Cobalt(II) and cobalt(III) complexes of thioether-containing hexadentate pyrazine amide ligands: C–S bond cleavage and cyclometallation reaction†‡

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Anaerobic reaction of $\mathrm{Co(O_2CMe)_2{\cdot}4H_2O}$ with the thioether-containing acyclic pyrazine amide hexadentate ligand 1,4-bis[*o*-(pyrazine-2-carboxamidophenyl)]-1,4-dithiobutane ($\mathrm{H_2\mathbf{L}^1}$) ($\mathrm{-CH_2CH_2-}$ spacer between the two pyrazine amide tridentate coordination units) furnishes $\mathrm{[Co^{II}(\mathbf{L}^1)]{\cdot}MeOH}$ (**1a**) having $\mathrm{CoN_2}$(pyrazine)$\mathrm{N'_2}$(amide)$\mathrm{S_2}$(thioether) coordination. It exhibits an eight-line EPR spectrum, attesting to a low-spin ($S = 1/2$) state of $\mathrm{Co^{II}}$. A similar reaction in air, however, furnishes $\mathrm{[Co^{III}(\mathbf{L}^{3a})(\mathbf{L}^{3b})]{\cdot}2MeOH}$ (**2a**) ($S = 0$), resulting from a C–S bond cleavage reaction triggered by an acetate ion as a base, having $\mathrm{CoN_2}$(pyrazine)$\mathrm{N'_2}$(amide)S(thioether)S′(thiolate) coordination. On the other hand, the reaction of $\mathrm{Co(O_2CMe)_2{\cdot}4H_2O}$ with 1,4-bis[*o*-(pyrazine-2-carboxamidophenyl)]-1,5-dithiopentane ($\mathrm{H_2\mathbf{L}^2}$) ($\mathrm{-CH_2CH_2CH_2-}$ spacer between the two pyrazine amide tridentate coordination units) in air affords a cobalt(II) complex $\mathrm{[Co^{II}(\mathbf{L}^2)]{\cdot}MeOH}$ (**1b**·MeOH) ($S = 1/2$); its structurally characterized variety has the composition $\mathbf{1b}{\cdot}\mathrm{C_6H_6}$. Interestingly, **1b**·MeOH undergoes facile metal-centred oxidation by aerial $\mathrm{O_2{-}H_2O_2{-}[Fe(\eta^5\text{-}C_5H_5)_2][PF_6]}$, which led to the isolation of the corresponding cobalt(III) complex $\mathrm{[Co^{III}(\mathbf{L}^2)][ClO_4]}$ (**2b**). When treated with methanolic KOH, **2b** affords a low-spin ($S = 0$) organocobalt(III) complex $\mathrm{[Co^{III}((\mathbf{L}^{2'})]}$ (**3**). Structures of all complexes, except **1a**, have been authenticated by X-ray crystallography. A five-membered chelate-ring forming ligand $\mathbf{L}^1(2-)$ effects C–S bond cleavage and a six-membered chelate-ring forming ligand $\mathbf{L}^2(2-)$ gives rise to Co–C bond formation, in cobalt(III)-coordinated thioether functions due to α C–H bond activation by the base. A rationale has been provided for the observed difference in the reactivity properties. The spectroscopic properties of the complexes have also been investigated. Cyclic voltammetry experiments in $\mathrm{MeCN{-}CH_2Cl_2}$ reveal facile metal-centred reversible-to-quasireversible $\mathrm{Co^{IV}{-}Co^{III}}$ (or a ligand-centred redox process; **2a**), $\mathrm{Co^{III}{-}Co^{II}}$ (**1a**, **1b**·MeOH, **2a**, **2b** and **3**), $\mathrm{Co^{II}{-}Co^{I}}$ (**1a**, **1b**·MeOH, **2a** and **2b**), and $\mathrm{Co^{I}{-}Co^{0}}$ (**1a**, **1b**·MeOH and **2b**) redox processes.

Introduction

There has been continued interest in the development of the coordination chemistry of peptide ligands containing the pyridine-2-carboxamide and pyridine-2,6-dicarboxamide functionality in their deprotonated form.[1–8] Many such complexes act as bioinorganic models[9] and catalysts for selective organic transformations.[4e,f] From the standpoint of exploring coordination chemistry of deprotonated pyridine amide ligands we[2,6] and others[3–5,7,8] have synthesized, structurally characterized and investigated properties of a large variety of interesting transition metal complexes. Herein we wish to disclose a full account of the coordination chemistry of cobalt with the ligands 1,4-bis[*o*-(pyrazine-2-carboxamidophenyl)]-1,4-dithiobutane ($\mathrm{H_2\mathbf{L}^1}$)[2a,b] and 1,4-bis[*o*-(pyrazine-2-carboxamidophenyl)]-1,5-dithiopentane ($\mathrm{H_2\mathbf{L}^2}$), in their deprotonated form. The chosen ligands differ in the size of the dithiaalkyl spacer chain length between the two tridentate units. The compounds synthesized include $\mathrm{[Co^{II}(\mathbf{L}^1)]{\cdot}MeOH}$ (**1a**), $\mathrm{[Co^{II}(\mathbf{L}^2)]{\cdot}MeOH}$ (**1b**·MeOH), $\mathrm{[Co^{III}(\mathbf{L}^{3a})(\mathbf{L}^{3b})]{\cdot}2MeOH}$ (**2a**), $\mathrm{[Co^{III}(\mathbf{L}^2)][ClO_4]}$ and $\mathrm{[Co^{III}(\mathbf{L}^{2'})]}$ (**3**). Noteworthy features of the complexes include: (i) a rare example of low-spin $\mathrm{Co^{II}}$ complexes coordinated by two pyrazine N, two deprotonated amide N and two thioether S donor atoms ($\mathbf{1b}{\cdot}\mathrm{C_6H_6}$) and its $\mathrm{Co^{III}}$ counterpart (**2b**), (ii) **2a** reveals a C–S bond cleavage reaction[10,11] in which a low-spin $\mathrm{Co^{III}}$ centre is coordinated by two dissimilar tridentate ligands, one containing the pyrazine amide vinyl thioether unit $\mathbf{L}^{3a}(1-)$ and the other a pyrazine amide thiolate unit $\mathbf{L}^{3b}(2-)$ and (iii) **3** provides a notable example of cyclometallation reaction.[11e,f,g,12]

Experimental

General considerations

All reagents were obtained from commercial sources and used without further purification, unless otherwise stated. The diamines 1,2-bis(2-aminophenylthio)ethane and 1,3-bis(2-aminophenylthio)propane[13] as precursors of thioether functionality and tetra-*n*-butylammonium perchlorate (TBAP)[2a–d] were

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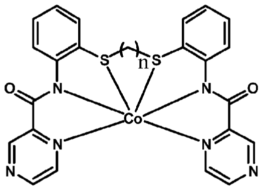
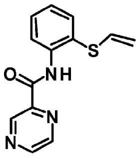
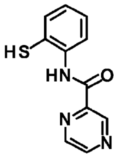
‡ Electronic supplementary information (ESI) available: ^{1}H (Fig. S1) and ^{13}C (Fig. S2) NMR spectrum of $\mathrm{H_2L^2}$; Absorption spectra of complexes (Fig. S3–S5); EPR spectra (solid, 120 K) of **1a** and **1b**·MeOH (Fig. S6); ^{1}H (Fig. S7) and ^{13}C (Fig. S8) NMR spectra of **2a** and **2b**, respectively; ^{13}C NMR spectra of **3** (Fig. S9) and **2a** (Fig. S10). See DOI: 10.1039/b709901k



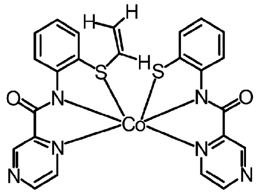
n = 2 : $[Co^{II}(L^1)]\cdot MeOH$ (**1a**)
n = 3 : $[Co^{II}(L^2)]\cdot MeOH$ (**1b**·MeOH)
$[Co^{III}(L^2)]X$ [X = ClO_4^- (**2b**); PF_6^- (**2c**)]



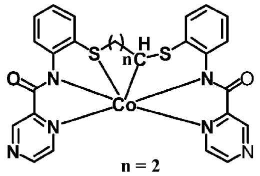
HL^{3a}



H_2L^{3b}



$[Co^{III}(L^{3a})(L^{3b})]\cdot 2MeOH$ (**2a**)



n = 2
$[Co^{III}(L^{2\prime})]$ (**3**)

prepared following reported procedures. The ligand 1,4-bis[*o*-(pyrazine-2-carboxamido-phenyl)]-1,4-dithiobutane (H_2L^1) was prepared as before.[2a,b] $[Fe(\eta^5\text{-}C_5H_5)_2][PF_6]$ was prepared following a reported procedure.[14]

Synthesis of 1,4-bis[*o*-(pyrazine-2-carboxamido-phenyl)]-1,5-dithiopentane (H_2L^2). Pyrazine-2-carboxylic acid (1.00 g, 8.06 mmol) was dissolved in pyridine (10 cm^3) and to it a suspension of 1,3-bis(2-aminophenylthio)propane (1.17 g, 4.03 mmol) in pyridine (5 cm^3) was added dropwise and the mixture was stirred for 10 min at 298 K. The temperature of the reaction mixture was then slowly raised to 383 K. To this, triphenylphosphite (2.50 g, 8.06 mmol) was added dropwise and the mixture was refluxed with stirring for 5 h. The volume was then reduced to *ca.* 7 cm^3, cooled and MeOH (10 cm^3) added. After 15 min of stirring the off-white solid that formed was filtered and washed several times with water. Final washing with MeOH (2 × 10 cm^3) afforded an off-white crystalline shiny solid (yield: 1.20 g, 60%). ^1H NMR (80 MHz; $CDCl_3$; standard $SiMe_4$): δ 11.03 (2H, s, NH), 9.59 (2H, d, pyrazine 3-H), 8.88–8.56 (4H, m, pyrazine 4,5-H), 7.63–7.00 (8H, m, phenyl ring protons), 2.97 (4H, t, $-SCH_2-$), 1.77 (2H, q, $-SCH_2CH_2CH_2-$). ^{13}C NMR (400 MHz; $CDCl_3$; standard $SiMe_4$): δ_C 28.853, 34.957, 120.132, 123.333, 124.657, 129.972, 135.534, 139.260, 142.617, 144.756, 147.512, 160.774.

