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Cobalt(III) complexes of some aromatic thiohydrazides – Synthesis, characterization and structure

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ABSTRACT

[Co(NH₃)₅Cl]Cl₂ forms neutral 1:3 complex by reaction with aromatic thiohydrazides, i.e. thiobenzhydrazide, *o*-hydroxythiobenzhydrazide, thiophen-2-thiohydrazide and furan-2-thiohydrazide. All these complexes are diamagnetic and have been characterized by elemental analysis and combination of spectroscopic methods. Cyclic voltammometry of the complexes shows irreversible metal centered and ligand centered electron transfer reactions. One complex, tris-o-hydroxythiobenzhydrazidocobalt(III), has been crystallized from DMSO solution to produce solvated crystals and its structure has been established by X-ray crystallography. Cobalt(III) ion is linked through three hydrazinic nitrogen and three sulfur atoms of three identical deprotonated ligand molecules in a distorted octahedral environment. Involvement of -OH group in intramolecular and intermolecular hydrogen bonding is crucial for crystal formation.

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1. Introduction

Transition metal ions form a large number of complexes with ligands having N and S as donor site. Thiourea binds to such metal ions through thioketo group [1–3] while thiosemicarbazides and thiosemicarbazones may offer various modes of coordination [4,5]. Moreover, these ligands constitute an important class of nitrogen-sulfur donor ligands, because of their highly interesting chemical [6-8] and biological properties [9]. The ligands and their metal complexes have gained special attention due to their activity against protozoa [10], influenza [11], small pox viruses [12], fungi [13] and cancer [14]. Thiohydrazides are ligands closely related to thiosemicarbazides and may be represented as $RC(S)NHNH_2$ [where R = an alkyl or aryl or a heterocyclic group]. These ligands are simpler than thiosemicarbazides in the sense that N⁴ NH₂ group is absent here. In the present communication synthesis of cobalt(III) complexes of thiobenzhydrazide (Htbh), o-hydroxythiobenzhydrazide (Hhtbh), thiophen-2-thiohydrazide (Htth) and furan-2-thiohydrazide (Hfth) and their characterization by combined spectroscopic method have been described. The structure of DMSO-solvated cobalt(III) complex of Hhtbh has been established by the single crystal X-ray diffraction.

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2. Experimental

Pentaamminechlorocobalt(III)choloride (99.99%) was purchased from Aldrich Chemicals and was used as a source of cobalt(III). All solvents used were purified according to standard methods. All other chemicals were of reagent grade and used without further purification.

2.1. Preparations

2.1.1. Synthesis of thiobenzhydrazide (Htbh) [15]

Carboxymethyldithiobenzoate (2.12 g) was dissolved in 15 ml 1 M NaOH and cooled in ice. An ice-cold mixture of 1 ml (80%) of hydrazine hydrate and 10 ml 1 M NaOH was added slowly to this. The mixture was allowed to stand on an ice bath for 2 h. It was then neutralized with ice-cold dilute HCl to pH 6. Thiobenzhydrazide separated on cooling the mixture in an ice bath for one hour. It was collected by filtration, washed with ice-cold water, crystallized from tepid water and dried in vacuum. Yield: 0.80 g. *Anal.* Calc. for $C_7H_8N_2S$: C, 55.26; H, 5.26; N, 18.43; S, 21.05. Found: C, 55.11; H, 5.20; N, 18.38; S, 20.97%.

2.1.2. Synthesis of o-hydroxythiobenzhydrazide (Hhtbh) [16]

Freshly distilled salicylaldehyde (10 ml) was dissolved in 30 ml of ethanol and heated to about 60 °C. To this was added 44 ml of ammonium polysulfide dropwise with vigorous shaking. The solution was refluxed for 10 min, cooled to room temperature and filtered. The filtrate was transferred to a separatory funnel, covered





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with ether and acidified with ice-cold 1:1 HCl. The *o*-hydroxydithiobenzoic acid formed was then extracted with ether. The dark brown ether layer was washed thoroughly with brine and then back extracted with several small portions of 10% hydrazine hydrate solution. Because of high solubility of the compound, the volume of combined extract is kept within 50 ml. After keeping the whole solution for about 40 min at room temperature, it was just acidified with glacial acetic acid and extracted with ether. *o*-Hydroxy-thiobenzhydrazide obtained on evaporation of ether was recrystallized from tepid water to afford light yellow crystals. Yield: 1.8 g. *Anal.* Calc. for $C_7H_8N_2OS$: C, 50.00; H, 4.76; N, 16.67; S, 19.05. Found: C, 49.85; H, 4.69; N, 16.57; S, 18.98%.

