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Synthesis and spectroscopic characterisation of cobalt(III) complexes with S-benzyl dithiocarbazate of 5-methyl-3-formyl pyrazole (HMPzSB): X-ray crystal structure of $[Co(MPzSB)_2]Cl$

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Abstract—The coordination mode of the title ligand, HMPzSB (synthesized for the first time and characterised by elemental analysis, mass, IR and PMR spectral parameters), is reported by solid state isolation and physicochemical identification of cobalt(III) complexes, $[Co(MPzSB)_2]X$ (X = Cl, ClO_4 and BF_4). Electronic spectral features of these diamagnetic Co^{III} species classify them as six-coordinate distorted octahedral ones. IR spectra (4000–200 cm^{-1}) of HMPzSB and its complexes are indicative of an uninegative tridentate NNS function of the title ligand through the Pyrazolyl (^2N) nitrogen, azomethine nitrogen and thiolato sulphur atom. ^1H-NMR data (in d_6-DMSO at 300 MHz) of the uncomplexed ligand and its Co^{III} species are commensurate with the tridenticity (NNS) of the deprotonated form of HMPzSB. X-ray crystallographic studies of $[Co(MPzSB)_2]Cl$ has authenticated that the geometry of the species is distorted octahedral, as envisaged, with the two deprotonated primary ligand systems ($MPzSB^-$). The Co—N (azomethine) and Co—N (pyrazolyl) bond lengths are 1.898(4) & 1.954(5) Å and 1.903(4) & 1.916(5) Å in ligand A & B, respectively where as that of Co—S (thiolato) is 2.217(2) and 2.255(2) Å in the two ligands. The extended planarity of the dithiocarbazate moiety and the pyrazolyl ring of the primary ligand system are maintained because of the ligation phenomenon to Co^{III}. © 1997 Elsevier Science Ltd

Keywords: cobalt(III); synthesis; spectroscopy; dithiocarbazate; pyrazole; X-ray crystal structure.

The structural nature of the metal ion complexes of heterocyclic thiosemicarbazones and S-alkyl dithiocarbazates have been correlated to their biological activity [1]. Moreover, biological implication of pyrazolyl compounds, often ascribed to chelation phenomena with trace metal ions, has generated a substantial amount of literature on the coordination chemistry of pyrazole-derived ligands, reflected through review article(s) of Trofimenko [2] with due citation of Saha's work [2]. In continuation of our earlier reports [3,4] on the transition metal ion complexes of pyrazolyl thiosemicarbazones, the present communication reports the synthesis and spectroscopic characterization of cobalt(III) complexes with S-benzyl dithiocarbazate of 5-methyl-3-formyl pyrazole together with X-ray crystal structure of $[Co(MPzSB)_2]Cl$.

EXPERIMENTAL

All the materials used as different stages for the preparation of the reported cobalt(III) complexes

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were GR/AR quality and were used without further purification. Spectrograde solvents were used for spectral and conductance measurements. DMSO-d_6 (Sigma) was used for recording ^{1}H-NMR data.

Synthesis of HMPzSB

S-Benzyl dithiocarbazate of 5-methyl-3-formyl pyrazole has been synthesized for the first time by a similar but appropriately modified method [3] involving: (1) the conversion of 5-methyl pyrazole-3-carbohydrazide [5] into its benzene sulfonyl derivative (m.p. 179–180°C), followed by (2) treatment with S-benzyl dithiocarbazate [6] in alkaline ethylene glycol (160°C): the recrystallised product (aqueous ethanol) melted at 185°C. Found C, 53.4; H, 5.0; N, 18.8 and calc. for $C_{13}H_{14}N_4S_2$ C, 53.7; H, 4.8; N, 19.3%.