Synthesis of cobalt complexes. $[Co^{II}(L^1)]\cdot MeOH$ (1a). Under anaerobic conditions in a glove box (UNIlab, mBraun, Germany) solid $Co(O_2CMe)_2\cdot 4H_2O$ (0.102 g, 0.409 mmol) was added in portions to a magnetically stirred solution of H_2L^1 (0.200 g, 0.409 mmol) in MeOH (10 cm^3). The dark brown solution obtained was stirred for 30 min at 298 K. The microcrystalline solid that precipitated was collected by filtration, washed with Et_2O and dried *in vacuo* (yield: 0.180 g, 84%).

$[Co^{II}(L^2)]\cdot MeOH$ (1b·MeOH). To a magnetically stirred solution of H_2L^2 (0.200 g, 0.398 mmol) in MeOH (10 cm^3), solid $Co(OAc)_2\cdot 4H_2O$ (0.099 g, 0.398 mmol) was added in portions. The dark brown solution obtained was stirred for 15 min with gentle warming at *ca.* 333 K. The microcrystalline solid that precipitated was collected by filtration, washed with Et_2O and dried *in vacuo* (yield: 0.178 g, 75%). Slow evaporation in air of a solution of the compound in a $MeCN–C_6H_6$ mixture (1 : 1, v/v) yielded single crystals suitable for X-ray diffraction studies having the composition $[Co^{II}(\mathbf{L^2})]\cdot C_6H_6$ (**1b**·C_6H_6).

$[Co^{III}(L^{3a})(L^{3b})]\cdot 2MeOH$ (2a)

Method A. The ligand $H_2\mathbf{L^1}$ (0.4 g, 0.819 mmol) was suspended in MeOH (15 cm^3) and to it was added solid $Co(O_2CMe)_2\cdot 4H_2O$ in portions. It was then stirred for 15 min with gentle warming at *ca.* 333 K resulting in a reddish brown solution. After 30 min the precipitate that formed was filtered. Slow evaporation of the filtrate in air yielded brown crystals, suitable for structural analysis (yield: 0.385 g, 75%).

Method B. The ligand $H_2\mathbf{L^1}$ (0.100 g, 0.205 mmol) was reacted with $CoCl_2\cdot 6H_2O$ (0.049 g, 0.205 mmol) in MeOH (5 cm^3) in open air with stirring. There was no apparent reaction and no colour change was observed. Then Et_3N (0.042 g, 0.410 mmol) diluted in MeOH (5 cm^3) was added. Gradually the colour of the reaction mixture changed and after a while a brown precipitate was obtained. It was filtered, washed with cold MeOH and dried *in vacuo* (yield: 0.084 g, 68%). The absorption and IR spectra of this solid were identical to that of $[Co^{III}(\mathbf{L^{3a}})(\mathbf{L^{3b}})]\cdot 2MeOH$ (**2a**) obtained following Method A.

$[Co^{III}(L^2)][ClO_4]$ (2b)

Method A. To a solution of $[Co^{II}(\mathbf{L^2})]\cdot MeOH$ (**1b**·MeOH) (0.100 g, 0.169 mmol) in an MeCN, CH_2Cl_2 and MeOH mixture [30 cm^3, 1 : 1 : 1 (v/v/v)], was added $NaClO_4\cdot H_2O$ (0.031 g, 0.254 mmol) and to it dioxygen was purged for 2 h. The volume of solvent was then reduced to *ca.* 5 cm^3 and the precipitate that formed was filtered through a frit, washed thoroughly with water to remove unreacted $NaClO_4\cdot H_2O$, washed with Et_2O and finally dried *in vacuo* (yield: 0.086 g, 77%).

Method B. To a stirred ice-cold solution of $[Co^{II}(\mathbf{L^2})]\cdot MeOH$ (**1b**·MeOH) (0.100 g, 0.169 mmol) in an MeCN, CH_2Cl_2 and MeOH mixture [12 cm^3, 1 : 1 : 1 (v/v)], was added 30% H_2O_2 solution (20 cm^3) dropwise and the reaction mixture was stirred in open air for 2 h. Solid $NaClO_4\cdot H_2O$ (0.031 g, 0.254 mmol) was then added to it and the solvent removed. The precipitate that formed was washed with water a couple of times, dried in open air first and then finally dried *in vacuo* (yield: 0.055 g, 49%). The absorption and IR spectra of this compound were identical to that of the $[Co^{III}(\mathbf{L^2})][ClO_4]$ (**2b**) obtained following Method A.

$[Co^{III}(L^2)][PF_6]$ (2c). To a magnetically stirred solution of $[Co^{II}(\mathbf{L^2})]\cdot MeOH$ (**1b**·MeOH) (0.05 g, 0.085 mmol) in a mixture (5 cm^3) of MeCN and CH_2Cl_2 (3 : 2; v/v) was added $[Fe(\eta^5\text{-}C_5H_5)_2][PF_6]$ (0.028 g, 0.085 mmol) as a solid. The reaction mixture was then stirred for 15 min. Removal of solvent under reduced pressure yielded a greenish brown solid which was washed thoroughly with Et_2O to wash off ferrocene formed during the reaction. The product was dried *in vacuo* (yield: 0.054 g, 86%). The absorption and ^1H NMR spectra of this compound were identical with that of the $[Co^{III}(\mathbf{L^2})][ClO_4]$ (**2b**) obtained following Method A and Method B.

$[Co^{III}(L^{2\prime})]$ (3)

Method A. To a solution of $[Co^{II}(\mathbf{L^2})]\cdot MeOH$ (**1b**·MeOH) (0.100 g, 0.169 mmol) in a $CH_2Cl_2–MeOH$ mixture [20 cm^3, 1 : 1 (v/v)] was added methanolic KOH solution (1 M, 20 cm^3) and dioxygen was purged through the reaction mixture for 2 h. The volume of solvent was then reduced to *ca.* 5 cm^3 and the precipitate that formed was filtered, washed thoroughly with water, then with Et_2O and finally dried *in vacuo* (yield: 0.090 g, 94%).

Method B. To a solution of $[Co^{III}(\mathbf{L}^2)][ClO_4]$ (**2b**) (0.066 g, 0.1 mmol) in a CH_2Cl_2–MeOH mixture [10 cm^3, 1 : 1 (v/v)] was added methanolic KOH solution (1 M, 20 cm^3), under a dinitrogen atmosphere. After stirring for 2 h the solvent was reduced down to *ca.* 5 cm^3 and the precipitate that formed was filtered, washed thoroughly with water, then with Et_2O and finally dried *in vacuo* (yield: 0.05 g, 89%).

Caution! *Perchlorate salts of compounds containing organic ligands are potentially explosive.*

Physical measurements

Elemental analyses were obtained using Thermo Quest EA 1110 CHNS–O, Italy. Conductivity measurements were done with an Elico type CM-82T conductivity bridge (Hyderabad, India). Spectroscopic measurements were made using the following instruments: IR (KBr, 4000–600 cm^{-1}), Bruker Vector 22; electronic, Agilent 8453 diode-array spectrophotometer; X-band EPR, Varian 109 C and Bruker EMX 1444 EPR spectrometer (fitted with a quartz dewar for measurements at 120 K or at 77 K). The EPR spectra were calibrated with diphenylpicrylhydrazyl, DPPH ($g = 2.0037$).