2.1.3. Synthesis of thiophen-2-thiohydrazide (Htth) [17]

Freshly distilled thiophen-2-aldehyde (10 ml) was dissolved in 30 ml of ethanol and heated to about 60 °C. To this 44 ml of ammonium polysulfide was added very slowly with continuous shaking. The solution was boiled for 10 min, cooled to room temperature and filtered. The filtrate was transferred to a separatory funnel, covered with ether and acidified with ice-cold 1:1 HCl. The free acid formed was then extracted with ether. The dark brown ether layer was washed several times with ice-cold brine and then back extracted with several 5 ml portions of 10% hydrazine hydrate solution. The aqueous layer was collected, allowed to stand for 30–40 min at room temperature. It was then neutralized with glacial acetic acid and crystallized from hot water to afford light yellow crystals. Yield: 3.0 g. *Anal.* Calc. for $C_5H_6N_2S_2$: C, 37.97; H, 3.80; N, 17.72; S, 40.51. Found: C, 38.22; H, 3.67; N, 17.80; S, 40.49%.

2.1.4. Synthesis of furan-2-thiohydrazide (Hfth) [17]

Freshly distilled furfural (10 ml) was dissolved in 30 ml of ethanol and heated to about 60 °C. Ammonium polysulfide (44 ml) was added to this with vigorous shaking. The solution was refluxed for 10 min, cooled to room temperature and filtered. The filtrate was transferred to a separatory funnel, covered with ether and acidified with ice-cold 1:1 HCl. The free acid thus formed was extracted with ether. The dark brown ether layer was washed thoroughly with brine and then back extracted with several small portions of 10% hydrazine hydrate solution. The aqueous layer was collected, allowed to stand for 40 min at room temperature. It was then neutralized with glacial acetic acid and the separated brown solid was collected by filtration. It was then crystallized from hot water to afford light brown crystals. Yield: 2.5 g. *Anal.* Calc. for $C_5H_6N_2OS$: C, 42.25; H, 4.23; N, 19.72; S, 22.54. Found: C, 42.00; H, 4.44; N, 19.61; S, 22.45%.

2.1.5. Synthesis of Co(tbh)₃

An aqueous solution of 25 mg (0.1 mmol) of $[Co(NH_3)_5Cl]Cl_2$ was acidified with 8–10 drops of concentrated HCl. The solution was heated nearly to boiling and calculated amount of ligand (670 mg, 4.5 mmol) dissolved in ethanol was added. The pH of the solution was adjusted between 6.4 and 6.6 by drop wise addition of 1:1 NH₄OH solution. The resulting solution was digested on a boiling water bath for 3–4 h. Brown precipitate was collected by filtration through a sintered glass frit (G-4) previously weighed, washed with hot water and dried to 110 °C. Yield: 98%. *Anal.* Calc. for Co(C₇H₇N₂S)₃: C, 49.27; H, 4.10; N, 16.41; S, 18.75. Found: C, 48.92; H, 3.93; N, 16.27; S, 18.42%.

2.1.6. Synthesis of Co(htbh)₃

To an aqueous solution of $[Co(NH_3)_5Cl]Cl_2$ (25 mg, 0.1 mmol) 8– 10 drops of concentrated HCl were added with constant stirring and the solution was heated nearly to boiling. Calculated amount of *o*-hydroxythiobenzhydrazide (760 mg, 4.5 mmol) dissolved in ethanol was added to the nearly boiling solution. The pH of the solution adjusted between 6.4 and 6.8 by adding drop wise 1:1 NH₄OH solution. The resulting solution was then digested on a boiling water bath for 3–4 h. Brown precipitate was collected by filtration through a previously weighed sintered glass frit (G-4), washed with hot water to remove excess reagent and dried to 110 °C. Yield: 98%. *Anal.* Calc. for $Co(C_7H_7N_2OS)_3$: C, 45.01; H, 3.75; N, 15.00; S, 17.15. Found: C, 44.88; H, 3.52; N, 14.85; S, 16.96%.