Synthesis of the complexes: [Co(*MPzSB*)2]*X* (*X* = Cl, ClO_4 & BF_4)

Alcoholic solution of the hydrated co^{II} salt (0.005 mol) was mixed with a solution of the ligand (0.01 mol, 2.90 g) in the same solvent; the resulting mixture was diluted with aqueous ethanol to double its volume and air was passed through this solution at ~90°C for 2–3 h for complete oxidation. The desired Co^{III} complex, in each case, precipitated out as larger reddish brown crystals upon slow evaporation; these were filtered off; washed with cold ethanol and dried over silica gel.

Physical measurements

Carbon, hydrogen and nitrogen of the HMPzSB and of the Co^{III} complexes were analysed at the Indian Association for the Cultivation of Science, Calcutta, with a Perkin–Elmer CHNS/O analyser 2400. The cobalt content of the complexes was determined gravimetrically as anhydrous $CoSO_4$, except for the perchlorate complex, where the metal was determined as the $CoHg(SCN)_4$ after decomposing the complex with conc. HNO_3 and H_2SO_4 mixture. The molar conductance of the complexes were measured in methanolic solution with a systronics Model 304 digital conductivity meter. The electronic spectra of the complexes in DMF solution (~30°C) were recorded on a Hitachi model UV2000 spectrophotometer (250–1100 nm). IR spectra were recorded on a Perkin–Elmer model 883 infrared spectrophotometer. PMR spectra were recorded in d_6-DMSo with Bruker AM 300L (300 MHz) super-conducting FTNMR. Mass spectrum of the ligand was recorded at IICB, Calcutta with JEOL JMS-AX500 mass spectrometer.

Structure determination

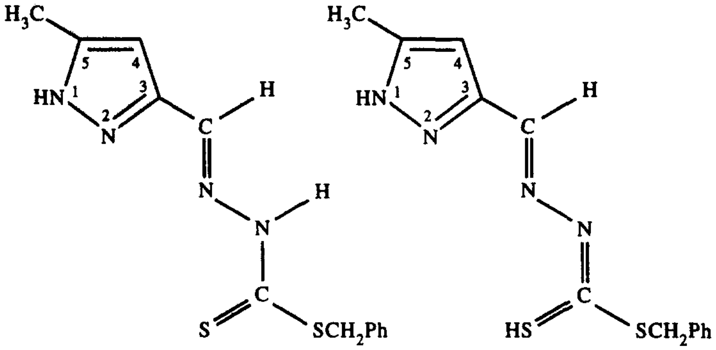
X-ray data were collected from a brown crystal of dimensions $0.12 \times 0.20 \times 0.22$ mm. On a Nonius MACH3 diffractometer, using graphite monochromatized Mo–K$_\alpha$ radiation [λ(Mo–K$_\alpha$) = 0.7103 Å].

The accurate cell parameters were determined by least squares refinement of the setting angles of 25 reflections in the range $25 \leqslant 2\theta \leqslant 35°$. The $\omega/2\theta$ scan technique was used to record intensities of reflections with a scan width of $(0.70+0.35 \tan\theta)$, scan aperture of $(2.0+1.0 \tan\theta)$ and maximum scan time of 60 s. Data were measured in the range of $2 \leqslant \theta \leqslant 25°$ with $-14 \leqslant h \leqslant 14$, $0 \leqslant k \leqslant 17$, $0 \leqslant l \leqslant 19$. Three standard reflections, 7 1 −1, 4 2 −1, 8 0 −2 were checked periodically to ensure the stability of the crystal. A total of 5380 reflections were measured of which 5178 were unique. Of these, 3428 showed $I > 2\sigma(I)$ and $R_{int} = 0.014$. Empirical absorption corrections were made with NRCVAX program ABSORB using psi-scan data. The structure of Co^{III} complex was solved by the Patterson heavy atom technique using the programme SHELX86 [7]. The position of the Co ion was determined from a three dimensional Patterson synthesis and this was used in a series of different Fourier synthesis to locate the other non-hydrogen atoms. The non-hydrogen atoms were initially refined isotropically by the full matrix least-squares procedure SHELX93 [8]. The position of the Cl$^-$ ion could not be ascertained unambiguously on account of it being disordered as was evident from the abnormally high isotropic temperature factor of this atom (Fig. 2). The chloride ion was, therefore, not refined anisotropically. The other non-hydrogen atoms, however, were refined anisotropically using SHELX93. The disordered Cl$^-$ ion probably accounts for the relatively high *R*-values. All the hydrogen atoms were generated using riding option of SHELX93 except the methyl hydrogens. These methyl hydrogens were generated using the rotating and the riding option of SHELX93. Least-squares refinement was carried out on F^2. The final least-squares cycle was calculated with 66 atoms and 356 parameters. Final residuals are $R = 0.1005$, $wR = 0.2114$ for all data and $R = 0.0735$ for $I > 2\sigma(I)$. Scattering factors were taken from the programme itself. The crystallographic data are summarized in Table 3 and the final positional parameters are available as supplementary material.

