

# Structural and spectral studies of novel Co(III) complexes of N(4)-substituted thiosemicarbazones derived from pyridine-2-carbaldehyde

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## Abstract

Seven bis(ligand) Co(III) complexes {[CoL<sub>2</sub><sup>1</sup>]NO<sub>3</sub> · H<sub>2</sub>O (**1**), [CoL<sub>2</sub><sup>1</sup>]Cl · 2H<sub>2</sub>O (**2**), [CoL<sub>2</sub><sup>1</sup>]ClO<sub>4</sub> (**3**), [CoL<sub>2</sub><sup>2</sup>]NO<sub>3</sub> (**4**), [CoL<sub>2</sub><sup>2</sup>]Cl · 2H<sub>2</sub>O (**5**), [CoL<sub>2</sub><sup>3</sup>]Br · 2H<sub>2</sub>O (**6**), [CoL<sub>2</sub><sup>3</sup>]ClO<sub>4</sub> · H<sub>2</sub>O (**7**)} of three thiosemicarbazone ligands {pyridine-2-carbaldehyde-N(4)-*p*-methoxyphenyl thiosemicarbazone [HL<sup>1</sup>], pyridine-2-carbaldehyde-N(4)-2-phenylethyl thiosemicarbazone [HL<sup>2</sup>] and pyridine-2-carbaldehyde-N(4)-(methyl),N(4)-(phenyl) thiosemicarbazone [HL<sup>3</sup>]} were synthesized and physico-chemically characterized. All complexes are assigned octahedral geometries on the basis of spectral studies. The ligands deprotonate and coordinate by means of pyridine nitrogen, azomethine nitrogen, and thiolate sulfur atoms. The single crystal X-ray structures of HL<sup>3</sup> and two nitrate compounds are discussed. The structural studies corroborate the spectral characterization.

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**Keywords:** Thiosemicarbazone; Co(III) complex; Pyridine-2-carbaldehyde; Crystal structure

## 1. Introduction

Schiff bases and their transition metal complexes are of much interest in inorganic chemistry and have been studied extensively. Thiosemicarbazones and their metal complexes are very promising compounds among Schiff bases, due to their beneficial biological applications [1]. It is known that the biological activity of the thiosemicarbazones varies with the N(4) substituent as well as the ketone or aldehyde from which they are derived [2,3]. There are reports that the presence of alkyl groups at the terminal N(4) position can considerably increase their activity [4]. Domag et al. [5] had reported that thiosemicarbazones possess antitubercular activity and after that many papers on the pharmacology of these compounds appeared, indicating that they

have wide inhibitory activity against smallpox [6] and several kinds of tumors [7]. They can also be used as pesticides [8] and fungicides [9–12]. The presence of various donor atoms and ability to change the denticity depending on the reaction conditions and starting reagents make thiosemicarbazones of various aldehydes and ketones a special category among organic ligands [13].

Due to the pronounced antibacterial, antimalarial, anti-tumor and antileukaemic activity of heterocyclic thiosemicarbazones and their metal complexes, these compounds have been attractive to a large number of research groups in recent years [14–22]. Pyridine-2-carbaldehyde thiosemicarbazone and its substituted derivatives and their metal complexes are important members in this series. A large number of complexes of different metals with the above ligands have been studied and biological activities of some of them have been explored [23,24]. In an earlier paper [25] we have reported the synthesis and crystal structure of one of the three present ligands, namely

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pyridine-2-carbaldehyde N(4)-phenylethyl thiosemicarbazone ( $HL^2$ ). Chattopadhyay et al. [26] have reported cobalt(III) complexes of the type  $[CoL_2]X$  ( $X = Cl, SCN$  and  $N_3$ ) where L is a deprotonated pyridine-2-carbaldehyde thiosemicarbazone. Here we report the synthesis and characterization of a novel ligand pyridine-2-carbaldehyde N(4)-methyl N(4)-phenyl thiosemicarbazone ( $HL^3$ ) and the cobalt(III) complexes of three pyridine-2-carbaldehyde based thiosemicarbazones. In order to characterize these compounds unequivocally we report the molecular and crystal structures of  $HL^3$  and two complexes,  $[CoL_2]NO_3$  and  $[CoL_2]NO_3$ .

## 2. Experimental

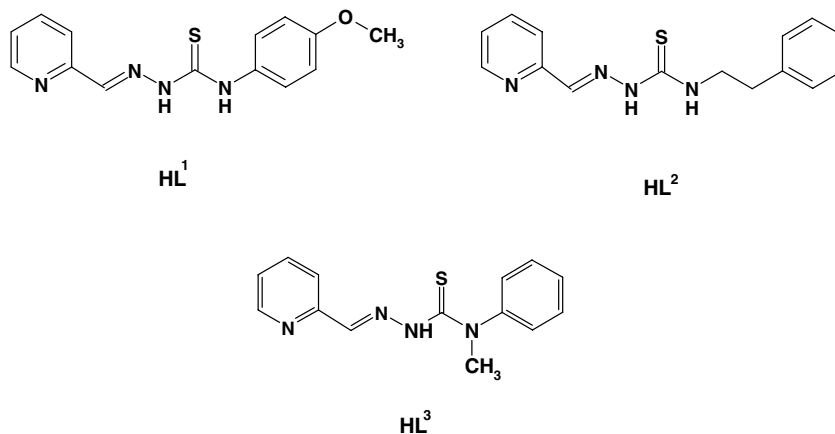
Pyridine-2-carbaldehyde (Aldrich) and *p*-anisidine (Fluka) were used as received. Cobalt(II) nitrate hexahydrate, cobalt(II) chloride hexahydrate, cobalt(II) perchlorate hexahydrate (Merck) were used as supplied. 4-Methyl-4-phenyl-3-thiosemicarbazide was prepared as reported previously [27] and solvents were purified by standard procedures before use. *Caution!* Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with care.

### 2.1. Synthesis of ligands

The thiosemicarbazone ligands (Scheme 1) were obtained by adopting and modifying a reported procedure of Scovill [27]. The synthesis and crystal structure of  $HL^2$  have been published earlier [25].

#### 2.1.1. Synthesis of $HL^1$

A solution of 1.00 g (5.52 mmol) of 4-methyl-4-phenyl-3-thiosemicarbazide in 5 ml of MeCN was refluxed with 0.679 g (5.52 mmol) of 4-methoxyaniline (*p*-anisidine) and 0.591 g (5.52 mmol) of pyridine-2-carbaldehyde for 1.5 h. The solution was chilled (overnight) and the crystals that separated were collected and washed well with MeCN. Yield: 58%. The compound was recrystallized from ethanol and dried *in vacuo* over  $P_4O_{10}$ .