Magnetism

Room-temperature magnetic susceptibility measurements on solid samples of **1a** and **1b**·MeOH were carried out with a locally-built Faraday balance equipped with an electromagnet with constant-gradient pole caps (Polytronic Corporation, Mumbai, India), Sartorius balance M-25-D/S (Göttingen, Germany), a closed-cycle refrigerator and a Lake Shore temperature controller (Cryo Industries, USA). All measurements were made at a fixed main field strength of ~6 kG. The calibration of the system and details of measurements are already reported in the literature.[2,6] Solution-state magnetic susceptibilities were obtained by the NMR technique of Evans[15a] in MeCN with a PMX-60 JEOL (60 MHz) NMR spectrometer. Corrections underlying diamagnetism were applied with use of appropriate constants.[15b]

Cyclic voltammetry

Cyclic voltammetric experiments were performed by using either a PAR model 370 electrochemistry system consisting of a M-174A polarographic analyzer, M-175 universal programmer and RE 0074 X–Y recorder or CH instruments, electrochemical analyzer/workstation M-600B series. The cell contained a glassy-carbon working electrode (PAR model G0021), a Pt wire auxiliary electrode and a saturated calomel electrode (SCE), as reference electrode. Details of the cell configuration are as previously described.[2,6] 1̃ mM solutions of the complexes and 0.1 M solutions of the supporting electrolyte, TBAP, were used. Under our experimental conditions, the $E_{1/2}$ values (V) for the ferrocenium/ferrocene couple were 0.40 (MeCN) and 0.49 (CH_2Cl_2) *vs.* SCE.

Crystal structure determinations†

Single crystals of suitable dimensions were used for data collection. Diffraction intensities were collected on a Bruker SMART APEX CCD diffractometer, with graphite-monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation at 100(2) K. The data were corrected for absorption. The structures were solved by SIR 92 expanded by Fourier-difference syntheses and refined with the SHELXL 97 package incorporated in WinGX 1.64 crystallographic collective package.[16] The positions of the hydrogen atoms were calculated assuming ideal geometries, but not refined. All non-hydrogen atoms were refined with anisotropic thermal parameters by a full-matrix least-squares procedure on F^2.

For **2a** severe disorder was encountered with the Co atom as well as with the S atoms. The cobalt atom was disordered over the crystallographically imposed 2-fold symmetry axis at two positions 0.525(2) Å apart. Each Co is coordinated to two S atoms, one thiolate and other vinyl thioether. However, each S atom is also disordered over two positions. So with each Co it shows two bonding interactions, one bond being longer than the other. The longer one corresponds to vinyl thioether S and the shorter one is due to thiolate S. In fact, to compensate and adjust the bond lengths of $Co–S_{thiolate}$ and $Co–S_{thioether}$, the Co atom is disordered. Two positions for Co and S were refined with each a site occupation factor of 0.5/0.5. Moreover, the vinyl group attached with the thioether S atom was disordered and spends equal time on both kinds of S atoms, thiolate and thioether, due to crystallographically imposed symmetry.

The data-set of **2b** was treated with the SQUEEZE filter of PLATON[17] due to the presence of severely disordered solvent molecule (probably benzene) which could not be modeled satisfactorily. PLATON estimated the electron count to be 18 electron $cell^{-1}$ in a volume of 85 $Å^3$ out of a unit volume of 1327.0 $Å^3$ (6.4%). Pertinent crystallographic parameters are summarized in Table 1 and metric parameters are collected in Table 2.

CCDC reference numbers 652240–652243.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b709901k

Results and discussion

Syntheses of cobalt(II) and cobalt(III) complexes

The hexadentate ligands used in the present work, in their deprotonated form, incorporate pairs of pyrazine, amide and thioether functions. The thioether function is a weak field ligand toward metal ions because of its poor σ-donor and π-acceptor character.[18] For viable thioether coordination, we have employed the dithiaalkyl fragment, $–S(CH_2)_2S–$,[2a,b] as part of pyridine[2c–2e,3–8]/pyrazine[2a,b,19] amide functionality. Thus using $\mathbf{L}^1(2-)$ we have developed low-spin Fe^{II}/Fe^{III} chemistry.[2a] In this work a new ligand $H_2\mathbf{L}^2$ has been synthesized having the same donor sites with a propylene spacer to provide extra flexibility in the ligand system. The hexadentate ligands $H_2\mathbf{L}^1$ and $H_2\mathbf{L}^2$ were prepared in high yield by treating 2-pyrazinecarboxylic acid with the diamine 1,2-bis(2-aminophenylthio)ethane/1,2-bis(2-aminophenylthio)propane, as a precursor of the thioether unit, in the presence of triphenylphosphite in pyridine. The purity of $H_2\mathbf{L}^2$ was checked by its ^1H and ^{13}C NMR spectra (Fig. S1 and

Table 1 Data collection and structure refinement parameters for [Co^{II}(**L**^{2})]·C_6H_6 (**1b**·C_6H_6), [Co^{III}(**L**^{3a})(**L**^{3b})]·2MeOH (**2a**), [Co^{III}(**L**^{2})][ClO$_4$] (**2b**), and [Co^{III}(**L**$^{2'}$)] (**3**)

	(**1b**·C_6H_6)	(**2a**)	(**2b**)	(**3**)
Chemical formula	$C_{31}H_{26}CoN_6O_2S_2$	$C_{26}H_{25}CoN_6O_4S_2$	$C_{25}H_{20}ClCoN_6O_6S_2$	$C_{25}H_{19}CoN_6O_2S_2$
M	637.63	608.57	658.97	558.51
Cryst size/mm	0.3 × 0.2 × 0.1	0.3 × 0.2 × 0.2	0.3 × 0.2 × 0.2	0.2 × 0.2 × 0.2
T/K	100(2) K	100(2) K	100(2) K	100(2) K
λ/Å	0.71069	0.71069	0.71069	0.71069
Crystal system	Monoclinic	Orthorhombic	Triclinic	Monoclinic
Space group	$C2/c$ (#15)	$Pccn$ (#56)	$P\bar{1}$ (#2)	$C2/c$ (#15)
a/Å	21.722(5)	19.135(5)	8.363(5)	29.151(5)
b/Å	12.058(5)	10.103(5)	10.980(5)	7.911(5)
c/Å	10.524(5)	13.099(5)	15.046(5)	22.885(5)
α/°	90	90	96.003(5)	90
β/°	104.864(5)	90	95.062(5)	120.892(5)
γ/°	90	90	103.491(5)	90
V/Å^3	2664.2(18)	2532.3(17)	1327.0(11)	4529(3)
Z	4	4	2	8
d_{calcd}/g cm^{-3}	1.590	1.596	1.649	1.638
μ/mm^{-1}	0.845	0.890	0.959	0.981
No. reflns collected	8566	15 892	8907	14 707
No. indep. reflns (R_{int})	3266 (0.0636)	3136 (0.0518)	6337 (0.0487)	5583 (0.0682)
No. reflns used [$I > 2\sigma(I)$]	2579	2605	4081	3814
Final R indices R_1 [$I > 2\sigma(I)$] R_1^{a}, wR_2^{b}	0.0565, 0.1247	0.0885, 0.1803	0.0921, 0.1738	0.0572, 0.1106
R indices (all data)	0.0805, 0.1595	0.1044, 0.1856	0.1475, 0.2238	0.0975, 0.1321
GOF on F^2	1.089	1.269	1.055	1.082

[a] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma[w(|F_o|^2)^2]\}^{1/2}$.

S2‡). This gives an opportunity to study the effect of chelate-ring size on the reactivity of Co^{II}/Co^{III} complexes.

The synthetic route followed for the syntheses of the present cobalt(II) and cobalt(III) complexes is outlined in Scheme 1. The synthesis of Co^{II} complexes [Co^{II}(**L**^{1})]·MeOH (**1a**) and [Co^{II}(**L**^{2})]·MeOH (**1b**·MeOH) involved the reaction of H_2**L**^{1}/H_2**L**^{2} with Co(O_2CMe)$_2$·4H_2O in MeOH. When H_2**L**^{1} was used, a similar reaction in air, however, furnished a diamagnetic Co^{III} complex [Co^{III}(**L**^{3a})(**L**^{3b})]·2MeOH (**2a**), resulting from a base-assisted C–S bond cleavage reaction. The oxidation of **1b**·MeOH by O_2–H_2O_2 led to the isolation of a Co^{III} complex [Co^{III}(**L**^{2})][ClO$_4$] (**2b**). [Co^{III}(**L**^{2})][PF$_6$] (**2c**) could easily be synthesized in a quantitative yield from the reaction between **1b**·MeOH and [Fe(η^5-C_5H_5)$_2$][PF$_6$]. Complexes **2b** and **2c** are indefinitely stable in the solid state and in neutral solutions. However, treatment of **1b**·MeOH with methanolic KOH in air led to the isolation of an organocobalt(III) complex [Co^{III}(**L**$^{2'}$)] (**3**). Interestingly, **3** could also be synthesized by anaerobic treatment of **2b** with methanolic KOH. It clearly indicates that dioxygen is necessary only for the oxidation of **1b**·MeOH to generate the corresponding Co^{III} complex **2b** and it is the base (methanolic KOH) which is crucial for the necessary transformation of a Werner-type cobalt(III) complex **2b** to the organocobalt(III) complex **3**.

