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Syntheses, structure and properties of cobalt-(II) and -(III) complexes of pentadentate N_4S ligands with appended pyrazolyl groups: evidence for cobalt(II)–dioxygen reversible binding

Sudeep Bhattacharyya,[a] **Dipesh Ghosh,**[a] **Suman Mukhopadhyay,**[a] **William P. Jensen,**[b,c]
Edward R. T. Tiekink[b] **and Muktimoy Chaudhury** *[a]

[a] *Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India. E-mail: icmc@mahendra.iacs.res.in*
[b] *Department of Chemistry, The University of Adelaide, 5005, South Australia*
[c] *Department of Chemistry, South Dakota State University, Brookings, DS 57007, USA*

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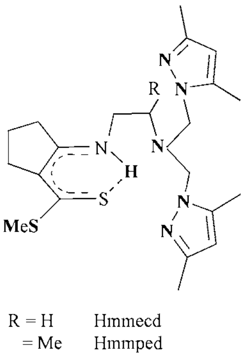
Cobalt-(II) and -(III) complexes of pentadentate N_4S ligands based on methyl 2-aminocyclopent-1-ene-1-carbodithioate with appended pyrazolyl groups $(3,5\text{-}Me_2C_3HN_2CH_2)_2NCH(R)CH_2NHC_5H_6C(=S)SCH_3$ (R = H, Hmmecd; CH_3, Hmmpcd) have been prepared and characterised by IR, ^{1}H NMR and electronic spectroscopy. Two of these compounds have also structurally been characterised by X-ray single crystal diffraction analyses. Cobalt(II) in [Co(mmpcd)]ClO_4, **1**, shows a five-coordinate, trigonal bipyramidal geometry while its cobalt(III) counterpart, [Co(mmpcd)Cl]ClO_4, **2**, reveals a six-coordinated distorted octahedral structure by the inclusion of a chloride ligand in its equatorial plane. In dmf or acetonitrile solution, **1** can bind dioxygen reversibly as indicated by EPR spectra recorded at cryogenic temperatures. Metal–dioxygen binding in **1** appears to be weak, possibly due to its trigonal bipyramidal structure and the presence of a sulfur donor in the ligand framework. Electronic spectra of the cobalt(III) complexes show two LMCT bands in the near UV region, tentatively assigned to $S\rightarrow Co^{III}$ charge transfer.

Introduction

Five-coordinated metal ions have been the topic of our recent research.[1–4] The N_4S ligands methyl 2-{2[bis(3,5-dimethylpyrazol-1-ylmethyl)amino]ethylamino}cyclopent-1-ene-1-carbodithioate (Hmmecd) and its propyl homologue (Hmmpcd) have a pair of appended pyrazolyl groups and a carbodithioate functionality behaving like thiol when coordinated.[1–5] With sufficient flexibility in the ligand backbone and an interesting hard–soft (N_4S) combination in the ligand donor set, these five-coordinating ligands are capable of offering several variations in their coordination patterns. Thus, with copper(II) and zinc(II) ions, the ligands use all five donor sites to generate geometries with varying degrees of distortions.[1] With nickel(II) and palladium(II), on the other hand, the situation is a little more complicated, especially in the presence of hydroxylated compounds as substrates.[2–4] The reaction proceeds through activation of otherwise unreactive C–N single bond(s) of the coordinated ligands to generate mono- or bi-nuclear complexes with square planar geometry. The structural anomeric effect is believed to have a significant role in this bond activation process.[4]



R = H Hmmecd
= Me Hmmped

Herein, we report the synthesis of cobalt(II) and cobalt(III) complexes of these Hmmpcd and Hmmecd. X-Ray crystallography, electronic spectroscopy, ^{1}H NMR and variable temperature (300–2 K) magnetic susceptibility measurements have been carried out to characterise these compounds. EPR studies in solution at temperatures below 77 K indicate reversible dioxygen binding by the cobalt(II) complex, [Co(mmpcd)]ClO_4.

Experimental

Materials

The ligands Hmmecd and Hmmpcd were synthesized following reported methods.[1] Unless stated otherwise, the reactions were carried out under an atmosphere of purified dinitrogen. Reagent grade solvents were dried from appropriate reagents[6] and distilled prior to their use. All other chemicals were reagent grade, available commercially and used as received.

