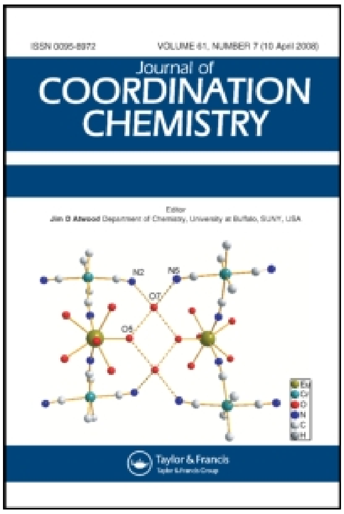

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Cobalt(III) and Low Spin Cobalt(II) Complexes of the Two Highly Flexible Hexadentate Ligands 1,3-di(*o*-salicylaldiminophenylthio)propane and 1,2-di(*o*-salicylaldiminophenylthio)xylene

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COBALT(III) AND LOW SPIN COBALT(II) COMPLEXES OF THE TWO HIGHLY FLEXIBLE HEXADENTATE LIGANDS 1,3-di(*o*-SALICYLALDIMINOPHENYLTHIO) PROPANE AND 1,2-di(*o*-SALICYLALDIMINOPHENYLTHIO)XYLENE

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The hexadentate dibasic Schiff base ligands 1,3-di(*o*-salicylaldiminophenylthio)propane (H_2DSAL PTP) and 1,2-di(*o*-salicylaldiminophenylthio)xylene (H_2DSAL PTX), with $N_2S_2O_2$ donor atoms, reacted with Co(II) salts, Co $X_2 \cdot 6H_2O$ ($X = Cl, ClO_4$), to give the complexes $[Co(DSAL\ PTP)]_2[CoCl_4]$ (**1**), $[Co(DSAL\ PTX)(NH_3)_2]$ (**2**) $[Co(DSAL\ PTP)]ClO_4$ (**3**) and $[Co(DSAL\ PTX)]ClO_4$ (**4**). H_2DSAL PTP reacted with $CoCl_2$ to provide a mixed valency complex containing Co(II) and Co(III) acceptor centres (**1**). The Co(III) centre in (**1**) is coordinated to the hexadentate ligand and the tetrachloro cobalt(II) ion is present as the counter anion. From the molecular structure of (**1**) it is observed that $[CoCl_4]^{2-}$ remains in channels in the crystal lattice. An interesting structural feature is that the anions and cations are linked in the crystal *via* hydrogen bonds. H_2DSAL PTX reacted with $CoCl_2$ in presence of NH_3 to give a low-spin, Co(II) complex (**2**) in which two NH_3 ligands are directly attached to the central metal ion. $Co(ClO_4)_2$ on the other hand, reacted smoothly with the ligands in absence of NH_3 and furnished the diamagnetic Co(III) complexes (**3**) and (**4**). Magnetic susceptibility measurements were carried out at 300 K. Cyclic voltammetric studies of all the complexes in DMF exhibit Co(II)/Co(III) redox couples at room temperature.

Keywords: Hexadentate $N_2S_2O_2$-donors; Low-spin Co(II) complex; Mixed valency Co(II)–Co(III) complex; X-ray crystal structure

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INTRODUCTION

Low-spin octahedral cobalt(II) complexes are not very common [1–3] and only a few low-spin octahedral complexes have been structurally characterised by X-ray crystallography. Although the low-spin forms are predominant at room temperature for some compounds, they generally exhibit spin equilibrium [4] at higher temperatures. Many Co(II) complexes have been shown to have ability to act as synthetic oxygen carriers. In some 1:1 cobalt(II) – oxygen adducts, tetradentate, potential oxygen-carrying, chelates are dissolved in presence of a Lewis base and then exposed to O_2. The Lewis base is found to occupy an axial position and molecular oxygen coordinated *trans* to the Lweis base [5].