Scheme 1. The thiosemicarbazones  $HL^1$ ,  $HL^2$  and  $HL^3$ .

#### 2.1.2. Synthesis of $HL^3$

A solution of 1.00 g (5.52 mmol) of 4-methyl-4-phenyl-3-thiosemicarbazide in 5 ml of MeCN was mixed with 0.591 g (5.52 mmol) of pyridine-2-carbaldehyde. The solution was heated at reflux for 1 h, chilled (overnight) and the crystals that separated were collected and washed well with MeCN. Yield: 64%. The compound was recrystallized from ethanol and dried *in vacuo* over  $P_4O_{10}$ . Single crystals of XRD quality were obtained by slow evaporation of an ethanol solution of the compound.

All analytical and spectroscopic data of the ligands are in good agreement with the expected values.

### 2.2. Synthesis of complexes

All complexes were prepared by the following general method. To a hot methanolic (20 ml) solution of thiosemicarbazone (0.5 mmol), 0.5 mmol of the cobalt(II) salt dissolved in 10 ml hot methanol was added. The mixture was refluxed for 2 h and allowed to stand for two days at room temperature. The compound formed was filtered, washed with water, methanol and ether. It was then dried *in vacuo* over  $P_4O_{10}$ . XRD quality single crystals of **1** and **4** were obtained by the slow evaporation of their methanol solutions.

### 2.3. Physical measurements

Elemental analyses were carried out using a Vario EL III CHNS analyzer at SAIF, Kochi, India. Infrared spectra were recorded on a Thermo Nicolet, AVATAR 370 DTGS model FT-IR spectrophotometer with KBr pellets and the ATR technique at SAIF, Kochi, India. Electronic spectra were recorded on a Cary 5000 version 1.09 UV-Vis-NIR spectrophotometer using a solution in chloroform.

### 2.4. X-ray crystallography

The crystallographic data and structure refinement parameters for the compounds are given in Table 1. The

Table 1  
Crystal refinement parameters of compounds HL<sup>3</sup>, [CoL<sup>1</sup>]<sub>2</sub>NO<sub>3</sub> · H<sub>2</sub>O (**1**) and [CoL<sup>2</sup>]<sub>2</sub>NO<sub>3</sub> (**4**)

Parameters	HL <sup>3</sup>	[CoL <sup>1</sup> ] <sub>2</sub> NO <sub>3</sub> ( <b>1</b> )	[CoL <sup>2</sup> ] <sub>2</sub> NO <sub>3</sub> ( <b>4</b> )
Empirical formula	C <sub>14</sub> H <sub>14</sub> N <sub>4</sub> S	C <sub>28</sub> H <sub>26</sub> CoN <sub>9</sub> O <sub>5</sub> S <sub>2</sub>	C <sub>30</sub> H <sub>30</sub> CoN <sub>9</sub> O <sub>3</sub> S <sub>2</sub>
Formula weight ( <i>M</i> )	270.35	691.63	687.68
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Mo Kα) (Å)	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub>
<i>Lattice constants</i>			
<i>a</i> (Å)	9.2038(10)	9.849(4)	14.7543(9)
<i>b</i> (Å)	9.6372(11)	13.193(5)	12.0675(18)
<i>c</i> (Å)	9.6497(12)	13.533(6)	27.424(8)
$\alpha$ (°)	63.773(2)	60.879(7)	90.00
$\beta$ (°)	65.060(2)	79.885(8)	91.109(11)
$\gamma$ (°)	75.410(2)	86.595(8)	90.00
<i>V</i> (Å <sup>3</sup> )	693.94(14)	1511.6(11)	4881.9(17)
<i>Z</i>	2	2	6
$\rho_{\text{calc}}$ (Mg m <sup>-3</sup> )	1.294	1.520	1.403
Absorption coefficient, $\mu$ (mm <sup>-1</sup> )	0.225	0.761	0.702
<i>F</i> (000)	284	712	2136
Crystal size (mm)	0.33 × 0.24 × 0.18	0.24 × 0.16 × 0.08	0.30 × 0.25 × 0.20
$\theta$ Range for data collection (°)	2.36–28.34	1.75–25.00	3.10–25.00
Limiting indices	–7 ≤ <i>h</i> ≤ 11, –12 ≤ <i>k</i> ≤ 12, –12 ≤ <i>l</i> ≤ 12	–11 ≤ <i>h</i> ≤ 11, –15 ≤ <i>k</i> ≤ 15, –16 ≤ <i>l</i> ≤ 16	–17 ≤ <i>h</i> ≤ 15, –14 ≤ <i>k</i> ≤ 14, –32 ≤ <i>l</i> ≤ 32
Reflections collected	4140	10660	20242
Independent reflections ( <i>R</i> <sub>int</sub> )	3024 (0.0112)	5240 (0.0752)	15034 (0.0378)
Refinement method	full-matrix least-squares on <i>F</i> <sup>2</sup>	full-matrix least-squares on <i>F</i> <sup>2</sup>	full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	3024/0/177	5240/0/408	15034/1/1216
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.050	1.034	0.804
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0440, <i>wR</i> <sub>2</sub> = 0.1214	<i>R</i> <sub>1</sub> = 0.0815, <i>wR</i> <sub>2</sub> = 0.1724	<i>R</i> <sub>1</sub> = 0.0479, <i>wR</i> <sub>2</sub> = 0.0733
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0516, <i>wR</i> <sub>2</sub> = 0.1274	<i>R</i> <sub>1</sub> = 0.1322, <i>wR</i> <sub>2</sub> = 0.1959	<i>R</i> <sub>1</sub> = 0.1134, <i>wR</i> <sub>2</sub> = 0.0848
Largest difference peak and hole (e Å <sup>-3</sup> )	0.251 and –0.197	0.629 and –0.469	0.328 and –0.211

data of HL<sup>3</sup> and **1** were collected using a Bruker Smart Apex CCD diffractometer equipped with graphite-monochromated Mo Kα ( $\lambda = 0.71073$  Å) radiation, while compound **4** was diffracted by CrysAlis CCD, Oxford Diffraction Ltd. with graphite-monochromated Mo Kα ( $\lambda = 0.71073$  Å) radiation at the National Single Crystal X-ray Diffraction Facility, IIT, Bombay, India. The trial structure was solved using SHELXS-97 [28] and refinement was carried out by full-matrix least-squares on *F*<sup>2</sup> (SHELXL) [28]. The molecular graphics employed were ORTEP-III [29] and PLATON [30].