Preparations

[Co(mmpcd)]ClO_4 1. The ligand Hmmpcd (0.44 g, 1 mmol) was dissolved in 20 cm^3 of methanol. To this solution was added a solution of cobalt(II) perchlorate hexahydrate (0.37 g, 1 mmol) also in methanol (5 cm^3). The solution turned red immediately. It was stirred for *ca.* 30 min at room temperature when a brown microcrystalline solid separated. The solid was filtered off, washed with diethyl ether, and dried *in vacuo*. The complex was recrystallised at 4 °C from methanol–dichloromethane (4:1 v/v) layered with ether. Yield: 0.29 g (48%). Found: C, 43.5; H, 5.6; N, 13.8. Calc. for $C_{22}H_{33}ClCoN_6O_4S_2$: C, 43.7; H, 5.5; N, 13.9%. IR (KBr disk): $\nu(C\overset{\cdots}{-}N)$/pyrazole ring, 1555s; $\nu(C\overset{\cdots}{-}N + C\overset{\cdots}{-}C)$, 1470s, 1445s; ν_{asym}(Cl–O), 1090vs; δ(O–Cl–O), 625s cm^{-1}. Λ_M (25 °C, CH_3CN): 110 S cm^2 mol^{-1}.

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[Co(mmpcd)Cl]ClO$_4$ 2. To a stirred methanolic solution of Hmmpcd (0.22 g, 0.5 mmol) was added slowly a methanolic solution of cobalt(II) chloride hexahydrate (0.12 g, 0.5 mmol). The resultant red solution was stirred at room temperature for 1 h and filtered. The filtrate was saturated with oxygen by bubbling air for *ca.* 20 min when a green solution was obtained. To this 0.1 g of NaClO$_4$ was added and then left to evaporate slowly in the air to yield a green microcrystalline solid. The product was collected by filtration, washed with *n*-hexane and finally recrystallised from hot methanol. Yield: 0.13 g (40%). Found: C, 41.1; H, 5.2; N, 13.2. Calc. for $C_{22}H_{33}Cl_2CoN_6O_4S_2$: C, 41.3; H, 5.2; N, 13.1%. IR (KBr disk): ν(C$\cdots$C), 1575s; ν(C$\cdots$N)/pyrazole ring, 1550s; ν(C$\cdots$N + C$\cdots$C), 1465vs; ν_{asym} (Cl–O), 1100vs; δ(O–Cl–O), 625s cm^{-1}. Λ_M(25 °C, CH$_3$CN): 105 S cm^2 mol^{-1}.

[Co(mmecd)Cl]ClO$_4$ 3. This compound was prepared using the same procedure as for **2** except that Hmmecd was used as ligand. The yield was 48%. Found: C, 40.9; H, 5.0; N, 13.4. Calc. for $C_{21}H_{31}Cl_2CoN_6O_4S_2$: C, 40.3; H, 5.0; N, 13.4%. IR (KBr disk): ν(C$\cdots$C), 1575s; ν(C$\cdots$N)/pyrazole ring, 1555s; ν(C$\cdots$N + C$\cdots$C), 1460vs, ν_{asym}(Cl–O), 1100vs; δ(O–Cl–O), 625s cm^{-1}. Λ_M(25 °C, CH$_3$CN): 110 S cm^2 mol^{-1}.

CAUTION: perchlorate salts of metal complexes are potentially explosive.[7] Complexes reported above were isolated in small quantities and handled with care.

Physical methods

IR spectra (4000–400 cm^{-1}) of the solid compounds were recorded on a Perkin-Elmer 783 Spectrophotometer as KBr disks, UV/VIS spectra in solutions on a Shimadzu UV-2100 Spectrophotometer. Solution electrical conductivities were measured with a Systronics Model 304 bridge. Magnetic moments of powdered samples at room temperature were calculated from data obtained on a PAR 155 vibrating-sample magnetometer. Variable temperature (300–2 K) magnetic susceptibility data were measured with a Quantum Design model MPMS 5 SQUID susceptometer at 1 T field strength. Diamagnetic corrections were applied using Pascal's constants. The X-band EPR spectra in solution (dmf–CH$_3$CN, 1 : 10 v/v) at room temperature as well as in the frozen state (up to 18 K) were recorded on a Varian E-line Century Series Instrument equipped with a Varian E-102 microwave bridge and Oxford Instrument ITC-4 temperature controller. The ^{1}H NMR spectra were recorded on a Bruker model Avance DPX 300 Spectrometer. Elemental analyses were performed with a Perkin-Elmer 240C elemental analyser.