This suggests that the role of the Lewis base is to stabilise the adduct by allowing octahedral coordination of the metal to be achieved upon oxygenation in solution. Square-planar and five coordinate low-spin Co(II) complexes are numerous [6], in contrast to six-coordinate species. We report here the synthesis and characterisation of a low-spin cobalt (II) complex [Co(DSAL PTX)$(NH_3)_2$] (**2**) containing two coordinated NH_3 molecules, two Co(III) complexes [Co(DSAL PTP)]ClO_4 (**3**) and [Co(DSAL PTX)]ClO_4 (**4**) along with another mixed valency complex $[Co^{III}(DSAL\ PTP)]_2[Co^{II}Cl_4]$ (**1**) in which the hexacoordinate cobalt(III) centre forms the cation and the anion is $[CoCl_4]^{2-}$. A structure determination of (**1**) by single-crystal X-ray diffraction techniques precludes any magnetic interaction between the two cobalt centres. In [Co(DSAL PTX)$(NH_3)_2$], the ligand field appears to approximate conditions suitable for the pairing of electrons thus inducing cobalt(II) to retain an essentially low-spin state.

EXPERIMENTAL

Synthesis of Ligands and Complexes

The ligands were prepared according to the method reported previously [7]. The complexes reported in the present study (**1**,**2**,**3** and **4**) were prepared by the following general procedure. To a stirred solution of the ligands (1 mmol) (H_2DSALPTP or H_2DSALPTX) in chloroform (20 cm^3), a methanolic solution (20 cm^3) of $CoCl_2 \cdot 6H_2O$ or $Co(ClO_4)_2 \cdot 6H_2O$ (1 mmol) was added and stirring was continued for 8–24 h. The products that separated out were filtered and recrystallised from methanol or acetonitrile (yields 75–80%). *Anal.* Calcd. for (**1**) (%): C, 53.1; H, 3.7; N, 4.3. Found: C, 52.9; H, 3.7; N, 4.2. Calcd. for (**3**) (%): C, 53.2; H, 3.7; N, 4.3. Found: C, 53.0; H, 3.7; N, 4.1. Calcd. for (**4**) (%): C, 56.9; H, 3.63; N, 3.9. Found: C, 56.8; H, 3.7; N, 3.8.

For the preparation of the low-spin Co(II) complex of the hexadentate ligand H_2DSALPTX (**2**), a few drops of 6(M) NH_3 were necessary to initiate the reaction and the brown compound separated out on adding pet.ether (60 – 80°) to the solution. *Anal.* Calcd. for (**2**) (%): C, 62.7; H, 4.9; N, 8.6. Found: C, 62.7; H, 5.0; N, 8.5.

Physical Measurements

Physical measurements were as reported in an earlier communication [8]. Magnetic susceptibilities were measured with a PAR 155 vibrating-sample magnetometer at 300 K. Thermal studies (TG-DTA) were performed on a Shimadzu DT-30 thermal analyser.

Crystal Structure Determination of [Co(DSAL PTP)]$_2$[CoCl$_4$] (1)

Single crystals were obtained by slow evaporation of a methanol-ether solution of [Co(DSAL PTP)]$_2$[CoCl$_4$] (**1**). A single crystal suitable for X-ray analysis was mounted on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator. CuKα($\lambda = 1.5418$ Å) radiation was employed. Unit cell parameters and the crystal orientation matrix were determined by least-squares refinements of the setting angles of 25 reflections ($10° < \theta < 20°$). Crystal and the instrument stabilities were monitored with a set of 3 standard reflections measured over 100 reflections; in all cases variations were insignificant. The collected intensity data were corrected for Lorentz and polarisation effects and an empirical absorption correction was also employed (T_{min}/T_{max} 0.466/0.991). Crystal data are summarised in Table I and non-hydrogen coordinates in Table II.

The structure was solved by the Patterson method followed by successive Fourier syntheses and refined through full-matrix least-squares on F^2 using SHELXL-97 [9] with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were constrained to ride on the respective carbon or nitrogen atom (C – H 0.93°Å) with isotropic displacement parameters equal to 1.2 times the equivalent isotropic displacement parameter of their parent atoms. The refinement of 178 least-squares variables converged to residual indices $R_1 = 0.064$ and $wR2 = 0.129$ for reflections with $I > 2\sigma(I)$. Final difference Fourier maps showed maximum and minimum peak heights as 0.586 e$Å^{-3}$ and -1.826 e$Å^{-3}$, respectively, the largest being within 1.03 Å

TABLE I Crystal data and structure refinement details for [Co(DSAL PTP]$_2$[CoCl$_4$] (**1**)