### 3. Results and discussion

The colors and partial elemental analysis data of all the complexes are listed in Table 2. All the complexes are brown in color and soluble in solvents like methanol, ethanol, chloroform and DMF. They are found to be diamagnetic which confirms oxidation to cobalt(III) during the preparation, as has been found previously with heterocyclic N(4)-substituted thiosemicarbazones, and hence corresponds to a d<sup>6</sup> ion in a strong field [31]. The molar conductivities of 10<sup>-3</sup> M DMF solutions of the complexes indicate

Table 2  
Stoichiometries and partial elemental analyses of the complexes

Compounds	Stoichiometries	Anal: Found (Calc.) %				<i>M</i> <sub>M</sub> <sup>a</sup>
		C	H	N	S	
[CoL <sup>1</sup> ] <sub>2</sub> NO <sub>3</sub> · H <sub>2</sub> O ( <b>1</b> )	C <sub>28</sub> H <sub>26</sub> CoN <sub>9</sub> O <sub>5</sub> S <sub>2</sub> · H <sub>2</sub> O	47.89 (47.39)	3.85 (3.98)	18.05 (17.76)	9.12 (9.04)	86
[CoL <sup>1</sup> ] <sub>2</sub> Cl · 2H <sub>2</sub> O ( <b>2</b> )	C <sub>28</sub> H <sub>26</sub> CoN <sub>8</sub> O <sub>2</sub> S <sub>2</sub> Cl · 2H <sub>2</sub> O	47.69 (47.97)	4.45 (4.31)	15.97 (15.98)	9.23 (9.15)	78
[CoL <sup>1</sup> ] <sub>2</sub> ClO <sub>4</sub> ( <b>3</b> )	C <sub>28</sub> H <sub>26</sub> CoN <sub>8</sub> O <sub>6</sub> S <sub>2</sub> Cl	45.89 (46.13)	3.73 (3.59)	15.29 (15.37)	8.79 (8.80)	80
[CoL <sup>2</sup> ] <sub>2</sub> NO <sub>3</sub> ( <b>4</b> )	C <sub>30</sub> H <sub>30</sub> CoN <sub>9</sub> O <sub>3</sub> S <sub>2</sub>	51.88 (52.40)	4.53 (4.40)	18.36 (18.33)	9.18 (9.33)	92
[CoL <sup>2</sup> ] <sub>2</sub> Cl · 2H <sub>2</sub> O ( <b>5</b> )	C <sub>30</sub> H <sub>30</sub> CoN <sub>8</sub> S <sub>2</sub> Cl · H <sub>2</sub> O	52.78 (53.05)	4.37 (4.75)	16.21 (16.50)	9.44 (9.75)	67
[CoL <sup>2</sup> ] <sub>2</sub> Br · 2H <sub>2</sub> O ( <b>6</b> )	C <sub>28</sub> H <sub>26</sub> CoN <sub>8</sub> S <sub>2</sub> Br · 2H <sub>2</sub> O	46.98 (47.13)	4.56 (4.24)	15.75 (15.70)	9.04 (8.99)	89
[CoL <sup>2</sup> ] <sub>2</sub> ClO <sub>4</sub> · H <sub>2</sub> O ( <b>7</b> )	C <sub>28</sub> H <sub>26</sub> CoN <sub>8</sub> O <sub>4</sub> S <sub>2</sub> Cl · H <sub>2</sub> O	46.58 (47.03)	4.06 (3.95)	15.82 (15.67)	9.08 (8.97)	75

<sup>a</sup> Molar conductivity of 10<sup>-3</sup> M DMF solution, in Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>.

that they are 1:1 electrolytes. The partial elemental analysis data and conductance measurement data are consistent with the general formulation of the complexes as  $[\text{CoL}_2]\text{X}$ , where  $\text{X} = \text{NO}_3, \text{Cl}, \text{Br}$  and  $\text{ClO}_4$ . For the compounds **1**, **5** and **7**, the elemental analysis data matches with the stoichiometry containing one molecule of water of crystallization/lattice water, two molecules in the case of **2** and **6**, whereas no water molecules are present in **3** and **4**. The relevant bond lengths and bond angles of  $\text{HL}^3$ ,  $[\text{CoL}_2^1]\text{NO}_3 \cdot \text{H}_2\text{O}$  (**1**) and  $[\text{CoL}_2^2]\text{NO}_3$  (**4**) are listed in Table 3. The asymmetric unit of **4** contains three molecules, only one of which is discussed.

### 3.1. Crystal structure of $\text{HL}^3$

The molecular structure of  $\text{HL}^3$ , with the atom numbering scheme, is given in Fig. 1. Its existence in the thione form is confirmed by the  $\text{C}=\text{S}$  bond length of

1.6750(14) Å [32]. The molecule exists in the *E* conformation about the  $\text{N}_2\text{--N}_3$  bond as evidenced by the  $\text{C}_6\text{--N}_2\text{--N}_3\text{--C}_7$  dihedral angle of  $177.66(16)^\circ$ . The intramolecular hydrogen bond  $\text{N}_3\text{--H1N}_3\cdots\text{N}_1$  and the intermolecular hydrogen bond  $\text{C}_6\text{--H}_6\cdots\text{N}_2^*$  facilitate this geometry. The core thiosemicarbazone moiety  $\text{C}_6, \text{N}_2, \text{N}_3, \text{C}_7, \text{S}_1, \text{N}_4$  is in a plane with a maximum deviation of  $-0.0576(15)$  Å for the  $\text{N}_2$  atom and makes an angle of  $16.79(8)^\circ$  with the pyridyl ring. The phenyl ring plane is almost perpendicular  $\{85.38(8)^\circ\}$  to this thiosemicarbazone plane. Relevant  $\text{C--H}\cdots\pi$  and  $\text{Cg}\cdots\text{Cg}$  interactions are given in Table 4.