2.1.7. Synthesis of $Co(tth)_3$

To the aqueous solution of 25 mg (0.1 mmol) $[Co(NH_3)_5Cl]Cl_2$, 8–10 drops of concentrated HCl was added with stirring. Calculated amount of thiophen-2-thiohydrazize (760 mg, 4.5 mmol) dissolved in ethanol was added to the stirred solution. 1:1 NH₄OH was added drop wise to maintain the pH near about 6.5–6.7. After the digestion for 3–4 h the solution afforded brown precipitate which was collected by filtration through a sintered glass frit (G-4) previously weighed, washed with hot water and dried to 110 °C. *Anal.* Calc. for Co(C₅H₅N₂S₂)₃: C, 33.97; H, 2.83; N, 15.85; S, 36.23. Found: C, 33.75; H, 2.69; N, 15.65; S, 36.07%.

2.1.8. Synthesis of $Co(fth)_3$

To the aqueous solution of 25 mg (0.1 mmol) $[Co(NH_3)_5Cl]Cl_2$, 8–10 drops of concentrated HCl was added with stirring. The solution was heated nearly to boiling and calculated amount of furan-2-thiohydrazide dissolved in ethanol was added. The pH of the solution adjusted to between 6.5 and 6.9 by adding drop wise 1:1 NH₄OH solution. The resulting solution was digested on a boiling water bath for 3–4 h. Brown precipitate was collected by filtration through a sintered glass frit (G-4) previously weighed, washed with hot water and dried to 110 °C. Yield: 98%. *Anal.* Calc. for $Co(C_5H_5N_2OS)_3$: C, 37.35; H, 3.11; N, 17.43; S, 19.92. Found: C, 36.93; H, 2.95; N, 17.17; S, 19.86%.

2.2. Physical measurements

Microanalyses (C, H, N, S) were done in IACS, Kolkata using 2400 series II Perkin Elmer, CHNS analyzer. Electronic spectra were recorded on a Hitachi 3210 UV–vis spectrophotometer. IR spectra were obtained on a Unicam 300S spectrometer (4000–300 cm⁻¹) with samples prepared as KBr pellets. ¹H NMR spectra in d_6 -DMSO solutions were obtained on a Brucker DRX 500 spectrometer using TMS as the internal standard. Cyclic Voltammometric measurements were made with a EG&G Potentiostat model 263A instrument using a platinum working electrode, a platinum wire auxiliary electrode and an Ag/AgCl (saturated KCl) as reference electrode. All cyclic voltammometric experiments were performed under a nitrogen atmosphere in distilled DMSO solution (0.1 M TBAP). Cyclic voltammometric data were collected at 298 K and are uncorrected for junction potential.

2.3. X-ray crystallography

Deep red flaky crystals of suitable for X-ray crystallography were obtained from a saturated solution of Co(htbh)₃ complex in DMSO. The crystalline compound was found to have the composition [Co(htbh)₃].3(CH₃)₂SO. *Anal.* Calc.: C, 31.74; H, 2.65; N, 10.58; S, 24.18. Found: C, 31.38; H, 2.34; N, 10.37; S, 23.95%.

Crystallographic data were collected with Mo K α (λ = 0.71073) radiation at 150 K using the Oxford Diffraction X-Caliber CCD system. The crystal was positioned at 50 mm from the CCD. Frames of 321 were measured with a counting time of 10 s. Data analysis was carried out with the CrysAlis program [18]. The structure was solved using direct methods with SHELXS97 [19]. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon and nitrogen were included in geometric positions and given thermal parameters equivalent to

1.2 times those of the atom to which they were attached. An absorption correction was carried out using the ABSPACK program [20]. The structure was refined on F^2 using SHELXL97 [19].