Empirical Formula	C29 H24 Co N_2 O_2 S_2 Cl_4Co_2
Formula Weight	1311.87
Crystal System	Tetragonal
Space Group	$P42_1c$
Unit cell dimensions	$a = 13.102(3)$ Å $b = 13.102(3)$ Å $c = 16.320(4)$ Å
Volume	2801.5(11) Å^3
Z	2
Density (calculated)	1.555 g cm^{-3}
Absorption coefficient	10.437 mm^{-1}
$F(000)$	1338
Crystal size	0.21 × 0.25 × 0.34 mm
Theta range for data collection	4.33 to 71.79
Index ranges	$0 \leq h \leq 15, 0 \leq k \leq 16, 0 \leq 1 \leq 20$
Reflections collected	2824
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1523/0/178
Goodness of fit on F^2	1.055
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0637$, $wR2 = 0.1291$
R indices (all data)	$R1 = 0.0761$, $wR2 = 0.138$

TABLE II Final atomic coordinates and equivalent isotropic displacement parameters (Å^2) of the non-hydrogen atoms in [Co(DSALPTP)]$_2$[CoCl$_4$]

Atom	*x/a*	*y/b*	*z/c*	*U/(eq)*
Co1	0	0	0	0.0173 (4)
Cl	0.03048 (14)	0.1398 (2)	0.07920 (11)	0.0299 (5)
Co2	1/2	0	0.63054 (7)	0.0140 (4)
S	0.62596 (15)	0.01352 (15)	0.71867 (9)	0.0252 (5)
O	0.3981 (4)	−0.0240 (4)	0.5502 (3)	0.0267 (16)
N	0.4886 (5)	0.1463 (4)	0.6318 (3)	0.0170 (14)
C1	0.3411 (6)	0.0465 (6)	0.5164 (4)	0.023 (2)
C2	0.2619 (6)	0.0136 (7)	0.4659 (4)	0.030(3)
C3	0.2034 (7)	0.0841 (7)	0.4237 (6)	0.040 (3)
C4	0.2200 (7)	0.1885 (7)	0.4309 (5)	0.039 (3)
C5	0.2976 (6)	0.2216 (6)	0.4825 (5)	0.026 (2)
C6	0.3568 (6)	0.1512 (6)	0.5261 (4)	0.022 (2)
C7	0.4314 (5)	0.1959 (5)	0.5808 (4)	0.0173 (19)
C8	0.5552 (6)	0.2026 (6)	0.6853 (4)	0.023 (2)
C9	0.5560 (7)	0.3090 (6)	0.6930 (5)	0.032 (3)
C10	0.6201 (8)	0.3558 (6)	0.7495 (5)	0.044 (3)
C11	0.6830 (8)	0.2971 (6)	0.7991 (6)	0.041 (3)
C12	0.6853 (7)	0.1927 (8)	0.7907 (5)	0.040 (3)
C13	0.6206 (5)	0.1462 (6)	0.7340 (4)	0.0213 (19)
C14	0.5917 (9)	−0.0403(7)	0.8171 (5)	0.051 (4)
C15	1/2	0	0.8622 (6)	0.074 (7)

U (eq) is defined as being 1/3 of the trace of the orthogonalized U tensor.

of the cobalt atoms. The absolute structure for the compound was chosen according to the Flack parameter [10] [x = 0.008(11)]. The largest shift/esd in the final cycle of refinement was 0.062. Complex neutral-atom scattering factors were used. All calculations were carried out using SHELXS-86 [11], SHELXL-97 [9], PARST [12] and ZORTEP [13] programs.

Structure Description

The complex [Co(DSAL PTP)]$_2$[CoCl$_4$] is comprised of [Co(DSAL PTP)]$^+$ cations and [CoCl$_4$]$^{2-}$ anions. The cation possesses distorted octahedral geometry. In the anion four chlorine atoms are coordinated to Co(II) in lightly distorted tetrahedral fashion. An ORTEP view of the cation with the atom numbering scheme is shown in Figure 1. The structure reveals that the two O-atoms and the two S-atoms (S, its symmetry related one S* ($^* = -x+1, -y, z$), O and O*] define the equatorial plane and two nitrogen atoms [N and N*] are in axial positions [N–Co2–N* = 178.8(3)°)]. The cation possesses C_2 symmetry as a two fold axis passes through Co2 atom