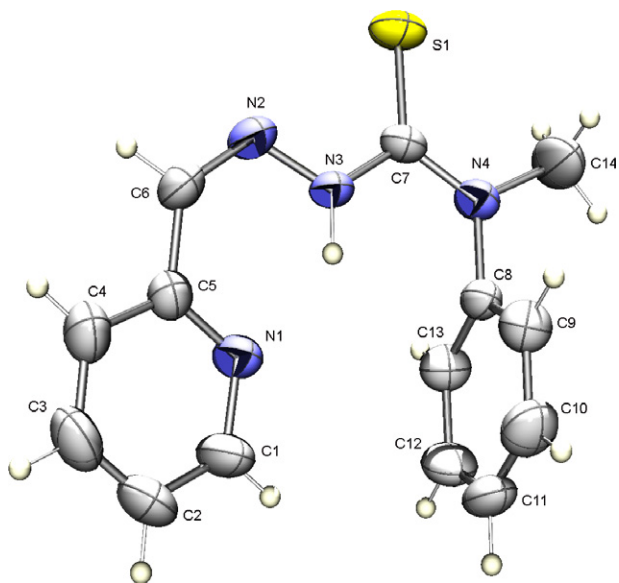
### 3.2. Crystal structures of $[\text{CoL}_2^1]\text{NO}_3 \cdot \text{H}_2\text{O}$ (**1**) and $[\text{CoL}_2^2]\text{NO}_3$ (**4**)

The molecular structures of **1** and **4** along with the atom numbering schemes are given in Figs. 2 and 3. The metal

Table 3  
Selected bond lengths (Å) and bond angles ( $^\circ$ ) of the compounds<sup>a</sup>

	$\text{HL}^2$	$\text{HL}^3$	$[\text{CoL}_2^1]\text{NO}_3 \cdot \text{H}_2\text{O}$ ( <b>1</b> )	$[\text{CoL}_2^2]\text{NO}_3$ ( <b>4</b> )
S(1)–C(7)	1.6849(13)	1.6750(14)	1.747(6)	1.732(6)
S(2)–C(21)			1.730(6)	
S(2)–C(22)				1.776(8)
N(2)–C(6)	1.2837(15)	1.285(2)	1.290(8)	1.305(6)
N(6)–C(20)			1.305(7)	
N(6)–C(21)				1.303(7)
N(2)–N(3)	1.3783(14)	1.3613(17)	1.360(7)	1.336(6)
N(6)–N(7)			1.371(7)	1.333(7)
N(3)–C(7)	1.3587(16)	1.3644(18)	1.321(7)	1.329(6)
N(7)–C(21)			1.330(8)	
N(7)–C(22)				1.292(8)
N(4)–C(7)	1.3401(16)	1.345(2)	1.344(8)	1.324(6)
N(8)–C(21)			1.347(8)	
N(8)–C(22)				1.370(8)
Co(1)–S(1)			2.232(2)	2.2348(17)
Co(1)–S(2)			2.2043(19)	2.2246(17)
Co(1)–N(1)			1.958(5)	1.963(5)
Co(1)–N(5)			1.956(5)	1.973(4)
Co(1)–N(2)			1.876(5)	1.889(4)
Co(1)–N(6)			1.885(5)	1.897(5)
C(6)–N(2)–N(3)	114.37(10)	117.75(13)	118.8(5)	120.3(5)
N(2)–N(3)–C(7)	120.47(10)	120.25(12)	111.6(5)	112.0(5)
N(4)–C(7)–N(3)	116.16(10)	113.87(12)	120.1(5)	116.4(6)
N(3)–C(7)–S(1)	119.25(8)	122.89(12)	123.3(5)	123.8(4)
N(4)–C(7)–S(1)	124.59(9)	123.22(11)	116.6(5)	119.8(5)
N(1)–Co(1)–N(5)			90.8(2)	90.10(18)
N(2)–Co(1)–N(6)			178.1(2)	178.4(2)
S(1)–Co(1)–S(2)			90.73(8)	92.24(7)
S(1)–Co(1)–N(1)			167.97(15)	168.17(16)
S(1)–Co(1)–N(5)			90.76(16)	89.53(13)
S(1)–Co(1)–N(2)			84.99(17)	85.07(16)
S(1)–Co(1)–N(6)			96.01(17)	94.80(15)
N(1)–Co(1)–N(2)			83.0(2)	83.3(2)
N(1)–Co(1)–N(6)			96.0(2)	96.9(2)
N(1)–Co(1)–S(2)			90.10(15)	90.45(14)
N(2)–Co(1)–N(5)			95.2(2)	98.6(2)
N(2)–Co(1)–S(2)			96.41(16)	92.75(13)
S(2)–Co(1)–N(5)			168.41(15)	168.60(17)
S(2)–Co(1)–N(6)			85.23(16)	85.62(19)
N(5)–Co(1)–N(6)			83.2(2)	83.0(2)

<sup>a</sup> Data for  $\text{HL}^2$  [25] is taken for comparison.

Fig. 1. ORTEP diagram of  $HL^3$  with 50% probability ellipsoids.Table 4  
Interaction parameters of the compound  $HL^3$ 

$\pi \cdots \pi$ interactions			
Cg(I)–Res(I) $\cdots$ Cg(J)	Cg–Cg (Å)	$\alpha$ (°)	$\beta$ (°)
Cg(1) [1] $\cdots$ Cg(1) <sup>a</sup>	3.6040	0.02	13.54
Equivalent position codes: a = $-x, 1 - y, 1 - z$ Cg(1) = N1, C1, C2, C3, C4, C5			
$CH \cdots \pi$ interactions			
X–H(I)–Res(1) $\cdots$ Cg(J)	H $\cdots$ Cg (Å)	X $\cdots$ Cg (Å)	X–H $\cdots$ Cg (°)
C(14)–H(14B) [1] $\cdots$ Cg(2) <sup>a</sup>	2.95	3.7088	137
Equivalent position codes: a = $1 - x, -y, 2 - z$ Cg(2) = C(8), C(9), C(10), C(11), C(12), C(13)			

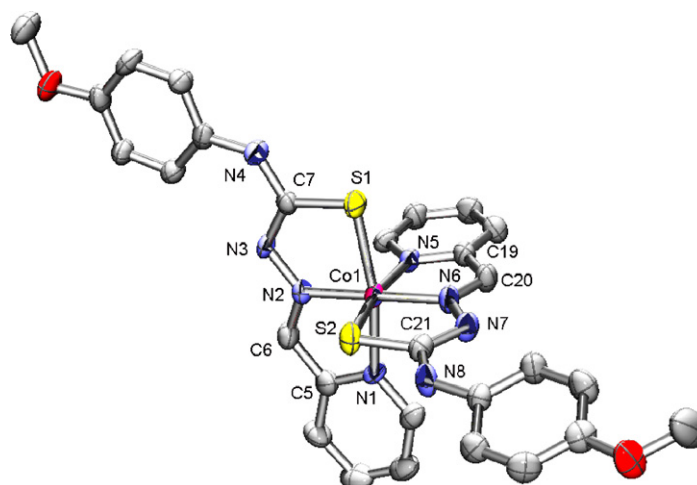
Cg = Centroid,  $\alpha$  = dihedral angles between planes I and J,  $\beta$  = angle Cg(1)–Cg(J).

centers in both the complexes possess an octahedral geometry with two deprotonated ligands. The Co(III) ion is coordinated in a *meridional* fashion [33–35] using pairs of