RESULTS AND DISCUSSION

Spectroscopic characterisation of HMPzSB

The primary ligand contains the thioamide function —NH—C(S)—SR and consequently it might exhibit thioene–thiol tautomerism (Fig. 1). IR spectral data are in quite good agreement with thioketo tautomer (1a) without showing any ν(S—H) band at *ca* 2575 cm^{-1} at least in the solid form of the ligand. However, the proton NMR in d_6-DMSO clearly indicates that the ligand (HMPzSB) has a second isomer (1b) as evidenced by appearance of a one proton singlet at low



(1a) Thione form **(1b) Thiol form**

Fig. 1. Thione form (1a) and thiol form (1b).

field ($\delta = 12.93$ ppm) pointing a hydrogen-bonded proton through thiol formation [9]. The mass fragmentation patterns are compatible with the proposed molecular formula of $C_{13}H_{14}N_4S_2$. The molecular ion peak appears at m/z 290 (53%). The presence of the peak at m/z 199 can be accounted for by a loss of benzyl group (m/z 91); this is followed by a secondary loss of —SC(=S)NH$_2$ to give the next peak at m/z 107 (100%); another peak at m/z 166 (100%) is due to loss of $PhCH_2SH$ (m/z 124) from the molecular ion and this is followed by further loss of the NCS unit affording a peak at m/z 108 (100%). The mass fragmentation peaks are thus reconcilable with the structural composition of the ligand (Fig. 1).