3. Results and discussion

3.1. Description of the structure of [Co(htbh)₃]·3(CH₃)₂SO complex

The crystal data, together with the data collection and structure refinement parameters are presented in Table 1. The selected bond lengths and angles were summarized in Table 2. The ORTEP diagram along with the numbering scheme of the compound is presented in Fig. 1.

The crystal structure of $[Co(C_7H_7N_2OS)_3]\cdot 3(CH_3)_2SO$ contains discrete $Co(C_7H_7N_2OS)_3$ entities and three DMSO molecules. The cobalt(III) ions are hexacoordinated with three nitrogen and three sulfur atoms from three identical ligands forming a facial structure.

The structure shows the cobalt atom in a distorted octahedral environment being bonded to three bidentate ligands through N and S. The bond lengths of Co(1)–S(11), Co(1)–S(21) and Co(1)–S(31) are 2.234(1), 2.214(1) and 2.217(1)Å respectively while those of Co(1)–N(14), Co(1)–N(24) and Co(1)–N(34) are 1.965(3), 1.969(3) and 1.963(3)Å respectively. These bond lengths are similar to those found in cobalt complexes with methylated isatin and ferrocene containing thiosemicarbazones [21,22].

The C–S bond lengths in the ligands of 1.736(3), 1.744(3) and 1.741(3) Å are within the normal range of C–S single bonds, indicating that the thiohydrazide moieties adopt the thiol tautomeric form [23]. In the ligands, the C–N distances are 1.294(4), 1.293(4) and 1.290(4) Å while the N–N bond lengths are 1.443(4), 1.451(3), 1.449(3) Å. Both sets of distances are intermediate between formal single bond and double bonds, but with the C–N distances closer to a double bond and the N–N distances closer to a single bond, thus pointing to an extensive electron delocalization over the molecular skeleton.

Furthermore, the bond angles in *o*-hydroxythiobenzhydrazide ligand of approximately around 117° are also compatible with the electron delocalization [24].

Table 1

Crystal data and refinement details of the Co(htbh)₃·3(CH₃)₂SO complex.

Empirical formula	C ₂₇ H ₃₉ N ₆ CoO ₆ S ₆
Crustel system	794.95 Trialinia
space group	<i>P</i> 1
Unit cell dimensions	a = 10.7535(17) Å
	b = 12.0000(13) Å
	c = 16.0388(15) Å $\alpha = 69.933(9)^{\circ}$ $\beta = 85.116(10)^{\circ}$ $\gamma = 66.705(12)^{\circ}$
Cell volume	1782.49 Å ³
Z	2
Calculated density	1.481
Absorption coefficient	0.881
F(000)	828
Theta range for data collection	2.30°-30.00°
Reflections collected/unique $[R_{int} = 0.0282]$	9933
Crystal size (mm)	$0.22 \times 0.03 \times 0.03$
Completeness to theta	95.6°
Data $[I > 2\sigma(I)]$ /parameters	6360/426
Goodness-of-fit (GOF) on F^2	0.913
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0563$
	$wR_2 = 0.1486$
R indices (all data)	$R_1 = 0.0880$
	$wR_{2} = 0.1583$
Largest differential neak and hole (e $\dot{\mathbf{A}}^{-3}$)	2.249 and -1.579

Table 2

Selected bond lengths (Å) and angles (°) in the metal coordination sphere.