*cis* pyridyl nitrogen, *trans* azomethine nitrogen and *cis* thiolate sulfur atoms from two monoanionic ligands. This coordination results in four five membered chelate rings in both complexes. The bond angles suggest a distorted octahedral coordination geometry in both complexes. The dihedral angle formed by the mean planes of the bicyclic chelate systems of each of the ligands is  $89.75(13)^\circ$  in **1** and  $83.45(1)^\circ$  in **4**. In **1**, each bicyclic chelate system, Co1, S1, C7, N3, N2, C6, C5, N1 and Co1, S2, C21, N7, N6, C20, C19, N5, are approximately planar as evidenced by the maximum deviation of  $-0.057(7)$  Å for C6 and  $0.080(7)$  Å for C21, respectively. In **4**, the bicyclic chelate system Co1, S1, C7, N3, N2, C6, C5, N1 is approximately planar with a maximum deviation of  $0.06297$  Å for N1, though its counterpart Co1, S2, C22, N7, N6, C21, C20, N5 show a distortion as evidenced by the maximum deviation of  $2.12988$  Å for C22. These results suggest the distortion in the octahedral geometry is more in **4** compared to **1**.

On complexation the ligand  $HL^2$  undergoes structural reorientation to coordinate the metal in a NNS manner in **4**. The azomethine nitrogen was in the *E* configuration with both pyridyl nitrogen and sulfur atoms in its metal free form of the ligand, but now is in the *Z* form with both the other donor atoms. The C–S bond length increases to  $1.732(6)$  Å [C7–S1] and  $1.776(8)$  Å [C22–S2] from  $1.6849(13)$  Å in  $HL^2$ . The N3–C7 bond length also changes from  $1.3587(16)$  Å to  $1.329(6)$  Å [ $1.292(8)$  Å for N7–C22] due to enolization of the ligand for coordination after deprotonation. The Co–S and Co–N bond lengths in both complexes are comparable. The Co–N<sub>azomethine</sub> bond lengths are shorter compared to Co–N<sub>pyridine</sub> bond lengths, indicating the greater strength of former bonds compared to the latter.

The molecules of **1** and **4** are packed in a ‘face to face’ manner within the unit cell, as is evident from Fig. 4 for the case of **1**, a result of diverse hydrogen bonding and C–H  $\cdots \pi$  ring interactions (Tables 5 and 6). The ‘face to face’ arrangement is along the *b* axis for the case of **1**

Fig. 2. ORTEP diagram for the compound  $[CoL_2]NO_3$  (**1**) with 50% probability ellipsoids. Hydrogen atoms and the nitrate ion are omitted for clarity.



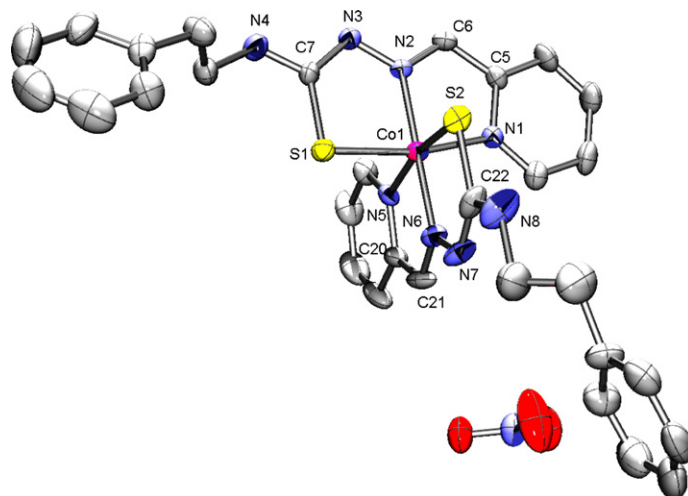


Fig. 3. ORTEP diagram for the compound  $[\text{CoL}_2]\text{NO}_3$  (**4**) with 25% probability ellipsoids. Hydrogen atoms are omitted for clarity.

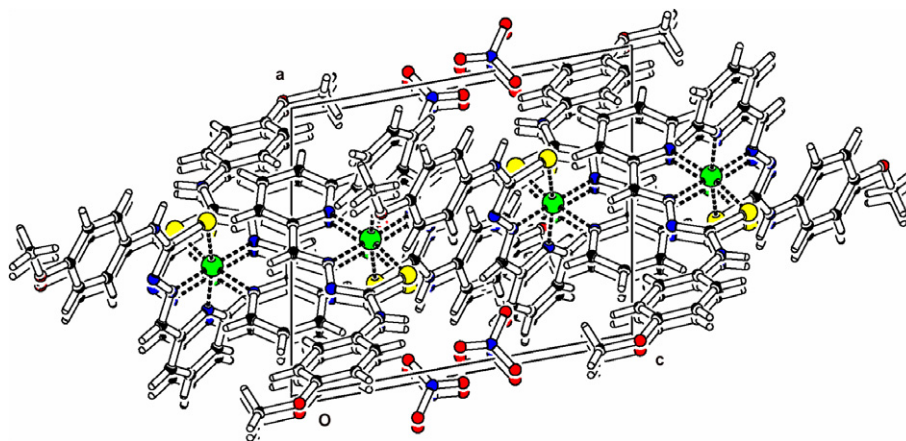


Fig. 4. A view of the molecule  $[\text{CoL}_2]\text{NO}_3$  (**1**) along the  $b$  axis showing face to face packing in the unit cell.

and along the  $c$  axis for the case of **4** (Fig. 5). Since the latter contains three different molecules in the asymmetric unit, a large number of diverse interactions are present compared to those present in **1**. However, no significant  $\pi \cdots \pi$  interactions are found in the packing of **4**. The relevant hydrogen bonding interactions of **1** and **4** along with  $\text{HL}^3$  are listed in Table 7.

### 3.3. Infrared spectra

The characteristic IR bands ( $50\text{--}4000\text{ cm}^{-1}$ ) for the free ligands ( $\text{HL}^1$ ,  $\text{HL}^2$  and  $\text{HL}^3$ ) differ from those of their complexes and provide significant indications regarding the bonding sites of the ligands. IR spectral assignments of the ligands and the complexes are listed in Table 8. A medium band in the range  $3129\text{--}3158\text{ cm}^{-1}$  in the free ligands due to the  $\nu(\text{N-H})$  vibration disappears in the spectra of complexes, providing strong evidence for ligand coordination around the cobalt(III) ion in its deprotonated form.