For all complexes the absence of *ν*(N–H) in their IR spectra confirms that the ligands are coordinated in their deprotonated form. Elemental analyses, IR and solution electrical conductivity data (except **2b** which is a 1 : 1 electrolyte, all are non-electrolyte)[20] are in good agreement with the above formulations (Table 3).

Crystal structure of [Co^{II}(L^2)]·C_6H_6 (1b·C_6H_6)

A view of the metal coordination environment in the crystal of [Co^{II}(**L**^{2})]·C_6H_6 is presented in Fig. 1. The crystal structure confirms the coordination by an intact hexadentate ligand H_2**L**^{2}, in its deprotonated form. The cobalt atom sits on a crystallographically imposed C_2 axis and six coordination sites are provided by two pyrazine nitrogens [N(1) and its symmetry related atom], two deprotonated amide nitrogens [N(3) and its symmetry related atom], and two thioether sulfur atoms [S(1) and its symmetry related atom]. Thus it affords a Co$^{II}N_2$(pyrazine)N_2'(deprotonated amide)S_2(thioether) coordination sphere. Appreciable distortions from ideal octahedral geometry are apparent (Table 2), as a result of expected Jahn–Teller distortion of a low-spin d^7 ion (see below). The angles between *trans* atoms at the metal centre are in the range 168.16(9)°–177.21(19)°. Similarly, the *cis* angles span a wide range, 81.81(12)°–96.29(12)°. Co–N$_{pyrz}$ (pyrz = pyrazine) and Co–N$_{amide}$ distances are 2.041(3) and 1.944(3) Å, respectively. Hence we observe that the average Co–N$_{amide}$ bond length is considerably shorter (~0.1 Å) than that of average Co–N$_{pyrz}$ distance, as expected. The Co–S$_{thioether}$ distance is 2.3617(12) Å. For a high-spin Co^{II} triazene 1-oxide complex the average thioether sulfur to cobalt(II) bond distance of 2.5335(3) Å was observed.[11f] The Co^{II}–S$_{thioether}$ bond length in **1b**·C_6H_6 is comparable to low-spin [Co(hexathia-18-crown-6)][picrate]$_2$ [equatorial bonds: 2.251(1) and 2.292(1) Å; axial bond: 2.479(1) Å; average of all Co–S bonds: 2.341(1) Å] and [Co(trithianonane)$_2$][BF$_4$]$_2$·CH_3NO_2 [average of equatorial bonds: 2.2545(3) Å; average of axial bonds: 2.6075(3) Å; average of all Co–S bonds: 2.431(3) Å] complexes.[23b,d] This clearly signifies that the thioether sulfurs in **1b**·C_6H_6 are tightly bound to the cobalt(II) ion, as they are part of a strongly coordinating deprotonated pyrazine amide functionality.[2a,b] Given the scarcity of low-spin six-coordinate cobalt(II) complexes[21,22] the structural characterization of [Co^{II}(**L**^{2})]·C_6H_6, the first low-spin six-coordinate Co^{II} with a pyridine/pyrazine carboxamido nitrogen and thioether sulfur coordination, deserves special attention.

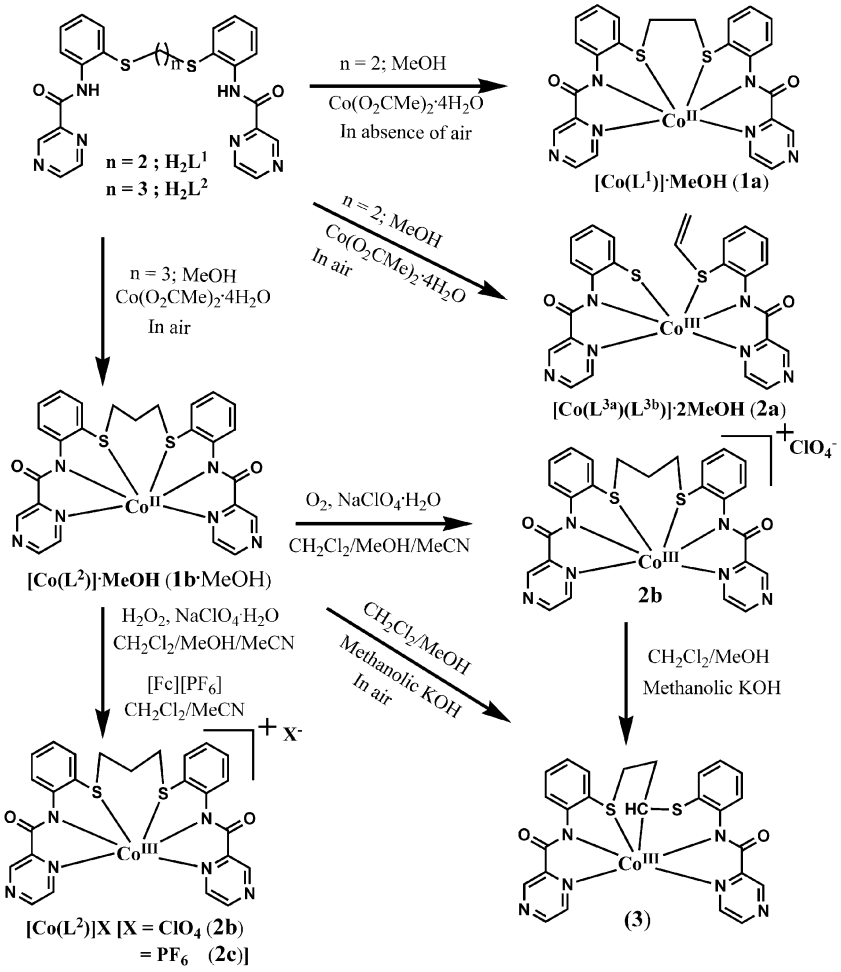
Table 2 Selected bond lengths and angles in $[Co^{II}(\mathbf{L}^2)]\cdot C_6H_6$ (**1b**·C_6H_6), $[Co^{III}(\mathbf{L}^{3a})(\mathbf{L}^{3b})]\cdot 2MeOH$ (**2a**), $[Co^{III}(\mathbf{L}^2)][ClO_4]$ (**2b**), and $[Co^{III}(\mathbf{L}^{2'})]$ (**3**)

Bond lengths/Å		Bond angles/°	
(**1b**·C_6H_6)			
Co–N(1)	2.041(3)	N(1)–Co–N(3)	81.81(12)
Co–N(3)	1.944(3)	N(1)–Co–S(1)	168.16(9)
Co–S(1)	2.3617(12)	N(1)–Co–N(1)^a	85.84(9)
		N(1)–Co–N(3)^a	96.29(12)
		N(1)–Co–S(1)^a	95.03(18)
		N(3)–Co–S(1)	86.35(9)
		N(3)–Co–N(3)^a	177.21(19)
		N(3)–Co–S(1)^a	95.53(9)
(**2a**)			
Co–N(1)	2.120(5)	N(1)–Co–N(1)^b	91.5(2)
Co–N(1)^b	1.773(5)	N(1)–Co–N(3)	79.8(2)
Co–N(3)	1.882(5)	N(1)–Co–N(3)^b	88.65(19)
Co–N(3)^b	2.008(5)	N(3)–Co–N(3)^b	164.93(8)
Co–S(1A)	1.927(3)	N(1)–Co–N(3)	104.3(2)
Co–S(1A)^b	2.217(3)	N(1)–Co–S(1A)	158.09(14)
Co–S(1B)	2.221(3)	N(1)–Co–S(1A)^b	88.86(13)
Co–S(1B)^b	2.614(3)	N(1)^b–Co–S(1A)	110.28(17)
C12–C13	1.284(13)	N(3)^b–Co–N(1)	88.65(19)
		N(3)–Co–S(1A)	96.07(19)
		N(3)^b–Co–S(1A)	91.08(18)
		S(1A)–Co–S(1A)^b	69.33(16)
		N(1)–Co–S(1B)	171.14(18)
		N(1)–Co-S(1B)^b	76.85(12)
		N(1)^b–Co–S(1B)	95.30(15)
		N(3)–Co–S(1B)	93.06(18)
		N(3)^b–Co–S(1B)	97.48(17)
		N(3)–Co–S(1B)^b	88.60(17)
		S(1A)–Co–S(1B)^b	81.57(13)
		S(1A)^b–Co–S(1B)	85.44(13)
		S(1B)–Co–S(1B)^b	97.93(14)
(**2b**)			
Co–N(1)	1.942(5)	N(1)–Co–N(3)	83.8(2)
Co–N(3)	1.925(6)	N(1)–Co–N(4)	96.0(2)
Co–N(4)	1.928(6)	N(1)–Co–N(5)	89.7(2)
Co–N(5)	1.927(5)	N(1)–Co–S(1)	171.69(17)
Co–S(1)	2.199(2)	N(1)–Co–S(2)	85.97(17)
Co–S(2)	2.234(2)	N(3)–Co–N(4)	176.0(2)
		N(3)–Co–N(5)	92.7(2)
		N(3)–Co–S(1)	88.47(17)
		N(3)–Co–S(2)	96.16(18)
		N(4)–Co–N(5)	83.3(2)
		N(4)–Co–S(1)	91.54(18)
		N(4)–Co–S(2)	87.80(18)
		N(5)–Co–S(1)	87.66(17)
		N(5)–Co–S(2)	169.61(17)
		S(1)–Co–S(2)	97.93(7)
(**3**)			
Co–N1	1.946(3)	N(1)–Co–N(3)	83.04(12)
Co–N3	1.926(3)	N(1)–Co–N(4)	97.02(12)
Co–N4	1.952(3)	N(1)–Co–N(5)	84.52(12)
Co–N5	2.046(3)	N(1)–Co–S(1)	171.00(9)
Co–S1	2.2017(16)	N(1)–Co–C(14)	90.23(14)
Co–C14	2.001(4)	N(3)–Co–N(4)	174.58(13)
		N(3)–Co–N(5)	93.47(12)
		N(3)–Co–S(1)	87.99(9)
		N(3)–Co–C(14)	90.43(14)
		N(4)–Co–N(5)	81.15(12)
		N(4)–Co–S(1)	91.98(9)
		N(4)–Co–C(14)	94.99(14)
		N(5)–Co–S(1)	96.80(9)
		N(5)–Co–C(14)	173.03(14)
		C(14)–Co–S(1)	89.10(12)

Symmetry code: $^a = -x, y, -z + 1/2$. $^b = -x + 1/2, -y + 3/2, z$.