Vibrational, electronic and PMR spectra

All these cobalt(III) complexes give satisfactory carbon, hydrogen, nitrogen and cobalt analyses (Table 1) and confirm to the desired general composition [Co(MPzSB)$_2$]X (X = Cl, ClO$_4$ & BF$_4$). The molar conductance values in methanol ($\sim 30°$C) classify them as 1 : 1 electrolytes and the complexes are diamagnetic as expected for a spin-paired d^6 ion. A comparative study of the IR spectral data of the complexes with the uncomplexed ligand provide meaningful information regarding the bonding sites of the primary ligand molecule. A decrease in ν(C=N) (~ 1580 cm^{-1}) in the spectrum of the free HMPzSB to *ca* 1560 cm^{-1} is consistent with coordination of the azomethine nitrogen to the central Co^{III} ion; the IR band at *ca* 470 cm^{-1} is then assignable to ν(Co—N) [10]. A second band around 1600 cm^{-1}, assignable to ν(C=N) is expected in the spectra of the complexes, since the anionic ligand while coordinated to Co^{III} generates a double bond between ^{2}N and ^{3}C (i.e. =^{1}N—^{2}NH—^{3}C(S)—SR). The coordination of the thiol sulfur atom to Co^{III} indicated by a decrease of the thioamide band from 850 cm^{-1} (free ligand) to *ca* 800 cm^{-1} in its complexes; moreover, a new band at *ca* 375 cm^{-1} is assignable to ν(Co—S). The positive shift of the ν(N—N)(Pz) frequency from 1010 cm^{-1} (in the free ligand spectrum) to *ca* 1030 cm^{-1} on complexation with Co^{III} ion indicates involvement of the pyrazolyl nitrogen (^{2}N) atom in bonding [11] as the presence of a band around 270–280 cm^{-1} is clearly assignable to ν(Co—N)(Pz) in terms of earlier reports [3,4]. The broad band(s) assignable to ν_3 (ClO$_4$ and BF$_4$) and weaker narrow band(s) due to ν_4 (ClO$_4$ & BF$_4$) are found at 1080 & 1070 cm^{-1} and 620 & 520 cm^{-1} respectively [12] showing ionic nature of the counterion. Electronic spectra of complex species recorded in DMF yield three bands in the region 36,300–36,600; 32,200–32,400 and 23,500–23,600 cm^{-1}. The high energy bands in view of high molar extinction coefficients, are likely to arise from charge transfer transitions. The free ligand (HMPzSB) has an $n \rightarrow \pi^*$ transition at 30,395 cm^{-1} due to a thiosemicarbazone moiety [13] which shows blue shifts to region 32,200–32,400 cm^{-1} in the spectra of complexes. The band in the range 23,500–23,600 cm^{-1} can be assigned as $^1A_{1g} \rightarrow {}^1T_{1g}$ transition of a d^6 system. The ^{1}H NMR spectra of complexes (Table 2) when compared with that of the free ligand point out the following: (i) —SCH$_2$— peak showing slightly downfield ($\delta = 4.45$–4.55) shift is ascribed to coordination of the thiol sulfur to Co^{III} resulting in reduced electron density at —SCH$_2$—; (ii) maximum downfield shift occurs with the methine proton appearing at *ca* $\delta = 8.94$ in the complex molecule corresponding to $\delta = 7.41$ in the free ligand as expected due to coordination of the azomethine nitrogen to the central Co^{III}; (iii) the shifting of ^{4}CH (the pyrazole ring) from $\delta = 6.31$ (free ligand) to *ca* $\delta = 6.77$ in complexes is reasonable with the proposition that ^{2}N (pyrazole) coordinates with cobalt(III) ion. ^{1}H NMR spectra thus provide support for the bonding characteristics of the primary ligand (HMPzSB) in forming complexes with cobalt(III) through pyrazolyl ring nitrogen (^{2}N), azomethine nitrogen and the thiolato sulphur atom.

Crystal structure of [Co(*MPzSB*)$_2$]Cl

A molecular view of the complex together with the atom numbering scheme is shown in Fig. 2. The struc-

Table 1. Analytical, conductance and far IR data for the complexes

Complex (color)	% C Found (Calc.)	% H Found (Calc.)	% N Found (Calc.)	% Co Found (Calc.)	Conductivity At 30°C in MeOH (Ω^{-1} cm^2 mol^{-1})	Far IR data (in cm^{-1}) ν(Co—N)(Pz)	ν(Co—N)(azomethine)	ν(Co—S)
[Co[MPzSB)$_2$]Cl (Reddish brown)	46.4 (46.3)	4.5 (4.8)	16.7 (16.6)	8.6 (8.7)	81.1	270	475	370
[Co(MPzSB)$_2$]ClO$_4$ (deep brown)	42.3 (42.2)	4.0 (3.2)	15.6 (15.1)	7.8 (7.9)	92.0	275	465	375
[Co(MPzSB)$_2$]BF$_4$ (brown)	42.8 (42.9)	4.1 (3.6)	15.5 (15.4)	7.9 (8.1)	84.6	273	480	375