Crystallography[8–12]

Diffraction quality crystals of complex **1** were grown by slow diffusion of *n*-hexane into an acetone solution of it. Crystals of **2** were obtained by slow evaporation of a methanolic solution.

Crystal data. $C_{22}H_{33}ClCoN_6O_4S_2$ **1**, $M = 604.1$, triclinic, space group $P\bar{1}$, $a = 9.981(2)$, $b = 15.610(4)$, $c = 8.943(2)$ Å, $\alpha = 100.06(2)$, $\beta = 93.74(2)$, $\gamma = 100.16(2)°$, $V = 1343.9(6)$ Å^3, $Z = 2$, $T = 293$ K, μ(Mo-Kα) = 9.34 cm^{-1}, 6565 reflections for a red crystal measured on a Rigaku AFC6R diffractometer, 6212 unique ($R_{int} = 0.040$), 3359 with $I \geq 3.0\sigma(I)$ used in subsequent calculations: final $R = 0.048$ and $R_w = 0.050$.

$C_{22}H_{33}Cl_2CoN_6O_4S_2$ **2**, $M = 639.5$, monoclinic, space group $P2_1/c$, $a = 12.86(1)$, $b = 13.13(1)$, $c = 16.01(2)$ Å, $\beta = 92.50(7)°$, $V = 2701(4)$ Å^3, $Z = 4$, $T = 135$ K, μ(Mo-Kα) = 10.29 cm^{-1}, 6801 reflections measured for a brown wedge as above, 6525 unique ($R_{int} = 0.130$), 3603 with $I \geq 3.0\sigma(I)$ used in subsequent calculations: final $R = 0.070$ and $R_w = 0.081$. The perchlorate was found to be disordered so that the O(4) atom (refined isotropically) was split over two sites with site occupancy factors of 0.52 and 0.48.

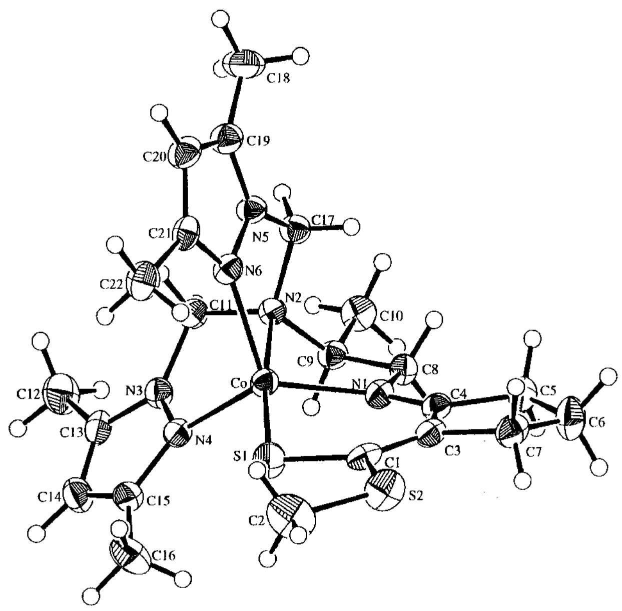

Fig. 1 An ORTEP drawing of the cation in [Co(mmpcd)]ClO$_4$, **1**, showing the atom-labelling scheme. Thermal ellipsoids shown are at the 35% probability level.

CCDC reference number 186/2249.

See http://www.rsc.org/suppdata/dt/b0/b005906o/ for crystallographic data in .cif format.

Results and discussion

Cobalt(II) complex

Synthesis of the cobalt(II) complex [Co(mmpcd)]ClO$_4$, **1** is straightforward: a brown crystalline product was obtained in moderate yield by mixing equimolar amounts of cobalt(II) perchlorate hexahydrate and the ligand in methanol solution. The corresponding cobalt(II) compound with Hmmecd as the ligand is relatively unstable. We were unable to develop any reproducible methodology for its isolation in the analytically pure form.