Crystal structure of $[Co^{III}(\mathbf{L}^{3a})(\mathbf{L}^{3b})]\cdot 2MeOH$ (2a)

In order to confirm the identity of the isolated complex obtained from the aerobic reaction between $Co(O_2CMe)_2\cdot 4H_2O$ and $H_2\mathbf{L}^1$ single crystal X-ray structure determination was carried out. In Fig. 2 a view of the metal coordination environment is presented. The Co atom sits on the 2-fold crystallographic axis. In spite of disordered Co and S atoms (Experimental) the metal–ligand distances obtained are in agreement with reported values (see below). The structural analysis of **2a** clearly shows the cleavage of a symmetrical hexadentate ligand $H_2\mathbf{L}^1$ into two unsymmetrical tridentate parts $H\mathbf{L}^{3a}$ (monoanionic) and $H_2\mathbf{L}^{3b}$ (dianionic), both of which provide an N_2S donor set. Salient features of **2a** are the presence of two dissimilar tridentate ligands, one containing a pyrazine amide vinyl thioether unit $\mathbf{L}^{3a}(1-)$ and the other having a pyrazine amide thiolate unit $\mathbf{L}^{3b}(2-)$. In essence, the reaction of $\mathbf{L}^1(2-)$ with $Co(O_2CMe)_2\cdot 4H_2O$ resulted in oxidative cleavage of the C–S bond,[10,11] affording distorted $Co^{III}N_2$(pyrazine)N'_2(deprotonated amide)S(thioether)S′(thiolate) coordination. The two deprotonated carboxamido nitrogens are *trans* to each other while the thiolate and thioether sulfurs occupy positions that are *trans* to pyrazine nitrogens, and are *cis* to each other. Due to the disorder encountered with both thioether and thiolate S atoms, average bond distances cannot be considered from two sets of Co–S(thiolate) [1.927(3) and 2.217(3) Å] and Co–S(thioether) [2.221(3) and 2.614(3) Å] data (Table 2). The $Co–N_{amide}$ [av: 1.945(5) Å] bond distance is well within the range noted for deprotonated amide complexes of trivalent cobalt.[7] Notably, the $Co–N_{pyrz}$ (pyrz = pyrazine) bond distance [av: 1.9465(5) Å] is shorter than the $Co–N_{py}$ (py = pyridine) distance reported for the nitrile hydratase model compound $[Me_4N][Co(PyPepS)_2]\cdot 0.5H_2O$ ($PyPepSH_2$ = *N*-2-mercaptophenyl-2′-pyridinecarboxamide) [1.9665 Å].[3d] A similar trend was observed previously between the low-spin Fe^{II} complexes of $\mathbf{L}^1(2-)$ and its pyridine analogue.[2a] The $Co^{III}–S_{thiolate}$ and $Co^{III}–S_{thioether}$ distances in **2a** are comparable to similar complexes obtained due to C–S bond cleavage reaction.[10,11] It is worth mentioning here the average $Co–S_{thiolate}$ bond length [2.222(12) Å] in $[Me_4N][Co(PyPepS)_2]\cdot 0.5H_2O$[3d] and the $Co–S_{thioether}$ bond length [2.2825(1) Å] in $[Et_4N][Co_2(PyPS(SMe))_2]\cdot 1.5Me_2CO\cdot 0.5MeCN$ [PyPS(SMe) is a trinegative pentadentate bridging ligand providing a pyridine, two deprotonated carboxamido nitrogens, a thioether sulfur and a thiolate sulfur].[7d]



Scheme 1

Table 3 Characterization data for cobalt(II) and cobalt(III) complexes

Complex	Microanalytical data (%)[a] C H N	Conductivity data[b] / Ω^{-1} cm^2 mol^{-1}	IR data ν_{max}/cm^{-1}	UV-VIS data[c] λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})
1a	$C_{25}H_{22}N_6O_3S_2Co$: 51.60 3.87 14.36 (52.00) (3.81) (14.56)	44	1611 ν(CO)	253 (39 200), 300 (sh) (22 000), 380 (sh) (5600), 510 (sh) (600), 760 (sh) (80)
1b·MeOH	$C_{26}H_{24}N_6O_3S_2Co$: 52.98 3.87 14.56 (52.80) (4.06) (14.22)	46	1613 ν(CO)	262 (26 500), 320 (sh) (13 000), 480 (sh) (2300), 580 (sh) (700), 760 (sh) (130)
2a	$C_{26}H_{25}N_6O_4S_2Co$: 50.13 4.13 13.57 (51.32) (4.11) (13.82)	40	1624 ν(CO)	255 (46 700), 300 (sh) (24 300), 390 (6600), 520 (sh) (1100), 800 (130)
2b	$C_{25}H_{20}N_6O_6S_2ClCo$: 45.87 3.31 12.56 (45.56) (3.04) (12.76)	140	3437 ν(OH); 1625 ν(CO); 1091, 624 ν(ClO_4^-)	262 (33 800), 324 (14 100), 430 (sh) (4700), 590 (sh) (800)
3	$C_{25}H_{19}N_6O_2S_2Co$: 53.82 3.61 14.86 (53.77) (3.41) (15.06)	48	3428 ν(OH); 1624 ν(CO)	266 (27 900), 320 (sh) (13 500), 420 (sh) (4500), 490 (sh) (2300), 600 (sh) (700)

[a] Calculated values are in parentheses. [b] Expected data for a 1 : 1 electrolyte in MeCN: 120–160 Ω^{-1} cm^2 mol^{-1}. [c] The data for **1a**, **1b**·MeOH, **2a** and **2b** in MeCN and for **3** in CH_2Cl_2.

Crystal structure of [Co^{III}(L^2)][ClO$_4$] (2b)

The structural analysis reveals the cation and a perchlorate counteranion. The ligand **L**^{2}(2−) employs distorted octahedral geometry around Co^{III} with two pyrazine nitrogens, two deprotonated amide nitrogens and two thioether sulfur atoms to afford a Co^{III}N$_2$(pyrazine)N$_2'$(deprotonated amide)S$_2$(thioether) coordination sphere (Fig. 1, Table 2). The angles between *trans* atoms at the metal centre are in the range 169.61(17)°–176.0(2)° and the *cis* angles span a wide range, 83.3(2)°–97.93(7)°.

Average Co–N$_{pyrz}$, Co–N$_{amide}$ and Co–S$_{thioether}$ distances are 1.9335(5), 1.927(6) and 2.2165(2) Å, respectively. For **1b**·C_6H_6, the Co^{II} analog of **2b**, the corresponding distances are 2.041(3), 1.944(3), and 2.239(15) Å, respectively. Due to the difference in charge of the cobalt ion the metal–ligand distances are shorter for the Co^{III} complex than that of Co^{II} complex, as expected.

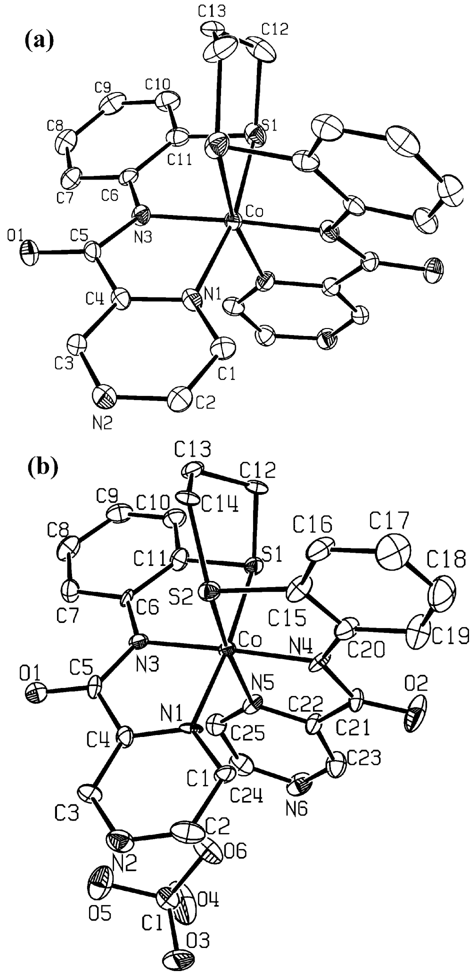


Fig. 1 Perspective views of (a) the metal coordination environment of $[Co^{II}(\mathbf{L^2})]\cdot C_6H_6$ ($\mathbf{1b}\cdot C_6H_6$) and (b) $[Co^{III}(\mathbf{L^2})][ClO_4]$ (**2b**), showing the atom-labeling scheme and 50% probability ellipsoids. Hydrogen atoms are omitted for the sake of clarity.