ture contains [Co(MPzSB)$_2$]$^+$ cation and Cl$^-$ anion. The Co^{III} atom is octahedrally coordinated by the two tridentate NNS ligands. The coordination is *via* the pyrazolyl (tertiary) nitrogen atoms [N(1A), N(1B)], in conformity with our earlier observations [14], the azomethine nitrogen atoms [N(2A), N(2B)] and the thiolato sulfur atoms [S(1A), S(1B)]. The pyrazolyl nitrogen [N(1B)], the thiolato sulfur [S(1B)] and two azomethine nitrogen atoms [N(2A) & N(2B)] are nearly coplanar. Table 3 summarises the relevant bond lengths (Å) and angles (°) for the non-hydrogen atoms with e.s.d.s in parentheses. The Co—N-(1A)(pyrazolyl) and Co—S(1A)(thiolato) distances are 1.954(5), 2.217(2) Å and N(1A)—Co—S(1A) angle is 166.8(2)°. The N—Co—N, N—Co—S and S—Co—S angular distributions indicate that the coordination polyhedron is distorted. This distortion in metal ion coordinated polyhedron results from the steric interactions, and the maximum distortions from the ideal octahedral geometry occurs for N(1B)—Co—N(2B) [81.3(2)°] and N(1A)—Co—N(2B) [98.8(2)°] angles. Similar distortion has been observed in literature [15]. Encapsulation of the metal atom by the coordination of six donor atoms results in the formation of four five membered chelate rings [Co, N(1), C(1), C(5), N(2) (IA, IB)]; [Co, N(2), N(3), C(6), S(1) (IIA, IIB)]. The torsion angles about the bonds in the chelate rings reveal the planar nature of the chelate rings. In both ligands, A and B, the chelate rings and the pyrazole ring lie nearly in the same plane. The pyrazole ring thus makes an extended coplanar system with the two chelate rings. This extended coplanar ring system of the two ligands approach each other orthogonally. This was evident from the analysis of the dihedral angles. The Co—S [2.217(2) & 2.255(2) Å] and the Co—N [1.898(4)–1.954(5) Å] coordination distances agree well with the values found in the literature [16–19].

The S(1)—C(6), C(6)—N(3) and C(5)—N(2) bond distances show partial double bond character. The S(1)—C(6)—N(3)—N(2) torsion angle indicate the *cis* conformation of the thiolate S(1) atom with respect to the hydrazinic N(2) atom. However, in uncomplexed thiosemicarbazide and thiosemicarbazones the S atom assumes the *trans* configuration with respect to the hydrazinic nitrogen. The N(2)—C(5)—C(1)—N(1) torsion angle show that the azomethine and pyrazolyl nitrogen atoms are also in the *cis* conformation in both the ligand molecules. This conformation of the ligand is necessary for its participation as a tridentate NNS ligand. The molecular conformation of this metal complex is fully extended in the fashion observed in the uncomplexed molecule. The partial double bond character of C(1)—C(5) in both ligand molecule favour the conjugation of the delocalized π-electrons of the heterocyclic ring with the dithiocarbazate skeleton. This conjugation results in near coplanarity of the pyrazole ring with the dithiocarbazate skeleton. The pyrazole ring is, therefore, restricted with respect to the dithi-