Bonds	Distance (Å)	Bonds	Distance(Å)
$\begin{array}{c} Co(1)-S(11)\\ Co(1)-S(21)\\ Co(1)-S(31)\\ Co(1)-N(14)\\ Co(1)-N(24)\\ Co(1)-N(34)\\ N(13)-N(14)\\ N(33)-N(34)\\ \end{array}$	2.234(1) 2.214(1) 2.217(1) 1.965(3) 1.969(3) 1.963(3) 1.443(4) 1.449(3)	C(12)-S(11) C(22)-S(21) C(32)-S(31) C(12)-N(13) C(22)-N(23) C(32)-N(23) N(23)-N(24)	1.736(3) 1.744(3) 1.741(3) 1.294(4) 1.293(4) 1.290(4) 1.451(3)
Bonds	Angles (°)	Bonds	Angles (°)
$\begin{array}{c} N(34)-Co(1)-N(14)\\ N(34)-Co(1)-N(24)\\ N(34)-Co(1)-S(21)\\ N(14)-Co(1)-S(21)\\ N(14)-Co(1)-S(31)\\ S(21)-Co(1)-S(31)\\ N(14)-Co(1)-S(11)\\ S(21)-Co(1)-S(11)\\ \end{array}$	90.17(11) 92.94(11) 90.94(8) 85.11(8) 93.28(8) 89.41(3) 84.98(8) 94.12(3)	$\begin{array}{l} N(14)-Co(1)-N(24)\\ N(14)-Co(1)-S(21)\\ N(14)-Co(1)-S(31)\\ N(24)-Co(1)-S(31)\\ N(34)-Co(1)-S(11)\\ N(24)-Co(1)-S(11)\\ S(31)-Co(1)-S(11) \end{array}$	92.22(11) 177.16(8) 85.73(8) 174.34(8) 173.25(8) 91.94(8) 89.85(3)



Fig. 1. The structure of Co(htbh)₃·3(CH₃)₂SO together with the atomic numbering scheme. Ellipsoids at 50% probability. Hydrogen bonds are shown as dotted lines.

Table 3	
Hydrogen bond lengths (\mathbf{A}) and angles (°)	

Donor (D)	Acceptor (A)	$H{\cdot}{\cdot}{\cdot}A$	$D{-}H{\cdot}{\cdot}{\cdot}A$	$D{\cdots}A$
O(20)-H(20)	N(13)	1.78	147	2.514
O(30)-H(30)	N(23)	1.92	145	2.634
O(40)-H(40)	N(33)	1.78	156	2.579
N(14)-H(14A)	O(20) ^a	2.09	169	2.977
N(14)-H(14B)	O(74)	2.06	152	2.879
N(14)-H(14B)	O(64)	2.53	116	3.033
N(24)-H(24A)	O(74)	2.15	141	2.902
N(24)-H(24B)	O(54)	2.09	142	2.854
N(34)-H(34A)	O(54)	2.07	145	2.861
N(34)-H(34B)	O(64)	2.06	150	2.872

^a Symmetry element -x, 1 - y, 1 - z.

There is an extensive set of hydrogen bonds in the structure which are detailed in Table 3. In the three ligands the O–H bonds

form hydrogen bonds to the nitrogen atoms, thus O(20)–H···N(13), O(30)–H···N(23) and O(40)–H···N(33) show O···N distances of 2.514, 2.634 and 2.579 Å respectively.

In addition the three DMSO molecules, each form two bifurcated hydrogen bonds, O(54) to N(24)–H(24B) and N(34)–H(34A) at 2.864 and 2.861 Å respectively, O(64) to N(34)–H(34B) and N(14)–H(14B) at 2.872, 3.033 Å and O(74) to N(14)–H(14B) and N(24)–H(24A) at 2.879, 2.902 Å. Five of these bonds are relatively strong with N–H···O angles in the range 141–152°. However N(14)–H(14B)···O(64) is much weaker with a N–H···O angle of 116°. The reason for this is readily apparent as O(64) is hydrogen bonded to H(14B) not H(14A) as might be expected. Instead N(14)–H(14A) forms a strong hydrogen bond to O(20) (–*x*, 1 – *y*, 1 – *z*) thus forming a centrosymmetric dimer held together by two hydrogen bonds.

These hydrogen bonds in between the –OH group of the benzene ring and the hydrazinic nitrogen is important for the successful crystallization. It well may be for that reason that the crystals of the other cobalt(III)–thiohydrazide complexes are not obtained since they do not possess the –OH group in ligand moiety. Also the inclusion of three solvent molecules with their hydrogen bonds to the complex may also have facilitated the crystallization.

3.2. Electronic spectra

Absorption maxima in the electronic spectra of the cobalt(III)– thiohydrazide complexes in ethanol and their assignments are listed in Table 4.