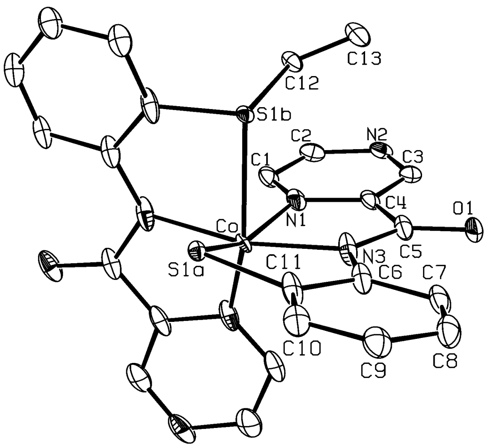


Fig. 2 Perspective view of the metal coordination environment in $[Co^{III}(\mathbf{L^{3a}})(\mathbf{L^{3b}})]\cdot 2MeOH$ (**2a**), showing the atom-labeling scheme and 50% probability ellipsoids. Hydrogen atoms are omitted for the sake of clarity.

We observe that the average Co–N_{amide} bond is shorter, albeit a small difference (~0.007 Å), than that of the average Co–N_{pyrz} bond length, as expected. The average Co^{III}–$S_{thioether}$ bond length observed here is shorter than a dithiaalkyl triazene 1-oxide coordinated compound reported in the literature [2.239(1) Å],[11f] indicating that the thioether sulfur is more tightly bound in the present compound.

Crystal structure of $[Co^{III}(\mathbf{L^{2'}})]$ (3)

The structure reveals that the Co^{III} centre is coordinated with two pyrazine nitrogens, two deprotonated amide nitrogens, a thioether sulfur and a carbon atom of the alkyl chain to provide a distorted octahedral $Co^{III}CN_4S$ coordination sphere (Fig. 3, Table 2). The uncoordinated thioether sulfur atom is 3.158 Å away from the metal centre. The angles between *trans* atoms at the metal center are in the range 171.00(9)°–173.03(14)° and the *cis* angles also span a wide range, 81.15(12)°–97.02(12)°. Thus the metal coordination geometry is appreciably distorted from a regular octahedron. The most striking feature of **3** is the presence of the cobalt–carbon bond Co–C14 [2.001(4) Å]. The observed distance lies within the range 1.94–2.05 Å found in organocobalt(III) species, where the coordinated alkyl carbon is part of a polydentate ligand chain.[11f,g,12] This bond is only slightly longer than the average Co–N_{pyrz} distance [1.996(3) Å] and appreciably longer (~0.06 Å) than that of Co–N_{amide} [1.939(3) Å] bond lengths. However, the Co–N_{pyrz} bond Co–N5 [2.046(3) Å], *trans* to the Co–C14 bond, is considerably longer than the other Co–N bonds. As reported previously,[12b] it is also observed here that an alkyl ligand has a strong *trans* influence in Werner-type alkyl-cobalt(III) complexes. The coexistence of the Co–S [2.2017(16) Å] and Co–C bonds in **3** indicates a strong Co–C bond, which probably provides the driving force for the organocobalt(III) complex formation by the displacement of a thioether site by a carbanionic site in the coordination sphere to form a comparatively more stable five-membered metallacycle. The observed Co–C bond length in **3** is slightly longer than that in the case of triazene 1-oxide system [1.969(5) Å].[11f,g] It is worth mentioning the Co–C bond length [1.977(4) Å] of a reported alkyl-cobalt(III) complex of a tetradentate 2-pyridinecarboxamido ligand,[23] in which the alkyl group is not part of a chelating ligand. Average Co–N_{pyrz} and Co–N_{amide} distances are 1.996(3) and 1.939(3) Å, respectively. The observed trend is as observed for **2a** and **2b**. To our knowledge,

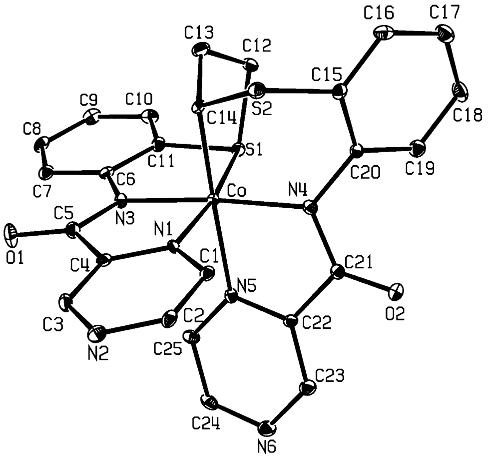


Fig. 3 Perspective view of the structure of $[Co^{III}(\mathbf{L^{2'}})]$ (**3**) showing the atom-labeling scheme and 30% probability ellipsoids. Hydrogen atoms are omitted for the sake of clarity.

compound **3** is the first example of a stable alkyl-cobalt(III) complex with a deprotonated hexadentate pyrazine amide ligand, with demonstrated potential to stabilize metal ions in high oxidation state, containing a dithaalkyl–S–$(CH_2)_3$–S functionality.

Absorption spectra

For low-spin cobalt(II) complexes **1a** and **1b**·MeOH in MeCN the observed shoulder at 760 nm may arise from the $^2E_g \rightarrow {}^4T_{1g}$ spin-forbidden transition and the shoulder at 510 nm and at 580 nm, respectively, can be assigned to $^2E_g \rightarrow {}^2T_{1g}$ and/or $^2E_g \rightarrow {}^2T_{2g}$ transitions (Fig. S3‡) in octahedral symmetry.[22,22] The higher intensity of this latter transition could be due to intensity stealing from a transition at 380 nm and 480 nm for **1a** and **1b**·MeOH, respectively. Notably, for the present cobalt(II) complexes absorption bands expected[21] for a high-spin octahedral cobalt(II) complex are not observed (Fig. S3‡). For **2a** and **2b** in MeCN the expected $^1A_{1g} \rightarrow {}^1T_{1g}$ (in octahedral symmetry) transition is observed at 800 nm and 590 nm, respectively (Fig. S4‡).[21] For the organocobalt(III) complex **3** the expected $^1A_{1g} \rightarrow {}^1T_{1g}$ transition was observed as a shoulder at 600 nm in CH_2Cl_2 (Fig. S5‡). In all the complexes the higher energy peaks are charge-transfer in origin. The data are collected in Table 3.

Magnetism and EPR spectra of cobalt(II) complexes

Octahedral cobalt(II) complexes are known to prefer high-spin ($S = 3/2$) configuration. Low-spin ($S = 1/2$) cobalt(II) complexes can be expected only in the presence of a sufficiently strong ligand field ($\Delta_o \geq 15\,000$ cm^{-1}) which is required to cause a ^2E ground state.[21,22] Room-temperature (300 K) magnetic susceptibility measurements for the Co^{II} complexes **1a** and **1b**·MeOH were carried out to define their spin-state properties. The effective magnetic moment (μ_{eff}) values in the solid-state are 2.41 for **1a** and 2.45 for **1b**·MeOH, slightly higher than that anticipated for authentic low-spin six-coordinate cobalt(II) complexes ($\mu_{eff} = 1.79$–$2.13\ \mu_B$).[22] The corresponding values in MeCN are 2.34 and 2.37, in reasonably good agreement with solid-state values. By comparison with analogous [Ni(**L**^{1})] ($\Delta_o \approx 12\,000$ cm^{-1})[2b] it is reasonable to assume[22a] Δ_o for the present complexes to be $\approx 15\,000$ cm^{-1}. Thus the room-temperature μ_{eff} values clearly demonstrate the $S = 1/2$ ground state of Co^{II} for both the complexes (see below). Notably, Kahn *et al.* predicted that for a spin-crossover transition to occur in a six-coordinate Co^{II} ion the metal ion should assume a (4 + 2) coordination environment, with a strong equatorial ligand field and a large axial distortion.[22c] Comparing the metric parameters of six-coordinate authentic $S = 1/2$ complexes [Co(hexathia-18-crown-6)][picrate]$_2$ and [Co(trithianonane)$_2$][BF$_4$]$_2$·CH_3NO_2 (see above) with that of **1b**·C_6H_6 we do not anticipate that these complexes would exhibit spin-crossover behaviour. The Co^{III} complexes **2a**, **2b**·MeOH and **3** are diamagnetic ($S = 0$).