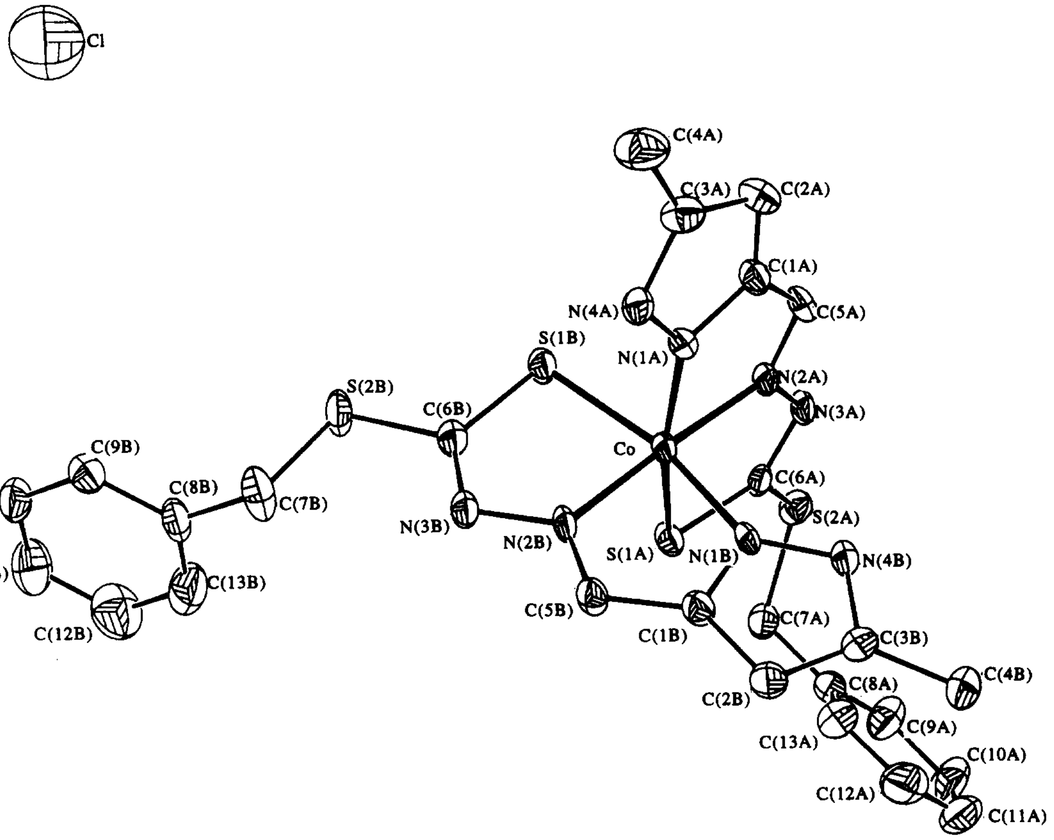


Fig. 2. ORTEP plot of the molecule showing the atom numbering scheme.

Table 2. PMR data of HMPzSB and its Co^{III} complexes values given (in δ ppm) relative to TMS

Compound	Imino proton	Position of pyrazole ring protons 1	4	5(CH$_3$)	methine proton	benzylic proton
HMPzSB	12.93 8.81	13.20	6.31	2.21	7.41	4.45
[Co(MPzSB)$_2$]Cl	—	14.40	6.76	2.30	8.92	4.52
[Co(MPzSB)$_2$]ClO$_4$	—	14.26	6.77	2.25	8.93	4.53
[Co(MPzSB)$_2$]BF$_4$	—	14.28	6.77	2.25	8.94	4.53

ocarbazate moiety due to coordination of pyrazolyl nitrogen atom.

The perspective view of the intermolecular hydrogen bonding interaction of the molecules in the unit cell is shown in Fig. 3. The crystal structure is stabilised by strong hydrogen bond interactions. The chloride ion accepts two hydrogen bonds: one from the pyrazolyl nitrogen atom of a translation related molecule and another from a pyrazolyl nitrogen atom of a glide related molecule. The geometrical details of the hydrogen bonds are given in Table 5.

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Table 3. Crystal data

Empirical formula	$[Co(C_{13}H_{13}N_4S_2)_2]Cl$
Formula weight	673.17
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Lattice parameters:	$a = 12.6100(8)$ Å $b = 15.083(2)$ Å $c = 16.0395(11)$ Å
Volume (Å^3)	2963.2(4) Å^3
Z	4
Density (calculated) (g/cm^3)	1.509
Absorption coefficient (cm^{-1})	9.84
$F(000)$	1384
Unique data measured	5178
Unique data with $I > 2\sigma(I)$	3623
Number of variables	356
S	0.971
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0735$, $wR2 = 0.1954$
R indices (all data)	$R1 = 0.1005$, $wR2 = 0.2114$
Largest diff. peak and hole (eÅ^{-3})	0.705 and -1.597