The electronic spectra of the ethanolic solutions of complexes exhibit two bands in the region of 252–270 nm (log ε = 4.185–4.362) and 310–330 nm (log ε = 4.112–4.1085 dm³ cm⁻¹ mol⁻¹) attributed to intraligand charge transfer bands ($\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$, respectively) [25]. The spectra also show peaks in the region of 420–432 nm (log ε = 2.996–3.663 dm³ cm⁻¹ mol⁻¹). These may arise due to S \rightarrow cobalt(III) charge transfer (LMCT) bands. The d–d transition bands could not be observed because those were obscured by strong charge transfer bands [26].

3.3. Infrared spectra

The characteristic IR bands $(4000-200 \text{ cm}^{-1})$ for the ligands when compared with those of its cobalt(III) complexes provided meaningful information regarding the bonding sites of the primary ligand molecule. Significant bands observed in the IR spectra of the ligands and the corresponding complexes with their probable assignments are listed in Table 5. Other peaks [v(C-C), v(C-H) of the benzene ring, out of plane(C–H), in plane(C–H) bending, v(N-N), and $\beta(C-N-N)$ vibrations] were of course observed in both reagent and corresponding complex. As their positions in the com-

Table 4	4
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Electronic absorption	data of	the	complexes	λmax	(nm)	in	ethanol.
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Complex	Absorption	Assignment
Co(tbh) ₃	257.6	$\pi \to \pi^*$
	310.4	$n \rightarrow \pi^*$
	420.4	LMCT
Co(htbh) ₃	252.8	$\pi \to \pi^*$
	316.6	$n \rightarrow \pi^*$
	420.4	LMCT
Co(tth) ₃	258.4	$\pi \to \pi^*$
	318.4	$n \rightarrow \pi^*$
	415.2	LMCT
Co(fth) ₃	270.8	$\pi \to \pi^*$
	330.8	$n \to \pi^*$
	432.0	LMCT

Table 5

Characteristic infrared absorption data for cobalt(III) thiohydrazide complexes (in cm^{-1}).

	v(N- H)	v(C–S)	ν(C– N)	v(M– N)	v(M– S)	v(S–H)	$\beta_{\rm NH2}$
H(tbh)	3280,	1180, 1070	1565,	-	-	2515vw	1595
	3200		1450				
Co(tbh)3	3340	1160, 1120,	1615,	540	420	-	1590
		1070, 760	1480				
H(htbh)	3300,	1175, 1105,	1580,	-	-	2590vw	1608
	3220	870	1465				
Co(htbh)3	3350	1160, 1100,	1610,	530	430	-	1690
		820	1480				
H(tth)	3280,	1295, 1160,	1535,	-	-	2530vw	1607
	3200	755	1500				
Co(tth)3	3330	1248, 1150,	1590,	510	420	-	1610
		730	1530				
H(fth)	3230	1255, 1150,	1585,	-		2510vw	1584
		820	1545				
Co(fth) ₃	3290	1241, 1125,	1600,	550	440		1590
		785	1575				

plex did not change significantly from those in the free ligands, these are not recorded. Board bands between 3300 and 3200 cm⁻¹ in the ligands are due to (N–H) stretching of NH₂ and NH groups. The number of bands in the complexes is usually greater than those in the ligands. The v(C–N) band (amide II) [27] is observed in the region 1580–1530 cm⁻¹ in the ligands. Their shifts to higher frequency on complex formation [28] suggest partial double bond character of C–N bond in the cobalt(III) complexes.

Bands involving v(C-S) are often difficult to assign [29]. Coordination of sulfur induces changes in positions and intensities of bands other than pure C–S stretching frequencies. The v(C-S) band is not found at a particular frequency. Because of coupled vibrations it may occur near v(C-N), aromatic v(C-C) and δ_{NH2} modes. In thiosemicarbazide, v(C-S) has been assigned [30] at 803 cm⁻¹ and is reported to have more than 50% contribution from the (C–S) stretching mode. The intensity ratio v(C=O)/v(C=S) ranges from 1.38 to 1.5 [31] enables assignment of v(C-S) bands in the ligands and their cobalt(III) complexes. Bands having contributions from v(C-S) are given in Table 5. A very weak band observed around 2510–2590 cm⁻¹ is assigned to v(S-H), attributed to the presence of keto-enol tautomerism in the ligand. The weakness of the band is most probably due to the following equilibrium lying to the left hand side

 $-C(=S)-NH-NH_2\leftrightarrow -C(SH)=N-NH_2.$

The absence of v(S–H) in the complex indicates coordination to occur through S atom and thioenolisation takes place before complex formation [31].