The X-band EPR spectra of **1a** and **1b**·MeOH display an eight-line well-resolved feature characteristic of hyperfine interaction with the ^{59}Co nucleus ($I = 7/2$) in a MeCN–toluene (1 : 1 v/v) glass (120 K).[11a] The EPR parameters are $g_{(av)} = 2.110$ and $a_{\parallel} \sim 95 \times 10^{-4}$ cm^{-1} for **1a** and $g_{(av)} = 2.134$ and $a_{\parallel} \sim 92 \times 10^{-4}$ cm^{-1} for **1b**·MeOH. However, in the polycrystalline state (120 K) **1a** and **1b**·MeOH display isotropic spectra with $g = 2.110$ and $g = 2.131$, respectively. The spectral feature of **1a** and **1b**·MeOH are displayed in Fig. 4 and Fig. S6‡, respectively. The $g_{(av)}$ values for frozen MeCN solutions (77 K) of **1a** and **1b**·MeOH are 2.110 and 2.134, respectively. In essence, **1a** and **1b**·MeOH do not show axial spectra (tetragonal elongation/compression), in conformity with the X-ray structure of **1b**·C_6H_6 (see above). The EPR data confirm the low-spin formulation of **1a** and **1b**·MeOH beyond doubt.[22]

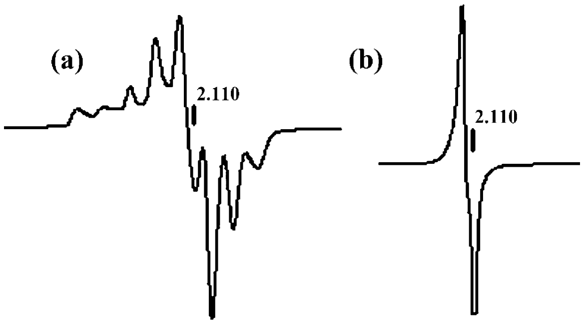


Fig. 4 EPR spectra of [Co^{II}(**L**^{1})]·MeOH (**1a**): (a) MeCN–$C_6H_5CH_3$ glass (1 : 1) and (b) polycrystalline sample at 120 K.

A comparison of observed *g* values in this work with those of authentic six-coordinate low-spin Co(II) complexes is in order. From the available $g_{(av)}$ values[22–24] based on donor atom type a trend in the extent of covalency in the Co–X bond emerges: Co–C ($g \approx 2.08$) > Co–S ($g \approx 2.12$) > Co–N ($g \approx 2.16$). In essence, within the class of six-coordinate low-spin cobalt(II) complexes with N/S donor containing ligands, the Co–S bond is more covalent than the Co–N bond, as expected.[22f]

^{1}H and ^{13}C NMR spectra of cobalt(III) complexes

All the three cobalt(III) compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy. As expected, in a $CDCl_3$ solution diamagnetic Co^{III} complexes **2a** (Fig. 5) and **2b** (Fig. S7‡) display clean ^{1}H NMR spectra. The former complex shows multiplets in the δ 5.1–5.54 region, diagnostic of vinyl function.[10,11a–c,11e,f] For the organocobalt(III) complex **3**, a multiplet due to –SCHCo proton was observed at δ 4.71 (Fig. 5). The spin structure arises due to coupling to two inequivalent adjacent methylene protons.[10,11e,f] Chemical shift and corresponding *J* values for ^{1}H spectral data of **2a** and **3** are collected in Table 4. The ^{13}C NMR spectra confirm that symmetric binding of **L**^{2}(2−) to Co^{III} in **2b** has been retained (Fig. S8‡) but in **3** it has been perturbed (Fig. S9‡). In **2a** the perturbation is maximum as the ligand **L**^{1}(2−) has been cleaved (Fig. 10).

Redox properties

To investigate the extent of stabilization of the cobalt(II) state towards oxidation and whether accessibility of higher (>3) oxidation states could be achieved, cyclic voltammetric (CV) studies were performed on all the complexes. The data are collected in Table 5.

The Co^{II} complexes **1a** and **1b**·MeOH in MeCN display at a glassy-carbon working electrode a reversible oxidative response corresponding to a Co^{III}–Co^{II} redox process at $E_{1/2} = -0.22$ V ($\Delta E_p = 80$ mV) and $E_{1/2} = -0.18$ V ($\Delta E_p = 80$ mV) *vs.* SCE, respectively. For **1a** two reductive reversible-to-quasireversible responses corresponding to Co^{II}–Co^{I} and Co^{I}–Co^{0} redox couples

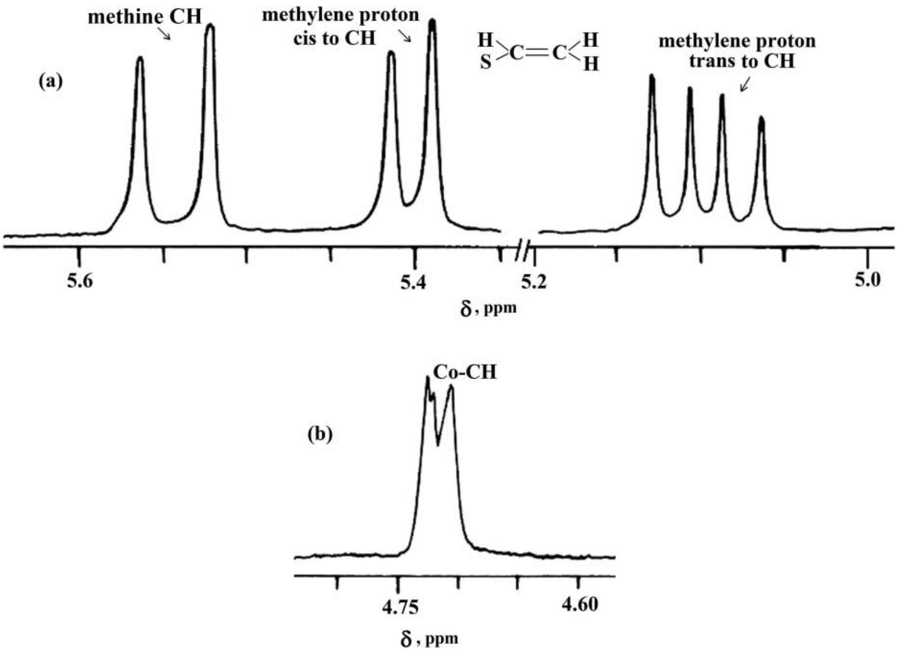


Fig. 5 ^{1}H NMR spectra (400 MHz) of selected regions of (a) [Co^{III}(**L**^{3a})(**L**^{3b})]·2MeOH (**2a**) and (b) [Co^{III}(**L**$^{2'}$)] (**3**) in CDCl$_3$ at 298 K.

Table 4 Chemical shifts (selected regions) in the ^{1}H NMR spectra of [Co^{III}(**L**^{3a})(**L**^{3b})]·2MeOH (**2a**) and [Co^{III}(**L**$^{2'}$)] (**3**)

Moiety	δ (ppm)
–CH=CH$_2$ in **2a**	5.54 (d): CH proton coupled with *trans* H of CH$_2$, J = 16.6 Hz 5.40 (d): CH$_2$ proton *cis* to CH, J = 8.8 Hz 5.10 (dd): CH$_2$ proton *trans* to CH, J_{12} = 9.28 Hz, J_{13} = 16.84 Hz
–SCHCo in **3**	4.71 (m): CH proton

Table 5 Cyclic voltammetric data for cobalt(II) and cobalt(III) complexes

	$E_{1/2}$/V *vs.* SCE for the redox processes			
Complex	Co^{III}–Co^{II}	Co^{II}–Co^{I}	Co^{I}–Co^{0}	Co^{IV}–Co^{III}/ligand oxidation
[Co^{II}(**L**^{1})]·MeOH (**1a**) in MeCN	−0.22	−1.38	−1.83	—
[Co^{III}(**L**^{3a})(**L**^{3b})]·2MeOH (**2a**) in MeCN	−0.76	−1.50	—	0.81
[Co^{II}(**L**^{2})]·MeOH (**1b**·MeOH) in MeCN	−0.18	−1.32	−1.70	—
[Co^{III}(**L**^{2})][ClO$_4$] (**2b**) in MeCN	−0.21	−1.32	−1.71	—
[Co^{III}(**L**$^{2'}$)] (**3**) in CH$_2$Cl$_2$	−1.28	—	—	—

are observed at $E_{1/2}$ = −1.38 V (ΔE_p = 80 mV) and $E_{1/2}$ = −1.83 V (ΔE_p = 100 mV), respectively (Fig. 6). The corresponding values for **1b**·MeOH are $E_{1/2}$ = −1.32 V (ΔE_p = 120 mV) and $E_{1/2}$ = −1.70 V (ΔE_p = 160 mV). As expected, due to the presence of a five-membered chelate-ring in **L**^{1}(2-) over a six-membered chelate-ring in **L**^{2}(2−), the Co^{III}–Co^{II} redox potential for **1a** is more negative than that of **1b**·MeOH by 40 mV. In other words, **L**^{1}(2−) stabilizes a Co^{III} state better than **L**^{2}(2−). This provides a rationale why in air initially formed '[Co^{II}(**L**^{1})]' is oxidized to its Co^{III} counterpart by dioxygen and in turn the acidity of the α-methylene proton of Co^{III}-coordinated **L**^{1}(2−) is likely to be enhanced relative to that in **1b**·MeOH. This difference might have eventually led to C–S bond cleavage in product **2a** (see below).