The IR spectrum (KBr disc) of complex **1** has several prominent features characteristic of coordinated N$_4$S ligand.[1] Two such bands appearing at 1555 and 1470 cm^{-1} are due to stretching modes associated with the pyrazolyl and cyclopentene rings, respectively. In addition, the complex displays two strong bands at 1090 and 625 cm^{-1}, confirming the presence of ionic perchlorate.[13] The molar conductivity in acetonitrile (110 S cm^2 mol^{-1}) is in accord with 1 : 1 electrolytic behaviour.[14]

Crystal structure. The molecular structure of the cation in [Co(mmpcd)]ClO$_4$ is shown in Fig. 1 and selected bond distances and angles are given in Table 1. The cobalt(II) centre is coordinated by a sulfur atom and four nitrogen atoms, *i.e.* one imine, two pyrazolyl and one tertiary amine nitrogen with the Co–N bond distances increasing in this order. The coordination geometry is best described as being based on a trigonal bipyramidal arrangement in which the axial positions are defined by the S(1) and N(2) atoms, the S(1)–Co–N(2) angle is 173.91(9)°. The angles in the trigonal plane range from 107.1(1) to 122.3(1)° and the cobalt atom lies 0.4540(6) Å out of this plane in the direction of the S(1) atom. The Co–S(1) distance of 2.311(1) Å is comparable to average Co–S distances in cobalt(II) thiolate complexes.[15,16] The S(1)–C(1) distance 1.707(5) Å also indicates thiolate character for the metal bound sulfur, a feature typical of the 2-aminocyclopentene based carbodithioate moiety.[1,5] The closest intermolecular contact in the lattice involving the non-hydrogen atoms of 3.212(6) Å

Table 1 Selected bond lengths (Å) and angles (°) for complexes **1** and **2**

	1	**2**
Co–S(1)	2.311(1)	2.210(2)
Co–N(1)	2.012(4)	1.911(5)
Co–N(2)	2.276(3)	2.016(5)
Co–N(4)	2.038(4)	1.955(6)
Co–N(6)	2.051(3)	1.939(6)
Co–Cl	—	2.288(2)
S(1)–C(1)	1.707(5)	1.719(7)
S(1)–Co–N(1)	95.5(1)	98.4(2)
S(1)–Co–N(2)	173.91(9)	173.5(2)
S(1)–Co–N(4)	104.7(1)	97.1(2)
S(1)–Co–N(6)	109.5(1)	97.8(2)
N(1)–Co–N(2)	78.7(1)	88.0(2)
N(1)–Co–N(4)	122.3(1)	91.1(2)
N(1)–Co–N(6)	115.9(1)	87.7(2)
N(2)–Co–N(4)	77.3(1)	81.9(2)
N(2)–Co–N(6)	75.0(1)	83.2(2)
N(4)–Co–N(6)	107.1(1)	165.1(2)
Cl–Co–S(1)		82.03(8)
Cl–Co–N(1)		177.7(2)
Cl–Co–N(2)		91.6(2)
Cl–Co–N(4)		91.2(2)
Cl–Co–N(6)		89.9(2)

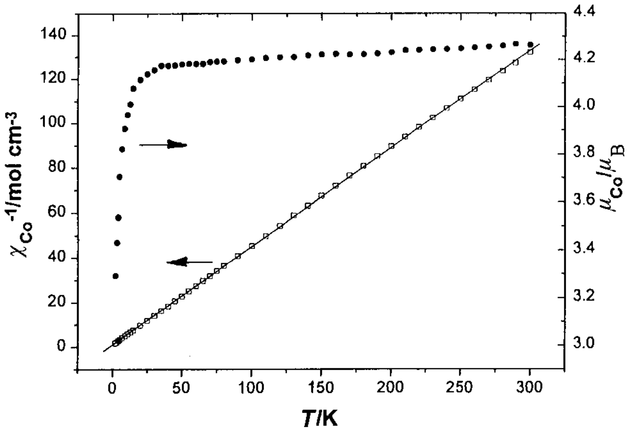

Fig. 2 Magnetic moments and reciprocal susceptibilities of [Co(mmpcd)]ClO$_4$, **1**, over the temperature range 2 to 300 K.

occurs between the perchlorate O(3) and N(3)^i atoms; symmetry operation i −1 + x, y, z.

Magnetic susceptibility and EPR measurements. The magnetic susceptibility of a powdered sample of complex **1** was measured over the temperature range 300 to 2 K using a SQUID susceptometer. Fig. 2 displays the plots of χ_{Co}^{-1} and μ_{Co} as a function of temperature. These show typical Curie–Weiss behaviour (linear regression yields $C = 2.27$ cm^3 K mol^{-1} and $\theta = -2.44$ K) with the magnetic moment remaining virtually independent of temperature in the higher temperature range, there being only a marginal drop from 4.26 μ_B at 300 K to 4.11 μ_B at 30 K. These values are typical for a high-spin cobalt(II) ($S = 3/2$) system, due to the orbital contribution of the excited E levels.[17] Below 30 K, however, there is a rapid reduction in magnetic moment to a value of 3.07 μ_B at 2 K. This behaviour is associated with significant zero-field splitting, leading to an unequal population of the Kramer's doublet of the spin quartet state. The results confirm **1** to be a high-spin species in the solid state throughout this temperature range.