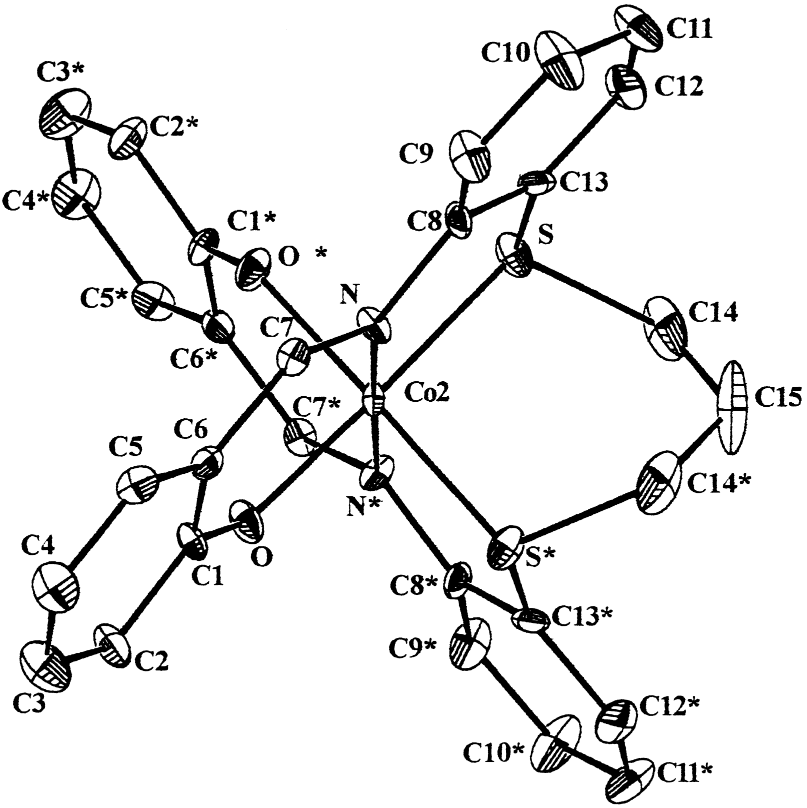

FIGURE 1 ORTEP diagram of [Co(DSAL PTP)]$_2$[CoCl$_4$].

and C15 atom (both in special position 1/2, 0,*z*). The S–Co2–S* angle for the chelating ligand is 98.18(11)° whereas O–Co2–O* is 92.6(3)°. Co–O, Co–S and Co–N bond distances are consistent with corresponding values of other analogous octahedrally coordinated cobalt complexes [14].

Another interesting structural feature is that the anions and cations are linked in the crystal structure *via* hydrogen bonds of the type Co1–Cl···H–C

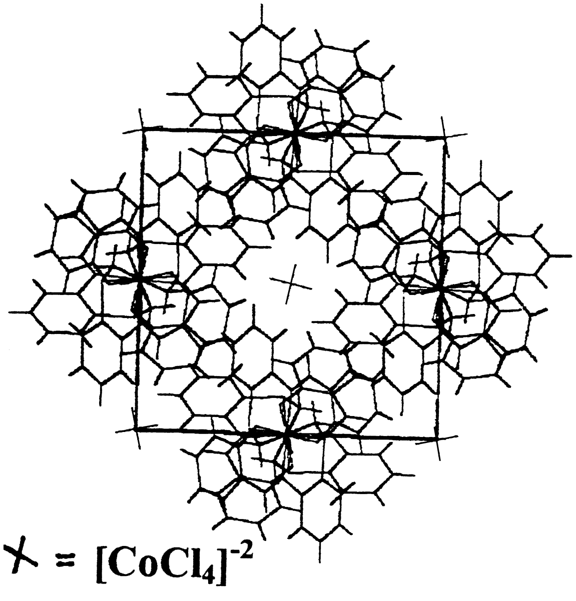

FIGURE 2 Molecular packing of $[\mathrm{Co(DSAL\ PTP)}]_2[\mathrm{CoCl_4}]$.

