical reductions of the complex 2

Electrochemical reduction (constant-potential coulometry) of complex **2** at −0.3 V *versus* SCE in acetonitrile solvent using a platinum-gauze working electrode under a dinitrogen atmosphere generated a red-brown solution and the observed Coulomb count corresponds to one-electron transfer ('*n*' value 1.09; $n = Q/Q'$ where Q' is the calculated Coulomb count for a one-electron transfer and Q is that found after exhaustive electrolysis). The resulting reduced solution displays a voltammogram which is superposable on that of the corresponding complex **2** which implies that the reduction here may be stereoretentive in nature. When the same red-brown reduced solution was coulometrically reoxidised at 0.0 V *versus* SCE the trivalent complex **2** was formed quantitatively. The reduced species is unstable at room temperature.

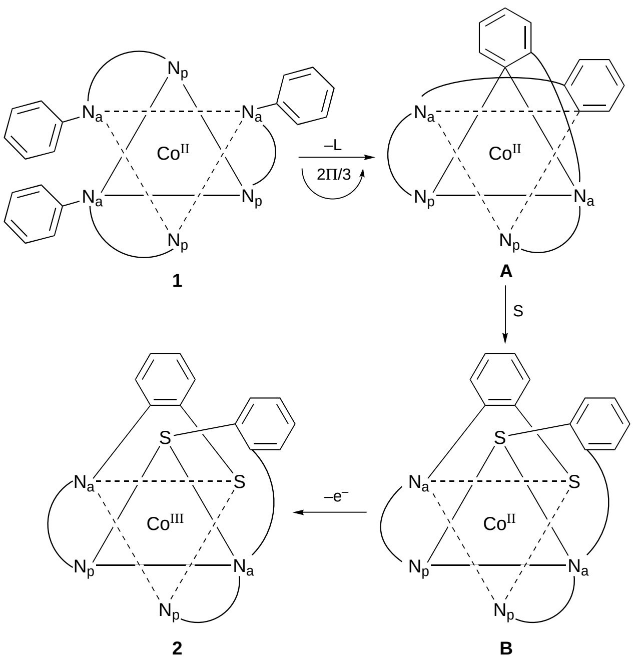
In order to confirm that the reduced solution consists of cobalt(II) species as opposed to the reduced ligand, the X-band EPR spectrum of the fresh solution (produced coulometrically in acetonitrile solvent followed by quick freezing at 77 K) was examined. It comprises eight lines characteristic of hyperfine splitting by the ^{59}Co nucleus (^{59}Co, 100% natural abundance, $I = \frac{7}{2}$).[14]

Chemical reduction of complex **2** by hydrazine hydrate in acetonitrile solvent produced the same red-brown solution. The reduced solution is unstable, however we have managed to record the EPR spectrum by freezing it immediately in liquid N_2 at 77 K. The spectrum (Fig. 5) is superposable on that of the electrochemically generated reduced solution. The centre-field *g* value and the average hyperfine splitting are 1.99 and 56 G respectively.

We were unable to grow suitable single crystals for X-ray characterisation. The complex appears to be crystalline but the crystals are invariably twinned and several attempts at structure solution met with failure. However, the spectral results match well with the structurally characterised similar ruthenium complex[3] which provides additional support in favour of the proposed stereochemistry of complex **2**.

The conversion of complex **1** into **2** formally involves several simultaneously operating functions such as (*i*) removal of molecule of ligand L from the starting **1**, (*ii*) cleavage of the C–S bond of the dithiocarbonate, (*iii*) formation of a new selective C–S centre and (*iv*) oxidation of the cobalt(II) ion to cobalt(III). As the reaction takes place particularly in high-boiling dmf and does not proceed through any stable intermediate, it is quite difficult to draw any conclusions regarding its mechanism. However, the available knowledge of the chemistry of the associated moieties may throw some light on possible reaction pathways. On that basis we assume that in high-boiling dmf and in the presence of dithiocarbonate, complex **1** may be transformed into a four-membered orthometallated reactive intermediate **A** (Scheme 2) as a first step of the C–H bond activation of the phenyl ring. Orthometallations from the pendant phenyl ring of L[15] and related ligands such as diphenyldiazene,[16] diphenyldiazene thiol,[2] $PhN{=}NC_6H_3(R)OH\text{-}2$[2] and phenolic Schiff bases[2] are known. The insertion of sulfur, generated by cleavage of the carbon–sulfur bond of the dithiocarbonate, into the M–C σ bond of the reactive four-membered cyclometallated species **A** (if it exists) would eventually lead to the formation of **B**. Insertion of small molecules into the reactive M–C bond has been documented.[15] 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 this ligand transformation the metal ion is oxidised from its bivalent to trivalent state. The low $Co^{II} \longrightarrow Co^{III}$ oxidation potential (<0.0 V) in complex **2** indicates the possibility of the existence of the cobalt(II) congener **B** as a reactive intermediate, which is spontaneously oxidised by air to the stable trivalent cobalt(III) state, **2**. This assumption obtains strong support from the experimentally observed fact that the chemically or electrochemically generated bivalent species **B** is spontaneously oxidised to the trivalent stable complex **2**.