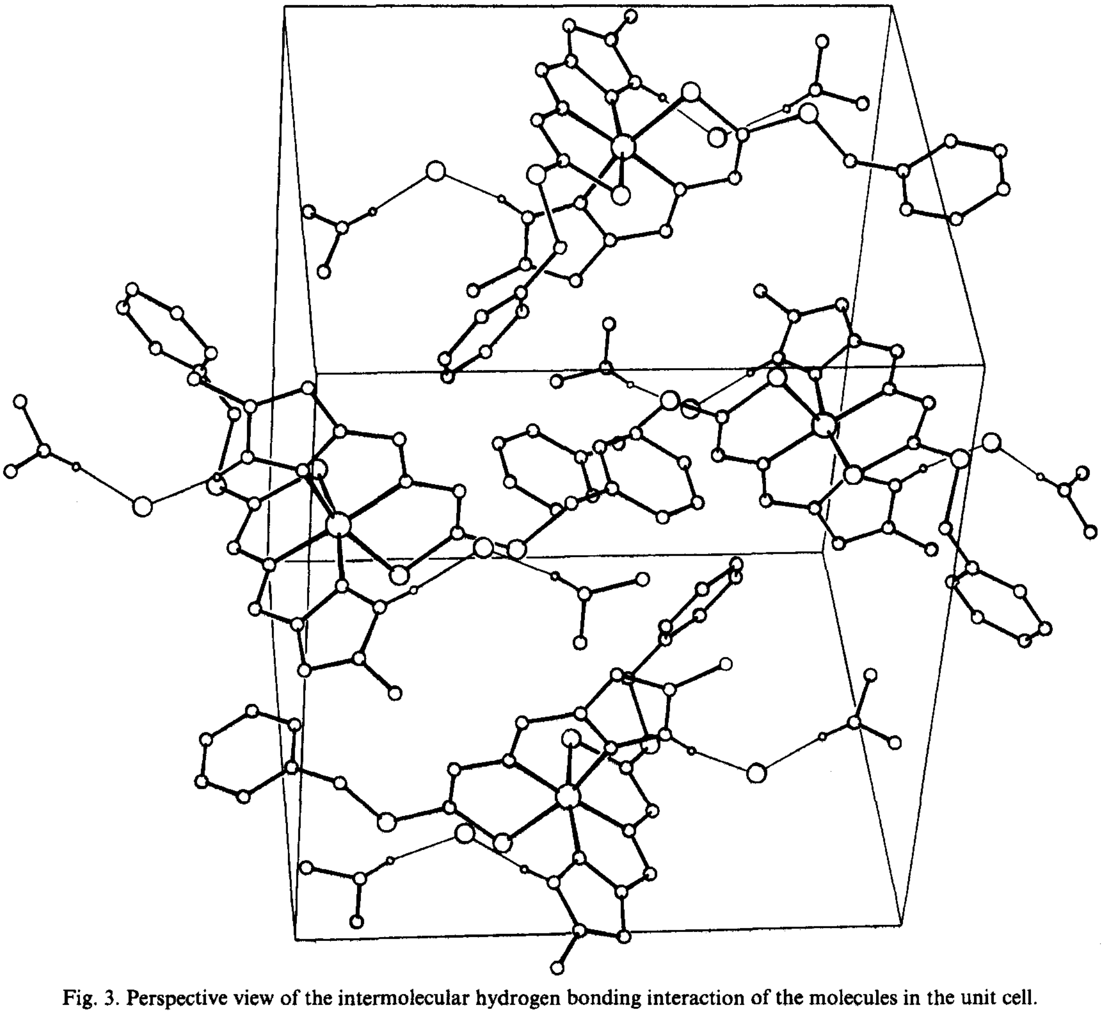

Fig. 3. Perspective view of the intermolecular hydrogen bonding interaction of the molecules in the unit cell.