TABLE III Selected bond distances (Å) and bond angles (°) for $[\mathrm{Co(DSALPTP)}]_2[\mathrm{CoCl_4}]$ (**1**)

Co1–C1	2.277(2)	Co1–C1	2.277(2)
Co1–C1	2.277(2)	Co1–C1	2.277(2)
Co2–O	1.898(5)	Co2–O*	1.898(5)
Co2–N	1.923(5)	Co2–N*	1.923(5)
Co2–S	2.196(2)	Co2–S*	2.196(2)
C1–Co1–C1	110.83(10)	C1–Co1–C1	108.80(5)
C1–Co1–C1	108.80(5)	C1–Co1–C1	108.80(5)
O–Co2–O*	92.6(3)	O–Co2–N	96.8(2)
O*–Co2–N	84.1(2)	O*–Co2–N*	84.1(2)
O*–Co2–N*	96.8(2)	N–Co2–N*	178.8(3)
O–Co2–S	174.0(2)	O*–Co2–S	84.8(2)
N–Co2–S	88.3(2)	N–Co2–S*	90.8(2)
O–Co2–S*	84.8(2)	O*–Co2–S*	174.0(2)
N–Co2–S*	90.8(2)	N*–Co2–S*	88.3(2)
S–Co2–S*	98.18(11)		

in which both donor and acceptor groups are influenced by the coordination to a metal centre. Each of the anions interacts with four surrounding cations *via* C–H···Cl hydrogen bonds. A crystal packing diagram is shown in Figure 2. The relative positions of the complex cations in the crystal lattice is quite evident from this diagram. Selected bond lengths and bond angles are given in Table III.

RESULTS AND DISCUSSION

With $CoCl_2 \cdot 6H_2O$ the ligands yielded complexes $[Co(DSALPTP]_2[CoCl_4]$ (**1**) (dark green; yield: 65%) and $[Co(DSAL\ PTX)(NH_3)_2]$ (**2**) (brown; yield: 60%). For the preparation of (**2**) few drops of 6M NH_3 solution had to be added because no reaction occurred even on prolonged refluxing without the presence of NH_3. On the other hand $Co(ClO_4)_2 \cdot 6H_2O$ reacted smoothly with the ligands in the absence of NH_3 to give the corresponding green cobalt(III) complexes $[Co(DSAL\ PTP)]ClO_4$ (**3**) and $[Co(DSAL\ PTX)]ClO_4$ (**4**).

Infrared and Electronic Spectra, Magnetic Moments and Conductance

The $\nu(C{=}N)$ stretching frequency of the ligands was lowered by $10-15\,cm^{-1}$ in the complexes indicating coordination of the azomethine nitrogen to the metal centres. The $\nu(S-CH_2)$ modes of the ligands observed as split bands at $700\,cm^{-1}$ and $650\,cm^{-1}$ for $H_2DSALPTP$ and at 660 and $640\,cm^{-1}$ for $H_2DSALPTX$, are red shifted by $20-15\,cm^{-1}$ in the ir spectra of the complexes (**1**), (**3**) and (**4**), pointing to the bonding of the thioether sulfur to the metal centre except in (**2**) where no such shift was noticed. An intense band at $300\,cm^{-1}$ was attributed to $\nu_3[CoCl_4]^{2-}$ [15]. Appearance of a strong broad band centered around $1100-1090\,cm^{-1}$ (ν_3), a weak one at $950\,cm^{-1}$ (ν_1) and a sharp one at 625 (ν_4) indicated the presence of ionic perchlorate [15] in complexes (**3**) and (**4**). A broad band centred at $3140\,cm^{-1}$ observed for (**2**) may be due to $\nu(NH_3)$ [15]. The complex was found to lose two molecules of ammonia in two steps, one at 180° and the other at about 190°. Ir spectra and elemental analyses of the residues obtained after each loss gave a clear indication that the loss occurred as described and after heating the sample beyond 190° the infrared band corresponding to $\nu(NH_3)$ was found to be absent. From the TG-DTA traces the weight loss corresponded to two molecules of ammonia, which was also substantiated by elemental analysis of the two products. The complex left after the removal of ammonia was stable up to 250°C and therefore is a potential acceptor of other Lewis bases. The complex was also found to be diamagnetic in contrast to the parent complex and therefore it can be concluded that the low-spin Co(II) complex was stable only when coordinated to the Lewis base.