In solution, both in the presence and absence of oxygen, the magnetic behaviour of complex **1** has been examined by ^{1}H NMR spectroscopy. Spectra obtained in CD$_3$CN, dmso-d_6 and dmf-d_7 have identical features in the temperature range 300–220 K and are characteristic of a high-spin cobalt(II) compound with very short spin–lattice relaxation time. Unfortunately, due to the frozen solution condition, we were unable to monitor the NMR spectra of the solutions below 220 K (freezing point of dmf-d_7, −61 °C) where a change in magnetic properties due to oxygenation (see below) is expected.

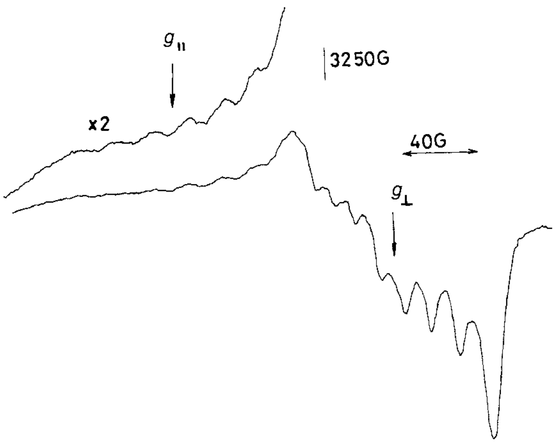

Fig. 3 X-Band EPR spectrum of the [Co(mmpcd)]ClO$_4$ dioxygen adduct in dmf–CH$_3$CN (1 : 10 v/v) solution at 18 K.

The X-band EPR spectrum of complex **1** in oxygenated solution (dmf–CH$_3$CN, 1 : 10 v/v) does not show any signal at room temperature. This is as expected for high-spin cobalt(II) complexes because of their very short spin–lattice relaxation time in all common stereochemistries, and very low temperatures are required to detect any characteristic signals.[18] At temperatures below 77 K a signal at $g \sim 2$ was observed (Fig. 3) containing two sets of well resolved eight line patterns characteristic of an unpaired electron being coupled to a cobalt nuclear spin (^{59}Co, $I = 7/2$). Corresponding spin-Hamiltonian parameters ($g_{\parallel} = 2.085$, $g_{\perp} = 2.010$, $A_{\parallel} = 17.5$ and $A_{\perp} = 12.0$ cm^{-1}) are characteristic of a radical based ($S = 1/2$) molecule with hyperfine coupling constants typically less than 20 cm^{-1}, compared to standard cobalt values.[19,20] The observed frozen solution spectrum with its typical shape and features is believed to originate from a superoxide radical[21–23] generated in the oxygenated solution by binding of dioxygen to cobalt(II) in **1**. Although supported by crystallographic evidence,[24] the explanation of superoxide ion involvement[22] has been contradicted by others.[25] According to the latter, the reduced EPR anisotropy results from a spin polarisation mechanism with the unpaired electron residing predominantly on O$_2$, *i.e.* this mechanism does not require a formal electron transfer from cobalt(II) to form the O$_2^-$ ion. The anisotropic features were only observed in polar solvents, *viz.* dmf and acetonitrile, at cryogenic temperatures and not in solvents like dichloromethane or nitromethane with poor or no coordinating properties. Similar solvent dependence of Co^{II}–dioxygen binding has been documented.[23] The spectrum disappears when the experimental solution of **1** is thoroughly flushed with argon and reappears upon introduction of dioxygen, thus confirming the reversible nature of this weak cobalt(II)–dioxygen binding in the present case.

A powdered solid of compound **1** does not show any EPR spectrum in the temperature range 300–10 K. This is as expected from the results of magnetic studies described above.