Table 4. Bond lengths (Å) and angles (°) for the non-hydrogen atoms with e.s.d.s in parentheses

	Ligand A	Ligand B
Co—S(1)	2.217(2)	2.255(2)
Co—N(1)	1.954(5)	1.916(5)
Co—N(2)	1.898(4)	1.903(4)

N(2A)—Co—N(2B)	176.5(2)	N(1B)—Co—S(1A)	90.3(2)
N(2A)—Co—N(1B)	95.2(2)	N(1A)—Co—S(1A)	166.8(1)
N(2B)—Co—N(1B)	81.3(2)	N(2A)—Co—S(1B)	98.6(2)
N(2A)—Co—N(1A)	81.1(2)	N(2B)—Co—S(1B)	84.9(2)
N(2B)—Co—N(1A)	98.8(2)	N(1B)—Co—S(1B)	166.1(1)
N(1B)—Co—N(1A)	91.6(2)	N(1A)—Co—S(1B)	90.7(1)
N(2A)—Co—S(1A)	85.7(2)	S(1A)—Co—S(1B)	90.6(1)
N(2B)—Co—S(1A)	94.4(2)		

	Ligand A	Ligand B
S(1)—C(6)	1.728(6)	1.731(6)
S(2)—C(6)	1.742(6)	1.745(6)
S(2)—C(7)	1.823(7)	1.816(7)
C(1)—N(1)	1.345(7)	1.336(7)
C(1)—C(2)	1.386(9)	1.399(9)
C(1)—C(5)	1.455(9)	1.426(8)
C(2)—C(3)	1.381(9)	1.380(9)
C(3)—N(4)	1.354(8)	1.358(8)
C(3)—C(4)	1.478(9)	1.497(9)
C(5)—N(2)	1.290(7)	1.281(7)
C(6)—N(3)	1.315(7)	1.290(8)
C(7)—C(8)	1.479(9)	1.517(10)
C(8)—C(13)	1.389(10)	1.367(12)
C(8)—C(9)	1.369(10)	1.391(10)
C(9)—C(10)	1.384(12)	1.392(10)
C(10)—C(11)	1.361(15)	1.337(13)
C(11)—C(12)	1.388(16)	1.366(14)
C(12)—C(13)	1.380(12)	1.380(13)
N(1)—N(4)	1.328(6)	1.347(7)
N(2)—N(3)	1.393(6)	1.390(6)
C(6)—S(1)—Co	94.9(2)	94.0(2)
C(6)—S(2)—C(7)	105.3(3)	102.5(3)
N(1)—C(1)—C(2)	110.2(5)	108.8(5)
N(1)—C(1)—C(5)	113.3(5)	113.8(5)
C(2)—C(1)—C(5)	136.5(5)	137.2(6)
C(3)—C(2)—C(1)	105.2(6)	104.5(5)
N(4)—C(3)—C(2)	107.0(6)	109.9(6)
N(4)—C(3)—C(4)	121.7(6)	120.2(6)
C(2)—C(3)—C(4)	131.1(7)	130.0(6)
N(2)—C(5)—C(1)	113.6(5)	114.0(5)
N(3)—C(6)—S(1)	125.3(4)	125.9(5)
N(3)—C(6)—S(2)	112.8(4)	120.0(5)
S(1)—C(6)—S(2)	121.8(4)	114.0(4)
C(8)—C(7)—S(2)	113.8(4)	108.4(5)
C(13)—C(8)—C(9)	118.2(7)	118.6(7)
C(13)—C(8)—C(7)	121.6(6)	120.8(7)
C(9)—C(8)—C(7)	120.2(7)	120.6(8)
C(8)—C(9)—C(10)	121.7(9)	119.2(8)
C(11)—C(10)—C(9)	120.1(9)	121.2(8)
C(10)—C(11)—C(12)	119.2(8)	120.1(9)
C(13)—C(12)—C(11)	120.6(9)	120.0(10)
C(8)—C(13)—C(12)	120.3(9)	120.9(9)
N(4)—N(1)—C(1)	106.4(5)	109.6(5)

Table 5. Details of hydrogen bonding distance (Å) and angles (°) D = proton donor, A = proton acceptor

D—H···A	D—H	D···A	H···A	D—H···A	Position
N(4A)—H(4A)···Cl	0.860(7)	2.764(8)	1.908(8)	173.9(6)	$-x+2,\ -y+1,\ -z+1$
N(4B)—H(4B)···Cl	0.860(7)	2.766(8)	1.915(8)	169.9(6)	$x,\ -y+1/2,\ +z+1/2$

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