Table 5  
Interaction parameters of compound **1**

$\pi \cdots \pi$ interaction			
Cg(I)–Res(I) $\cdots$ Cg(J)	Cg–Cg ( $\text{\AA}$ )	$\alpha$ ( $^\circ$ )	$\beta$ ( $^\circ$ )
Cg(5) [1] $\cdots$ Cg(7) <sup>a</sup>	3.6973	7.83	29.12
Cg(7) [1] $\cdots$ Cg(5) <sup>a</sup>	3.6973	7.83	22.39
Cg(7) [1] $\cdots$ Cg(7) <sup>b</sup>	3.6339	0.02	18.97

Equivalent position codes:  $a = 1 - x, -y, 1 - z$ ;  $b = 1 - x, -1 - y, 1 - z$   
 Cg(5) = N(1), C(1), C(2), C(3), C(4), C(5); Cg(7) = C(8), C(9), C(10), C(11), C(12), C(13)

$\text{CH} \cdots \pi$ interactions			
X–H(I)–Res(1) $\cdots$ Cg(J)	H $\cdots$ Cg ( $\text{\AA}$ )	X $\cdots$ Cg ( $\text{\AA}$ )	X–H $\cdots$ Cg ( $^\circ$ )
C(1)–H(1) [1] $\cdots$ Cg(2) <sup>a</sup>	2.81	3.0983	99
C(15)–H(15) [1] $\cdots$ Cg(1) <sup>a</sup>	2.88	3.1389	98
C(15)–H(15) [1] $\cdots$ Cg(3) <sup>a</sup>	2.87	3.1094	96

Equivalent position codes:  $a = x, y, z$   
 Cg(1) = Co(1), S(1), C(7), N(3), N(2); Cg(2) = Co(1), S(2), C(21), N(7), N(6); Cg(3) = Co(1), N(1), C(5), C(6), N(2)

Cg = Centroid,  $\alpha$  = dihedral angles between planes I and J,  $\beta$  = angle Cg(1)–Cg(J).

Table 6  
Interaction parameters of compound **4**

<i>CH...<math>\pi</math> interactions</i>			
<i>X–H(I)–Res(1)...</i> Cg( <i>J</i> )	H...Cg (Å)	X...Cg (Å)	X–H...Cg (°)
C(1)–H(1) [1] $\rightarrow$ Cg(1) <sup>a</sup>	2.88	3.1630	99
C(1)–H(1) [1] $\rightarrow$ Cg(4) <sup>a</sup>	2.99	3.2167	96
C(1)–H(1) [1] $\rightarrow$ Cg(2) <sup>a</sup>	2.93	3.1831	97
C(1)–H(1) [1] $\rightarrow$ Cg(3) <sup>a</sup>	2.78	3.0836	100
C(2)–H(2) [1] $\rightarrow$ Cg(15) <sup>a</sup>	2.90	3.4591	120
C(3)–H(3) [1] $\rightarrow$ Cg(7) <sup>b</sup>	2.61	3.5363	171
C(31)–H(31) [2] $\rightarrow$ Cg(10) <sup>a</sup>	2.96	3.1897	96
C(31)–H(31) [2] $\rightarrow$ Cg(12) <sup>a</sup>	2.83	3.1076	99
C(31)–H(31) [2] $\rightarrow$ Cg(9) <sup>a</sup>	2.88	3.1745	100
C(31)–H(31) [2] $\rightarrow$ Cg(11) <sup>a</sup>	2.96	3.2015	97
C(32)–H(32) [2] $\rightarrow$ Cg(7) <sup>b</sup>	2.92	3.4221	115
C(33)–H(33) [2] $\rightarrow$ Cg(15) <sup>b</sup>	2.58	3.4932	168
C(76)–H(76) [3] $\rightarrow$ Cg(17) <sup>a</sup>	2.93	3.2103	99
C(76)–H(76) [3] $\rightarrow$ Cg(19) <sup>a</sup>	2.99	3.2095	95
C(62)–H(62) [3] $\rightarrow$ Cg(24) <sup>c</sup>	2.79	3.5533	140
C(63)–H(63) [3] $\rightarrow$ Cg(24) <sup>b</sup>	2.64	3.5568	168
C(61)–H(61) [3] $\rightarrow$ Cg(18) <sup>a</sup>	2.95	3.2068	97
C(61)–H(61) [3] $\rightarrow$ Cg(20) <sup>a</sup>	2.84	3.1071	98

Equivalent position codes: a = *x*, *y*, *z*; b = *x*, 1 + *y*, *z*; c = 1 – *x*, 1/2 + *y*, –*z*.

Cg(1) = Co1, S1, C7, N3, N2; Cg(2) = Co1, S2, C7, N7, N2; Cg(3) = Co1, N1, C20, C6, N2; Cg(4) = Co1, N1, C5, C6, N2; Cg(7) = C10, C26, C27, C13, C14, C15.

Bands ranging from 1600 to 1350 cm<sup>-1</sup> suffer significant shifts in the spectra of the complexes, which can be attributed to  $\nu(\text{C}=\text{C})$  and  $\nu(\text{C}=\text{N})$  vibration modes, and their mixing patterns are different from that in the spectra of the ligands. The positive shift of bands corresponding to  $\nu(\text{C}=\text{N})$  in the range 1584–1590 cm<sup>-1</sup> in the free ligands to 1602–1614 cm<sup>-1</sup> in the complexes is consistent with the coordination of the azomethine nitrogen to the central Co(III) ion [36,37]. Medium bands at ca. 439–450 cm<sup>-1</sup>

corresponding to  $\nu(\text{Co}-\text{N})$  further support azomethine nitrogen coordination [38,39]. The enolization of the ligands is supported by the increase in  $\nu(\text{N}-\text{N})$  by 58–115 cm<sup>-1</sup>. The bands in the ranges 1307–1334 and 779–897 cm<sup>-1</sup> due to  $\nu(\text{C}=\text{S})$  and  $\delta(\text{C}=\text{S})$ , respectively, of the free ligands are shifted to lower values, indicating coordination of the thiolate sulfur to the Co(III) ion. The downward shift of the bands in the complexes corresponding to  $\nu(\text{C}=\text{S})$  and  $\delta(\text{C}=\text{S})$  in the free ligands can be attributed to a change of bond order and strong electron delocalization upon chelation [40]. Medium bands in the range at 375–385 cm<sup>-1</sup> are assignable to  $\nu(\text{Co}-\text{S})$  [41]. A positive shift corresponding to out-of-plane bending vibrations of the pyridine ring in the free ligands (613–622 cm<sup>-1</sup>) to higher frequencies (617–635 cm<sup>-1</sup>) in the complexes is confirmative of pyridine nitrogen coordination to the cobalt(III) ion [42]. Medium bands at ca. 255–268 cm<sup>-1</sup> corresponding to  $\nu(\text{Co}-\text{N}_{\text{pyridyl}})$  point towards the coordination of the pyridyl nitrogen to the cobalt(III) ion [43].