The cobalt(III) complex **2a** displays in MeCN two quasireversible (ΔE_p = 80 mV) reductive CV responses at $E_{1/2}$ = −0.76 V and $E_{1/2}$ = −1.50 V *vs.* SCE, corresponding to the Co^{III}–Co^{II} and Co^{II}–Co^{I} redox processes, respectively. A reversible oxidative response (ΔE_p = 60 mV) is also observed at $E_{1/2}$ = 0.81 V, which could be either due to a Co^{IV}–Co^{III} or a ligand-centered redox process (Fig. 6). It is well-documented that a combination of deprotonated amide nitrogen and thiolate sulfur donors is well-suited to substantially stabilize the Co^{III} state.[9b]

In MeCN solution the Co^{III} complex **2b**, however, displays three reversible reductive responses at $E_{1/2}$ = −0.21 V (ΔE_p = 60 mV), $E_{1/2}$ = −1.32 V (ΔE_p = 60 mV), and $E_{1/2}$ = −1.71 V (ΔE_p = 90 mV), corresponding to the Co^{III}–Co^{II}, Co^{II}–Co^{I}, and Co^{I}–Co^{0} redox processes, respectively (Fig. 7). The observed $E_{1/2}$ values exactly match with the corresponding Co^{II} complex **1b**·MeOH. This is understandable given the fact that the metal coordination geometry is expected to be invariant in these two complexes. As the cobalt(III) centre in **2b** is in a low-spin state the reversible redox behaviour at ≈−0.20 V strengthens our contention that the cobalt(II) centre in **1b**·MeOH has low-spin character.

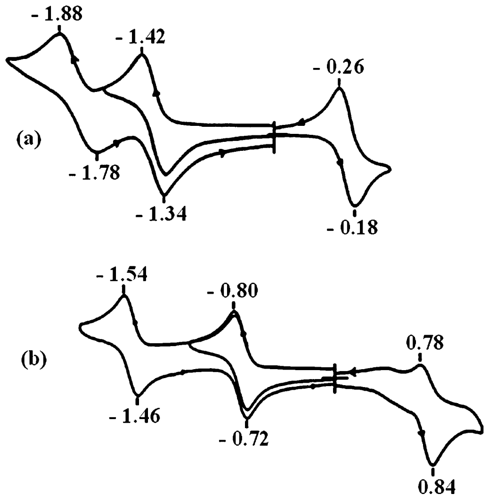


Fig. 6 Cyclic voltammograms (100 mV s^{-1}) of ~1 mM solutions of (a) [Co^{II}(**L**^{1})]·MeOH (**1a**) and [Co^{III}(**L**^{3a})(**L**^{3b})]·2MeOH·H_2O (**2a**) in MeCN (0.1 M in TBAP) at a glassy-carbon working electrode. Indicated potentials (in V) are *vs.* SCE.

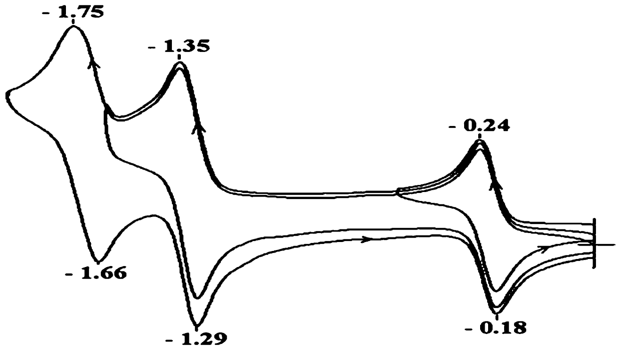
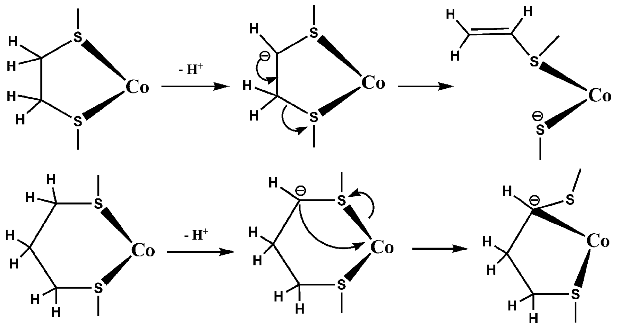


Fig. 7 Cyclic voltammograms (100 mV s^{-1}) of ~1 mM solutions of [Co^{III}(**L**^{2})][ClO$_4$] (**2b**) in MeCN (0.1 M in TBAP) at a glassy-carbon working electrode. Indicated potentials (in V) are *vs.* SCE.

The organocobalt(III) complex **3** shows, in CH_2Cl_2, a reductive response at $E_{1/2} = -1.28$ V ($\Delta E_p = 120$ mV) corresponding to a Co^{III}–Co^{II} redox process. Due to enhanced σ donation by three anionic donor sites (two deprotonated amide nitrogens and a carbanion) it is understandable why the Co^{III} state in **3** is substantially stabilized.

The C–S bond cleavage and cyclometallation reaction: a rationale

On the basis of the present findings taken collectively with that reported in the literature (d^6-ion-promoted thioether activation *via* base attack),[10,11] a rationale for the chelate-ring size dependent reactivity of cobalt(II) complexes with a base under aerobic conditions is provided (Scheme 2). Interestingly, the cobalt(II) complexes [Co(**L**^{1})]·MeOH (**1a**) and [Co(**L**^{2}]·MeOH (**1b**·MeOH) are low-spin, attesting the fact that **L**^{1}(2−) and **L**^{2}(2−) are strong-field ligands. Thus during facile oxidation of Co^{II} to the Co^{III} state (CV result) initial activation of expected low acidity of a C–H bond α to a coordinated thioether unit appended to a strong-field ligand framework will be facile due to the strong-field nature of **L**^{1}(2−) and **L**^{2}(2−). In the case of **1a** the coordinated ligand **L**^{1}(2−) cleaves into two unsymmetrical ligand components *via* scission of the C–S bond affording the Co^{III} complex **2a**. It has a Co^{III}(N_2S)(N_2S') coordination sphere involving both thioether (S) and thiolate (S′) sulfur, the possible formation of an unfavourable and more strained four-membered metallacycle is bypassed *via* migration of the anionic charge to a sulfur site with concomitant ligand cleavage. The ligand **L**^{2}(2−), capable of providing N_4S_2 coordination, has a –CH_2– group stereochemically suitably positioned such that deprotonation, with subsequent carbanion coordination, could lead to an N_4CS donor set around cobalt(III) with all five-membered chelate-rings. Indeed it happens in the synthesis of **3**. In essence, an activated five-membered chelate-ring leads to C–S bond cleavage whereas a six-membered chelate-ring affords the organocobalt(III) complex.



Scheme 2

Concluding remarks

A new class of five (four structurally characterized) mononuclear bivalent and trivalent cobalt complexes having distorted octahedral CoN_4S_2/CoN_4CS coordination spheres have been successfully synthesized with diathiaalkyl appended hexadentate acyclic pyrazine amide ligands. The complexes [Co^{II}(**L**^{1})]·MeOH (**1a**) and [Co^{II}(**L**^{2})]·MeOH (**1b**·MeOH) join the rare family of low-spin Co^{II} octahedral complexes. Metal-ion mediated activation of C–H bonds of organic molecules is a fundamentally important chemical process. Notably, ring-size-specific differentiation in reactivity has been observed for **1a** and **1b**·MeOH on base treatment. The ligand **L**^{2}(2−) forming a six-membered chelate-ring is capable of stabilizing Co^{II} state even in air, whereas the ligand **L**^{1}(2−) which forms a five-membered chelate-ring with Co^{II} undergoes a facile oxidation to Co^{III} in air, followed by cleavage of a C–S bond affording the complex [Co^{III}(**L**^{3a})(**L**^{3b})]·2MeOH (**2a**). This complex has a Co^{III}(N_2S)(N_2S') coordination sphere involving both thioether (S) and thiolate (S′) sulfurs. The complex **1b**·MeOH, on treatment with a base, affords an organocobalt complex [Co^{III}(**L**$^{2'}$)] (**3**). Notably, this is the third report of C–H bond activation that shows both reactivity patterns in a cobalt(III)-coordinated thioether function, triggered by base treatment.[11e–g] We plan to carry out detailed temperature-dependent magnetic and EPR spectral studies on the cobalt(II) compounds. Inspired by the findings of this study we are currently engaged in the exploration of the coordination chemistry of **L**^{1}(2−) and **L**^{2}(2−) towards Ru(II).

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