Metal–nitrogen v(M-N) and metal–sulfur v(M-S) stretching frequencies have also been assigned. The v(M-N) vibrations may be tentatively assigned [32] at around 510–550 cm⁻¹. In several coordination compounds the v(M-S) band has been assigned at around 380–450 cm⁻¹ [33]. In complexes under study, the bands observed in the region 420–440 cm⁻¹ may therefore be assigned to the (M–S) stretch.

The bending mode of vibration for $-NH_2 (\beta_{NH2})$ is observed near 1600 cm⁻¹ in free ligands and these sharp bands suffer a shift towards higher frequency in the complexes indicating complexation occurs through hydrazinic $-NH_2$ group [34].

3.4. Proton NMR spectra

Table 6 presents chemical shift data for ¹H NMR spectra of the ligands and their cobalt(III) complexes.

From the ¹H NMR data of all the free ligands and its complexes it is suggested that position of protons i.e., aromatic and –OH

Table 6

¹H NMR data for ligands and complexes. Chemical shifts (δ) are given in ppm, relative to TMS. Spectra were recorded in d_6 -DMSO as solvent.

Compound/ligand	Hydrazinic proton	Amidic proton
H(tbh)	6.2	10.80
Co(tbh) ₃	7.26	-
H(htbh)	5.75	11.75
Co(htbh) ₃	7.008	-
H(tth)	6.2	8.2
Co(tth) ₃	7.06	-
H(fth)	5.24	8.25
Co(fth) ₃	7.105	-

protons for H(htbh) remain almost unaltered on complexation and hence are not recorded in the table. Amidic proton resonance signals observed in the region δ = 8.20–11.75 in the ligands are absent in the complexes. It signifies involvement of deprotonated ligands in complexation. The NMR signal of hydrazinic proton underwent a downfield shift by more than 0.8 ppm in the complexes compared to the corresponding ligand. The fact suggests that coordination occurs through hydrazinic nitrogen atom [35–37].

3.5. Electrochemistry

Voltammometric behavior of the cobalt(III)-thiohydrazide complexes was studied in the potential range from +1.0 V to -2.0 V (vs. Ag/AgCl) in DMSO solution using TBAP (0.1 M) as supporting electrolyte. A scan initiated in the negative direction reveals an irreversible cobalt(III)/cobalt(II) reduction wave at -0.5 V in all the complexes. In addition, a ligand centered irreversible reduction wave was observed in the range of -1.0 to -1.3 V depending upon the ligand.

The irreversibility may be due to the process:

 $Co^{III}(htbh)_3 + e + H^+ \rightarrow Co^{II}(htbh)_2(DMSO)_2 + H(htbh)$ [38].

The reduction of the cobalt(III) to cobalt(II) complex results in the loss of a ligand molecule in the coordinating solvent DMSO. In the reverse sweep since a new species is formed during anodic process the electrochemical behavior of these complexes becomes irreversible.

4. Conclusion

The present study shows that cobalt(III) ion forms sufficiently stable, diamagnetic, innermetallic, 1:3 complexes with thiohydrazide ligands binding through hydrazinic nitrogen and sulfur atoms. From the crystal structure of the Co(htbh)₃·3(CH₃)₂SO it is evident that inter and intra molecular hydrogen bonding involving –OH group of the *o*-hydroxythiobenzhydrazide ligand is responsible for crystallization. That the other cobalt(III)–thiohydrazide complexes cannot be crystallized may be due to the absence of the –OH group in the ligand moiety. The electronic, IR and proton NMR spectrum of the other cobalt(III)–thiohydrazide complexes are similar to those of Co(htbh)₃. Therefore it appears that other thiohydrazide complexes have similar structure.

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Appendix A. Supplementary material

CCDC 737525 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010. 01.011.

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