Electronic spectroscopy. Electronic spectral data for [Co(mmpcd)]ClO$_4$ **1** are collected in Table 2. In deoxygenated acetonitrile (thoroughly flashed with argon) solution it shows a prominent band maximum at 720 nm (ε 65 dm^3 mol^{-1} cm^{-1}) associated with a d–d transition, followed by a medium intensity band at 450 nm (ε 1750 dm^3 mol^{-1} cm^{-1}). This latter band, we believe, also has ligand field origin[26,27] and gains intensity from the tail of a nearby LMCT band at 371 nm (ε 10900 dm^3 mol^{-1} cm^{-1}) attributable to S→Co^{II} charge

Table 2 Summary of electronic spectroscopic data[a]

Complex	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})
1 [Co(mmpcd)]ClO$_4$	720 (65), 450 (1750), 371 (10900), 310 (8600), 245 (14350)
2 [Co(mmpcd)Cl]ClO$_4$	700 (170), 565 (210), 432 (4400), 414 (3450), 292 (25000), 230 (26100)
3 [Co(mmecd)Cl]ClO$_4$	705 (170), 565 (215), 432 (4400), 412 (3550), 290 (25300), 232 (27500)

[a] Spectra recorded in acetonitrile.

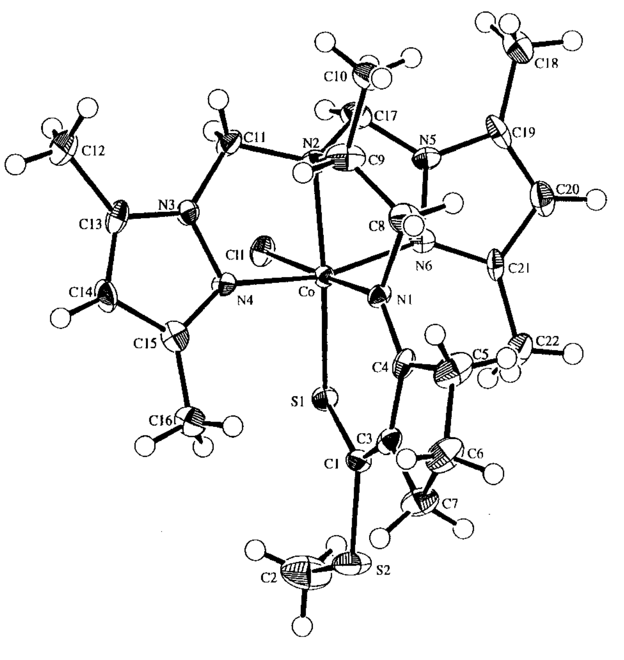

Fig. 4 An ORTEP drawing of the cation in [Co(mmpcd)Cl]ClO$_4$, **2**, with the atom numbering. Thermal ellipsoids shown are at the 50% probability level.

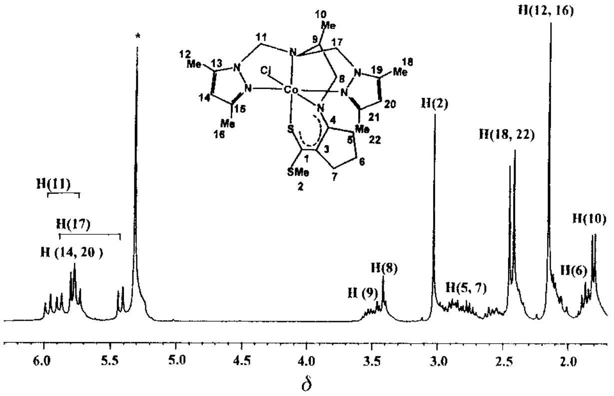

Fig. 5 300 MHz ^{1}H NMR spectrum of [Co(mmpcd)Cl]ClO$_4$, **2**, in dichloromethane-d_2 solution at 25 °C. The asterisk indicates protio solvent impurity.

transfer. Remaining band maxima appearing near or below 300 nm are due to ligand internal transitions, based on similarities with the absorptions of the "free" ligand. These spectral features remain unchanged when molecular oxygen is bubbled through the solution for *ca.* 20 min at temperatures 303–283 K. Thus we are unable to see the expected change(s) in the electronic spectrum due to oxygenation which, in the present case, can only occur at cryogenic temperatures.

Cobalt(III) complexes. Indications of reversible dioxygen binding by complex **1** at cryogenic temperatures have prompted us to isolate the cobalt(III) complexes of these N$_4$S ligands. Initial attempts involving aerial oxidation of the red solution mixtures obtained by mixing Co(ClO$_4$)$_2$·6H$_2$O with N$_4$S ligands in methanol proved unsuccessful. The above procedure when followed with a minor modification by replacing Co(ClO$_4$)$_2$·6H$_2$O with CoCl$_2$·6H$_2$O as the metal ion precursor resulted in green crystalline complexes of composition [Co(mmpcd)-Cl]ClO$_4$, **2**, and [Co(mmecd)Cl]ClO$_4$, **3**. Their elemental analyses, IR spectra and molar conductivity values in solution (see Experimental section) are in good agreement with the assigned compositions.