In view of the well known lability of cobalt(II) species, alternatively we may also assume the formation of the complex $[Co^{II}L_2\{SC(S)OR\}]^+$ as a possible short-lived intermediate. At the high reaction temperature (boiling dmf) and in the presence of air, redox processes such as $Co^{II} \longrightarrow Co^{III}$ and $ROC(S)S^-$ to ROC(S)S–SC(S)OR could occur and then the disulfide could act as an ‘S’ donor as in rubber vulcanisation processes to yield the final thiolated complex **2**.



Scheme 2

This cobalt-mediated aromatic thiolation reaction is itself complex in nature. To obtain direct experimental evidence in favour of the proposed reaction pathways requires further study particularly the development of other systems where the thiolation reaction can take place under more facile experimental conditions. Work in this direction is in progress.

Conclusion

We have observed cobalt-ion-assisted carbon–sulfur bond cleavage of dithiocarbonate and direct selective activation of the C–H bond of the phenyl ring of L. This activation process in turn enables the one-pot synthesis of aromatic thiol. The thiolated compound **2** itself is reactive, particularly with respect to metal reduction and ligand oxidation. It can undergo various kinds of interesting second-stage reactions of the co-ordinated thiolated ligand (L′) and act as a stepping stone for the formation of sulfur-bridged heteropolynuclear complexes.

Experimental

Materials

Cobalt carbonate (J. T. Baker, Colorado, USA) was converted into cobalt perchlorate by the standard method. The complex $[Co^{II}L_3][ClO_4]_2\cdot H_2O$ **1**,[11] potassium salts K[SC(S)OR] (R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^i or benzyl), $Na[S_2P(OEt)_2]$ and $Na[S_2PPh_2]$ were prepared according to the reported procedures.[17,18] 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.[19] Dinitrogen gas was purified by successive bubbling through alkaline dithionite and concentrated sulfuric acid.

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 spectra on a Nicolet spectrophotometer with samples prepared as KBr pellets. Magnetic susceptibility was measured with a PAR vibrating-sample magnetometer. The ^{1}H and ^{13}C NMR spectra were obtained with a 300 MHz Varian Fourier-transform IR spectrometer. Cyclic voltammetric measurements were carried out using a PAR model 362 scanningpotentiostat electrochemistry system with a platinum-wire and auxiliary electrodes and an aqueous saturated calomel reference electrode (SCE) in a three-electrode configuration. A PAR model 279 digital coulometer was used for coulometry. The supporting electrolyte was NEt_4ClO_4 and the solute concentration ≈10^{-3} mol dm^{-3}. The half-wave potential E°_{298} was set equal to $0.5(E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are the anodic and cathodic cyclic voltammetric peak potentials respectively. The scan rate used was 50 mV s^{-1}. 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 measurement at 77 K (liquid nitrogen), and calibrated by using tetracyanoethylene ($g = 2.0023$). The elemental analyses (C, H, N, S) were carried out with a Carlo Erba (Italy) elemental analyser.

Preparation of complex 2

Complex **1** (100 mg, 0.12 mmol) was dissolved in dmf (15 cm^3) and the solution magnetically stirred with gentle heating for 10 min. To the warm solution was added potassium *O*-ethyl dithiocarbonate (99 mg, 0.61 mmol). The mixture was then heated to reflux with stirring for 4 h. The initial brown colour of **1** gradually turned to green. The progress of the reaction was monitored periodically by TLC. The solvent was removed under reduced pressure and the solid mass thus obtained was dried *in vacuo* over P_4O_{10}. The dried product was extracted by the minimum volume of chloroform and purified by using a silica gel column (60–120 mesh). With benzene (as eluent) a yellow solution due to liberated L separated first. Using chloroform–acetonitrile (8 : 1) as eluent a green band was eluted leaving behind a dark band at the top of the column. The green fraction was collected and evaporation of the solvents under reduced pressure afforded a crystalline solid. The pure product was dried *in vacuo* over P_4O_{10}. Finally the product was recrystallised from acetonitrile–benzene (1 : 6). Yield: 46 mg (65%) (Found: C, 45.2; H, 2.5; N, 14.25; S, 10.85. Calc.: C, 45.0; H, 2.7; N, 14.3; S, 10.9%). Electronic spectral data in MeCN: λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 786 (4318), 664 (3339) (sh), 404 (26 603) and 280 (54 625).

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