The perchlorate complexes **3** and **7** show single broad bands at 1120 and 1123 cm<sup>-1</sup> and strong bands at 620 and 625 cm<sup>-1</sup>, indicating the presence of ionic perchlorate [44]. The bands at 1120 and 1123 cm<sup>-1</sup> are assignable to  $\nu_3(\text{ClO}_4)$  and unsplit bands at 620 and 625 cm<sup>-1</sup> assignable to  $\nu_4(\text{ClO}_4)$ . Moreover, no bands assignable to  $\nu_1(930 \text{ cm}^{-1})$  or  $\nu_2(460 \text{ cm}^{-1})$  are observed in their spectra. This, along with unsplit  $\nu_3$  and  $\nu_4$  bands, show the exclusive presence of a non-coordinated perchlorate group having  $C_{3v}$  symmetry and it is supposed to be descended from  $T_d$  symmetry due to lattice effects [45].

In the spectra of the complexes **1** and **4** the absence of the combination bands ( $\nu_1+\nu_4$ ) in the region 1700–1800 cm<sup>-1</sup> rules out the possibility for a coordinated

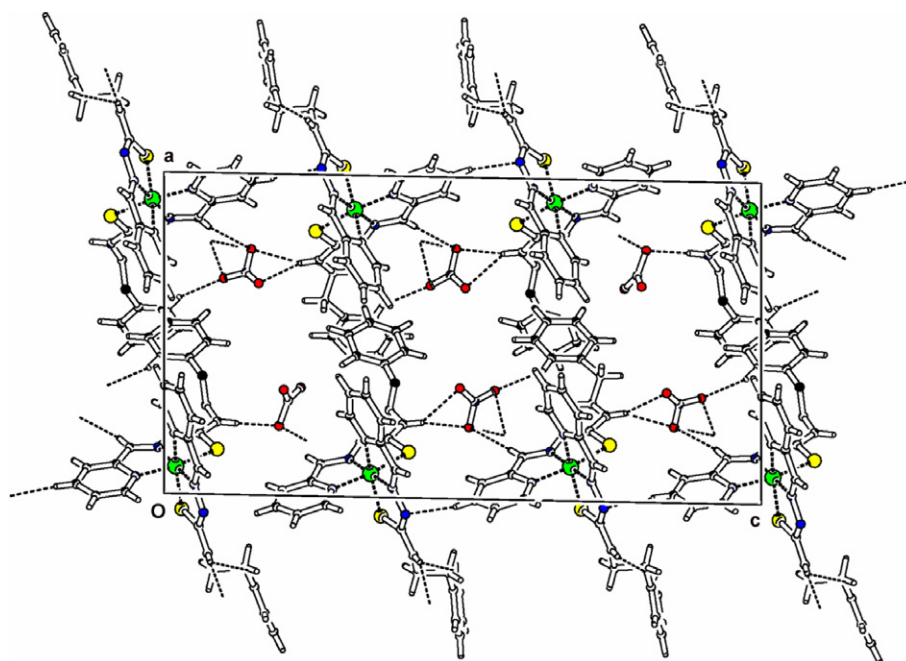


Fig. 5. Unit cell packing of the molecule  $[\text{CoL}_2]\text{NO}_3$  (**4**) along the *b* axis showing hydrogen bonding interactions.

Table 7  
H-bonding interactions in the compounds

	Residue	D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
HL <sup>3</sup>	1	N3–H1N3···N1 <sup>a</sup>	0.88	1.98	2.6768	135
	1	C6–H6···N2 <sup>b</sup>	0.93	2.61	3.3540	137
[CoL <sub>2</sub> ] <sup>1</sup> NO <sub>3</sub> · H <sub>2</sub> O (1)	1	N8–H8A···O3 <sup>c</sup>	0.86	2.10	2.922(10)	159
	1	N4–H4A···O4 <sup>d</sup>	0.86	2.12	2.964(9)	167
	1	C17–H17···O4 <sup>e</sup>	0.93	2.46	3.350(10)	160
	1	C28–H28···S1 <sup>f</sup>	0.96	2.86	3.556(10)	131
	1	C18–H18···O1 <sup>g</sup>	0.93	2.46	3.221(9)	139
	1	C6–H6···S2 <sup>h</sup>	0.93	2.71	3.477(7)	140
	1	C9–H9···N3 <sup>a</sup>	0.93	2.24	2.845(10)	122
	1	C23–H23···N7 <sup>a</sup>	0.93	2.36	2.929(10)	119
[CoL <sub>2</sub> ] <sup>2</sup> NO <sub>3</sub> (4)	1	N4–H4N···O5 <sup>i</sup>	0.86	2.09	2.9152	160
	1	N8–H8N···O7 <sup>a</sup>	0.86	2.16	2.9978	163
	1	N8–H8N···O9 <sup>a</sup>	0.86	2.45	3.1914	145
	1	C18–H18···N11 <sup>j</sup>	0.93	2.44	3.3499	166
	1	C6–H6···O1 <sup>i</sup>	0.93	2.52	3.4235	164
	1	C8–H8A···S1 <sup>a</sup>	0.97	2.60	3.0852	111
	1	C8–H8B···N7 <sup>a</sup>	0.97	2.40	2.8034	104
	1	C26–H26···O3 <sup>j</sup>	0.93	2.58	3.8880	146
	2	N12–H12···O1 <sup>k</sup>	0.86	2.25	3.0343	151
	2	N12–H12···O3 <sup>k</sup>	0.86	2.41	3.1487	144
	2	N16–H16N···O1 <sup>a</sup>	0.86	2.22	3.0474	161
	2	N16–H16N···O2 <sup>a</sup>	0.86	2.45	3.1740	143
	2	C48–H48···N19 <sup>a</sup>	0.93	2.47	3.3572	160
	2	C51–H51···O5 <sup>a</sup>	0.93	2.42	3.3256	164
	2	C56–H56···O4 <sup>a</sup>	0.93	2.46	3.3890	172
	2	C38–H38A···S3 <sup>a</sup>	0.97	2.59	3.0969	112
	3	N20–H20B···O5 <sup>a</sup>	0.86	1.99	2.8412	169
	3	N20–H20N···O8 <sup>l</sup>	0.86	2.27	3.0763	156
3	N20–H20N···O9 <sup>l</sup>	0.86	2.53	3.2167	137	
3	C86–H86···O8 <sup>l</sup>	0.93	2.51	3.4043	161	
3	C63–H63···N3 <sup>l</sup>	0.93	2.48	3.3965	167	
3	C66–H66···O9 <sup>l</sup>	0.93	2.54	3.4389	161	
3	C68–H68A···S5 <sup>a</sup>	0.97	2.68	3.1332	109	

D = donor; A = acceptor; equivalent position codes: a = x, y, z; b = -x, -y, 1 - z; c = 1 - x, 1 - y, 1 - z; d = -1 + x, -1 + y, z; e = 2 - x, 1 - y, -z; f = -x, 1 - y, -z; g = x, 1 + y, -1 + z; h = 1 - x, -y, 1 - z; i = 1 + x, y, z; j = 1 - x, -1/2 + y, 1 - z; k = -x, 1/2 + y, 1 - z; l = 1 - x, 1/2 + y, -z.