Crystal and molecular structure. The molecular structure and the atom numbering scheme for the cation in complex **2** are shown in Fig. 4 and selected geometric parameters are listed in Table 1. Oxidation of the cobalt(II) centre in **1**, to Co^{III}, and subsequent introduction of a chloride ligand in the coordination sphere leads to **2**. The coordination geometry for the cation is distorted octahedral with N(2) and S(1) atoms defining the axial positions (N(2)–Co–S(1), 173.5(2)°) while the imino nitrogen N(1) and the pyrazolyl nitrogen atoms N(4) and N(6) lie in the basal plane along with the 'incoming' Cl(1) atom. The cobalt atom is situated almost in the equatorial plane lying only 0.1042(6) Å above the least-squares plane in the direction of the S(1) atom. Consistent with the increase in oxidation state of the cobalt atom, there is a uniform contraction in the Co–ligand bond distances going from structure **1** to **2** (Table 1). A number of changes in the angles subtended at the cobalt centre could be anticipated owing to reorganisation of the ligand donor set in **2**, however the most significant changes involve atoms that define the trigonal plane in **1**. Thus the angles N(1)–Co–N(4) and N(1)–Co–N(6) have contracted by approximately 30°, while the remaining angle N(4)–Co–N(6) has expanded by *ca.* 60° in **2** compared to **1** due to introduction of Cl(1) into the coordination geometry. The slightly shorter Co–S(1) distance 2.210(2) Å in **2** is in accord with similar distances found in cobalt(III)–thiolate complexes.[28,29] In the lattice the closest non-hydrogen intermolecular contact occurs between O(2) and C(11)^{ii} atoms, 2.998(6) Å; symmetry operation *ii* $-x$, $-0.5 - y$, $-0.5 - z$.

^{1}H NMR spectroscopy. The proton NMR spectrum of [Co(mmpcd)Cl]ClO$_4$ **2** (Fig. 5) has several interesting features compared to that of free Hmmpcd. The broad signal due to the N–H···S functionality appearing at δ 11.18 in the "free" ligand spectrum is missing in that of the complex. Also the methylenic protons H(11) and H(17), which together appear as a singlet at δ *ca.* 5.0 for the "free" ligand, are diastereotopic in the complex due to restricted rotation of the metal-bound pyrazolyl arms and each appears as a AB quartet with values for H(11) protons at δ 5.97 and 5.75 (J_{AB} = 12 Hz). Corresponding values for the H(17) protons are δ_A 5.89 and δ_B 5.43 (J_{AB} = 10.8 Hz). The least shielded pyrazolyl ring protons H(14) and H(20), which appear collectively as a singlet at δ 5.79 for the "free" ligand, appear in the spectrum of **2** as a pair of singlets at δ 5.80 and 5.78. The latter resonance overlaps with a doublet at δ 5.75, due to one of the H(11) protons, to give the appearance of a triplet at δ 5.77. The spectrum in the upfield region δ 3.6–1.6 is a little more complicated and required ^{1}H–^{1}H COSY NMR data to corroborate the proposed assignments (see below). Thus, a cluster of resonances due to three protons in the δ 3.6–3.35 region is assigned to the H(8) methylenic

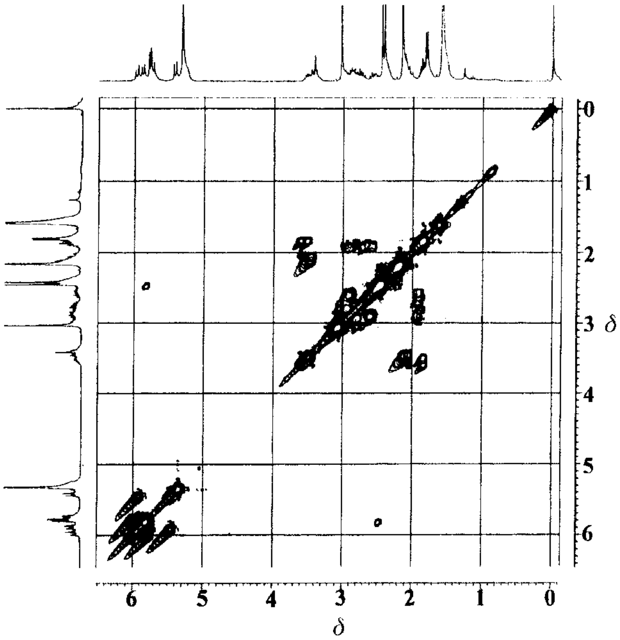

Fig. 6 ^{1}H–^{1}H 2-D-COSY NMR spectrum (300 MHz, 25 °C, dichloromethane-d_2) of [Co(mmpcd)Cl]ClO$_4$, **2**.