Electronic spectra of the complexes were recorded in DMF. The band observed at 15330 cm^{-1} for (**1**) is presumably due to the $^3T_{1g} \leftarrow {}^1A_{1g}$ transition in the octahedral cobalt(III) complex, as supported by the X-ray crystallographic data. Another high intensity band found at 16778 cm^{-1} may be due to d–d transitions in the tetrahedral Co(II) centre of the same complex. Other higher energy bands are charge-transfer transitions. For complex (**2**) two shoulders at 17241 and 21739 cm^{-1} are doublet–doublet transitions [16]. The transitions for Co(III) complexes (**3**) and (**4**) are in keeping with the presence of octahedral Co(III) centres.

Magnetic susceptibilities of (**1**) and (**2**) were determined at 300 K and μ_{eff} values of (**1**) and (**2**) were found to be 3.46 and 2.91 BM respectively. From the X-ray crystal structure it was found that complex (**1**) contains two cobalt centres, one present in an octahedral ligand environment as Co(III) and the another in a tetrahedral $CoCl_4^{2-}$ unit. Thus the magnetic susceptibility value arises from the tetrahedral Co(II) centre. Compounds (**3**) and (**4**) are diamagnetic with Co(III) centres having the usual hexacoordinate structure. Molar conductance values of complexes (**3**) and (**4**) are consistent with 1:1 electrolytes (Tab. IV). Complex (**2**) behaves as a non-electrolyte in nitromethane solution. The low conductance value observed for (**1**) may arise because of hydrogen bonding between the cation and anion as seen from its crystal structure. Moreover, the dissociated anionic part may strongly associate itself with solvent molecules imparting low mobility to the solvated anion and thus resulting in a low conductance value.

Electrochemical Studies

Cyclic voltammetric behaviours of (**1**)–(**4**) were examined in DMF solution containing TEAP as supporting electrolyte at a scan rate of 200 mV/s

TABLE IV Electrical conductivity* and magnetic moments for the complexes

	Λ_M (ohm^{-1} cm^2 mol^{-1})	μ_{eff} (300°K) ($B.M.$)
[Co(DSAL PTP)]$_2$[CoCl$_4$] (**1**)	64.4	3.46
[Co(DSALPTX)(NH$_3$)$_2$] (**2**)	3.2	2.91
[Co(DSALPTP)]ClO$_4$ (**3**)	81.6	Diamagnetic
[Co(DSALPTX)]ClO$_4$ (**4**)	81.8	Diamagnetic

* Measured in nitromethane.

TABLE V Electrochemical data† for the complexes

Complex	$E_{1/2}(V)$	$\Delta E_p(mV)$	$E_{pa}(V)$	$E_{pc}(V)$
$[Co(DSALPTP)]_2[CoCl_4]$ (**1**)	−0.14	65	0.75	
$[Co(DSALPTX)(NH_3)_2]$ (**2**)			0.2	−0.7
$[Co(DSALPTP)]ClO_4$ (**3**)	−0.15	60		
$[Co(DSALPTX)]ClO_4$ (**4**)	−0.17	60		

† In DMF (0.1 MTEAP) at a platinum electrode with an Ag/AgCl reference electrode; scan rate 200 mVs^{-1}; $E_{1/2} = 0.5(E_{pa} + E_{pc})$, $\Delta E_p = E_{pc} - E_{pa}$, where E_{pc} and E_{pa} are cathodic and anodic peak potentials, respectively.

(Tab. V). Cyclic voltammograms of (**1**) exhibited one well-defined reversible reduction couple at −0.14 V ($\Delta E_p = 65$ mV) corresponding to the Co(III)/Co(II) couple. An irreversible anodic peak is observed at 0.75 V (E_{pa}) probably due to oxidation of the Co(II) site to Co(III). For complex (**2**) one irreversible Co(II)/Co(I) reduction couple is located at −0.70 V (E_{pc}). On the positive side an irreversible oxidation corresponding to the Co(II)/Co(III) couple was observed at 0.2 V (E_{pa}), absent on initial positive scan but appearing after the cathodic process. This is most probably due to Co(II) to Co(III) oxidation after the ligand has undergone change. Complexes (**3**) and (**4**) display one reversible Co(III)/Co(II) reduction couple at −0.15 and −0.17 V ($\Delta E_p = 60$ mV), respectively.

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Supplementary Data

Full lists of crystallographic data are available from the authors upon request.

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