Table 8  
IR spectral data of the ligands and their complexes (cm<sup>-1</sup>)

Compound	$\nu(\text{C}=\text{N}) + \nu(\text{N}=\text{C})$	$\nu(\text{N}-\text{N})$	$\nu/\delta(\text{C}-\text{S})$	py(ip)	py(op)	$\nu(^2\text{N}-\text{H})$	$\nu(^4\text{N}-\text{H})$	$\nu(\text{Co}-\text{N}_{\text{azo}})$	$\nu(\text{Co}-\text{N}_{\text{py}})$	$\nu(\text{Co}-\text{S})$
HL <sup>1</sup>	1584	1024	1334, 837	613	401	3134	3310			
[CoL <sub>2</sub> ] <sup>1</sup> NO <sub>3</sub> · H <sub>2</sub> O (1)	1604	1137	1315, 827	617	408		3428	446	262	378
[CoL <sub>2</sub> ] <sup>1</sup> Cl · 2H <sub>2</sub> O (2)	1605	1132	1298, 833	627	410		3402	445	255	383
[CoL <sub>2</sub> ] <sup>1</sup> ClO <sub>4</sub> (3)	1602	1139	1303, 826	620	412		3419	439	268	385
HL <sup>2</sup>	1586	1079	1324, 897	622	406	3129	3374			
[CoL <sub>2</sub> ] <sup>2</sup> NO <sub>3</sub> (4)	1605	1141	1315, 892	630	416		3405	448	255	375
[CoL <sub>2</sub> ] <sup>2</sup> Cl · 2H <sub>2</sub> O (5)	1631	1137	1291, 892	630	413		3426	450	258	378
HL <sup>3</sup>	1590	1035	1307, 779	614	421	3158				
[CoL <sub>2</sub> ] <sup>3</sup> Br · 2H <sub>2</sub> O (6)	1603	1137	1292, 770	632	453			443	260	382
[CoL <sub>2</sub> ] <sup>3</sup> ClO <sub>4</sub> · H <sub>2</sub> O (7)	1603	1137	1292, 764	635	433			440	264	374

nitrate group. The presence of bands at ca. 840 ( $\nu_2$ ), 1384 ( $\nu_3$ ) and 706 cm<sup>-1</sup> ( $\nu_4$ ) for **1** and bands at 725, 1384 and 842 cm<sup>-1</sup> for **4** clearly points out the uncoordinated nature of the nitrate group [46]. According to Stefov et al., coordinated water should exhibit bands at 825, 575 and 500 cm<sup>-1</sup>. The absence of bands in these regions in the spectra of complexes **1**, **2**, **5**, **6** and **7** shows that the water molecules are not coordinated but are present as lattice water [47].

### 3.4. Electronic spectra

The electronic spectral assignments of the ligands and their complexes are given in Table 9. The electronic spectra of spin paired trivalent cobalt complexes of approximate  $O_h$  symmetry have the following assignments of d–d bands:  $\nu_1$ :  $^1\text{T}_{1g} \leftarrow ^1\text{A}_{1g}$ ;  $\nu_2$ :  $^1\text{T}_{2g} \leftarrow ^1\text{A}_{1g}$ ;  $\nu_3$ :  $^3\text{T}_{1g} \leftarrow ^1\text{A}_{1g}$ ;  $\nu_4$ :  $^3\text{T}_{2g} \leftarrow ^1\text{A}_{1g}$  [45]. The  $\nu_1$  bands are assigned values  $\sim 19\,646$ – $21\,052$  cm<sup>-1</sup> and  $\nu_2 \sim 25\,000$  cm<sup>-1</sup>. The band



Table 9

Electronic spectra ( $\text{cm}^{-1}$ ) of the ligands and their complexes

Compound	${}^1T_{1g} \leftarrow {}^1A_{1g}$	${}^1T_{2g} \leftarrow {}^1A_{1g} + \text{LMCT}$	${}^3T_{2g} \leftarrow {}^1A_{1g}$	$n \rightarrow \pi^*$	$\pi \rightarrow \pi^*$
HL <sup>1</sup>				30769	42735
[CoL <sup>1</sup> ] <sub>2</sub> NO <sub>3</sub> · H <sub>2</sub> O (1)	19701	24708	16548	30982	43206
[CoL <sup>1</sup> ] <sub>2</sub> Cl · 2H <sub>2</sub> O (2)	19646	24691	16393	30960	43103
[CoL <sup>1</sup> ] <sub>2</sub> ClO <sub>4</sub> (3)	20107	25008	16804	31206	42986
HL <sup>2</sup>				30960	42194
[CoL <sup>2</sup> ] <sub>2</sub> NO <sub>3</sub> (4)	21052	24519	17793	31347	43859
[CoL <sup>2</sup> ] <sub>2</sub> Cl · 2H <sub>2</sub> O (5)	20619	25000	17513	29240	41667
HL <sup>3</sup>				30948	42796
[CoL <sup>3</sup> ] <sub>2</sub> Br · 2H <sub>2</sub> O (6)	20576	25063	17953	31408	43212
[CoL <sup>3</sup> ] <sub>2</sub> ClO <sub>4</sub> · H <sub>2</sub> O (7)	20534	25000	17422	31396	43096

assigned to  $\nu_2$  is a combination band between it and the more intense  $S \rightarrow \text{Co}^{\text{III}}$  charge-transfer bands. Very weak bands at  $\sim 16393$ – $17953 \text{ cm}^{-1}$  correspond to spin forbidden  ${}^3T_{2g} \leftarrow {}^1A_{1g}$  transitions. From the spectra it can be concluded that two well separated high energy bands corresponding to spin allowed singlet  $\rightarrow$  singlet transitions have been observed with the occasional presence of low energy spin forbidden bands.

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### Appendix A. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center. CCDC 605916, 605917 and 605918 contain the supplementary crystallographic data for compounds **1**, HL<sup>3</sup> and **4**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.poly.2006.08.029](https://doi.org/10.1016/j.poly.2006.08.029).

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