and H(9) methine protons of the ethylenic backbone of the coordinated ligand. Another cluster of signals in the region δ 2.90–2.50, integrating to four protons, is ascribed to the methylene protons H(5) and H(7) of the cyclopentene ring. The remaining ring protons H(6) also appear as multiplet centred at δ 1.85. The rest of the spectrum involves a number of sharp signals all due to various methyl protons as per the atomic labelling scheme shown in Fig. 5.

In order to reinforce the assignments of the clustered signals in Fig. 5 and to resolve the complex connectivities involved, ^{1}H–^{1}H COSY NMR experiments were performed on complex **2**. The spectrum (Fig. 6) contains eight cross peaks of which two are due to geminal couplings of H(11) and H(17) methylene protons (proton labels as shown in Fig. 5). Three upfield cross peaks are due to mutual interactions among the H(5), H(6) and H(7) methylene protons of the cyclopentene ring, thus confirming their appearances as a cluster of signals. The methine proton H(9) is involved in two cross peaks which explains its appearance as a multiplet. While the first cross peak confirms its interactions with the adjoining H(10) methyl protons to generate an expected doublet at δ 1.80, the other owes its origin from relatively long range interactions involving the methyl protons H(18) and H(22) of the nearby pyrazolyl moiety. The 2-D experiment also confirms distant interactions between one of the diastereotopic H(11) protons and the methyl protons H(12) and H(16) of the adjacent pyrazolyl ring.

Optical spectroscopy. Table 2 summarises the electronic spectral data for complexes **2** and **3**. Their spectral features in acetonitrile solution are almost identical. Two lower energy bands at 700 and 565 nm have intensities consistent with spin-allowed d–d transitions $^1A_{1g} \longrightarrow {}^1T_{1g}$ and $^1A_{1g} \longrightarrow {}^1T_{2g}$, respectively as expected for low-spin pseudo-octahedral cobalt(III) complexes.[30] The more intense bands appearing at 432 (ε 4400) and 414 nm (3500 dm^3 mol^{-1} cm^{-1}) are indicative of charge transfer transitions, probably originating from S→Co^{III} charge transfer as reported.[28,29] The remaining bands in the UV region are due to ligand-localised transitions.

Concluding remarks

The five-coordinated trigonal bipyramidal cobalt(II) complex [Co(mmpcd)]ClO$_4$ in a N$_4$S donor environment has been described. It can bind molecular oxygen reversibly in solution as reflected from its characteristic EPR spectra recorded at temperatures below 77 K. At room temperature, however, there is no evidence in support of such metal–dioxygen bonding as has been observed by others.[31,32] Those studies involved square pyramidal cobalt(II) precursors which allowed the dioxygen molecule to approach the metal centre along the available axial site where a metal d$_{z^2}$ electron is available to bind the incoming ligand. In the present trigonal bipyramidal precursor complex both axial sites are blocked. The incoming oxygen molecule is probably allowed to approach the metal centre through one of the equatorial sites, as observed in the analogous cobalt(III) complex [Co(mmpcd)Cl]ClO$_4$, leading to weak metal–oxygen bonding. Also, the presence of a sulfur donor in the ligand framework is capable of removing electron density from the cobalt(II) centre *via* a π-bonding mechanism,[20,33] thereby favouring weak dioxygen bonding in the present case. In the solid state, the cobalt(II) compound shows magnetic moment values in the temperature range 300–2 K, which are typical for a high spin cobalt(II) (S = 3/2) system. The diamagnetic cobalt(III) complexes are in a distorted octahedral ligand field and display a pair of high intensity electronic spectral bands in the near UV region, tentatively due to S→Co^{3+} charge transfer. Similar spectral features are characteristic of thiol-coordinated low-spin non-corrin cobalt(III) chromophore(s) found in a group of nitrile hydratase enzymes of bacterial origin.[34,35]

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