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# Synthesis, Physico-Chemical Characterization and Bio-Activity of Cobalt(II) Tetrathiocyanato Diargentate(I) Complexes with Some Acylhydrazones

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Heterobimetallic complexes of the type  $\text{Co}[\text{Ag}(\text{SCN})_2]_2 \cdot \text{L}$  (where L = acetophenone benzoylhydrazone (abh), acetophenone isonicotinoyl hydrazone (ainh), acetophenone salicyloyl hydrazone (ash), acetophenone anthraniloyl hydrazone (aah), *p*-hydroxy acetophenone benzoylhydrazone (phabh), *p*-hydroxy acetophenone isonicotinoyl hydrazone (phainh), *p*-hydroxy acetophenone salicyloyl hydrazone (phash), *p*-hydroxy acetophenone anthraniloyl hydrazone (phaah) were synthesized and characterized by various physico-chemical techniques. The complexes are non-electrolytes and form a polymeric structure by bridging SCN groups between two metal centers. The ligands are coordinated through  $>\text{C}=\text{O}$  and  $>\text{C}=\text{N}$ -groups. Magnetic susceptibility measurements and electronic spectra suggest a tetrahedral geometry for  $\text{Co}[\text{Ag}(\text{SCN})_2]_2$  and spin free octahedral geometry for all the complexes. Thermal analysis (TGA and DTA) of  $\text{Co}[\text{Ag}(\text{SCN})_2]_2$  complex shows multi-step exothermic decomposition patterns. X-ray powder diffraction parameters of two of the complexes correspond to a tetragonal and orthorhombic crystal lattices. The complexes show fair antifungal activity against *Rizoctonia sp.*, and *Stemphylium sp.* and moderate antibacterial activity against *Clostridium sp.*, and *Pseudomonas sp.* The activity increases with increasing concentration of the compounds.

**Keywords:** cobalt(II) and silver(I); bimetallic complexes; polymeric; bio-activity; characterization; thermal studies

## 1 Introduction

Cobalt is a unique element present in vitamin B<sub>12</sub> and is vital for living beings, though in minute quantities. It plays a significant role in activating small inorganic molecules (1), particularly molecular oxygen. The best studied examples are cobalt(II)-Schiff base complexes which take up O<sub>2</sub> in DMF or pyridine solution (2). Considerable significance is attached to the study of cobalt complexes in view of the synthesis of cobalmines responsible for erythrocytes (RBC) formation in the human body (3, 4). Our interest in the complexes of hetero-bimetallic thiocyanates with acylhydrazones has grown because of the possibility to synthesize more biologically active compounds by the combination of two metal thiocyanates  $\text{Co}(\text{NCS})_2$  and  $\text{AgSCN}$  and a hydrazone ligand. Accordingly, a number of  $\text{Co}[\text{Ag}(\text{SCN})_2]_2 \cdot \text{L}$  complexes were synthesized, characterized and their biological activities (antifungal and antibacterial) are discussed in this paper.

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## 2 Experimental

### 2.1 Materials

All chemicals were of AnalaR (BDH) or equivalent grade. Benzoic acid hydrazide ( $\text{C}_6\text{H}_5\text{CONHNH}_2$ ), salicylic acid hydrazide ( $\text{HO-C}_6\text{H}_4\text{CONHNH}_2$ ) and anthranilic acid hydrazide ( $\text{H}_2\text{NC}_6\text{H}_4\text{CONHNH}_2$ ) were synthesized by the reported methods (5). Isonicotinic acid hydrazide ( $\text{NC}_5\text{H}_4\text{-CONHNH}_2$ ) was obtained from S.D. Fine Chemicals, Mumbai and used after recrystallization in ethanol.

### 2.2 Preparation of Ligands

#### 2.2.1 Acetophenone Acylhydrazones

Acetophenone benzoyl hydrazone (abh),  $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)=\text{NN-HCOC}_6\text{H}_5$ ; acetophenone isonicotinoyl hydrazone (ainh),  $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)=\text{NNHCOC}_5\text{H}_4\text{N}$ ; acetophenone salicyloyl hydrazone (ash),  $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)=\text{NNHCOC}_6\text{H}_4(\text{OH})$  and acetophenone anthraniloyl hydrazone (aah),  $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)=\text{NNHCOC}_6\text{H}_4(\text{NH}_2)$  were synthesized by reacting their corresponding acid hydrazides with acetophenone in 1:1 molar ratio in 50 mL ethanol in a RB flask. The reaction mixture was refluxed at 60°C for 2–4 h and then allowed to cool in

a beaker and filtered the product by suction on a Buckner funnel. The abh and aah ligands were recrystallized from hot benzene, while ash and ainh were recrystallized from hot ethanol and dried in a desiccator over anhydrous  $\text{CaCl}_2$ .

### 2.2.2 *p*-Hydroxy Acetophenone Acylhydrazones

*p*-hydroxy acetophenone benzoylhydrazone (phabh),  $\text{C}_6\text{H}_4(\text{OH})\text{C}(\text{CH}_3)=\text{NNHCOC}_6\text{H}_5$ ; *p*-hydroxy acetophenone isonicotinoyl hydrazone (phainh),  $\text{C}_6\text{H}_4(\text{OH})\text{C}(\text{CH}_3)=\text{NNHCOC}_5\text{H}_4\text{N}$ ; *p*-hydroxy acetophenone salicyloyl hydrazone (phash),  $\text{C}_6\text{H}_4(\text{OH})\text{C}(\text{CH}_3)=\text{NNHC}_6\text{H}_4(\text{OH})$ ; *p*-hydroxy acetophenone anthraniloyl hydrazone (phaah),  $\text{C}_6\text{H}_4(\text{OH})\text{C}(\text{CH}_3)=\text{NNHCOC}_6\text{H}_4(\text{NH}_2)$  were synthesized by reacting their corresponding acid hydrazide with *p*-hydroxy acetophenone in 1:1 molar ratio in 50 mL ethanol. The reactants were refluxed for 4–6 h in a RB flask at  $60^\circ\text{C}$ . The crude product was filtered after cooling, recrystallized from hot ethanol and dried in a desiccator. The ligands were characterized by their melting points, C H N analyses and IR spectra (Table 1).

### 2.3 Preparation of Metal Thiocyanates

Cobalt(II) thiocyanate was prepared by dissolving  $\text{CoNO}_3 \cdot 6\text{H}_2\text{O}$  (10 mmol, 2.90 g) in 50 ml absolute ethanol and  $\text{KSCN}$  (20 mmol, 1.94 g) in 25 mL absolute ethanol separately. Both the solutions were mixed in a beaker at room temperature.  $\text{KNO}_3$  was thus formed as a white solid and removed by filtration. The filtrate containing  $\text{Co}(\text{NCS})_2$  was slowly evaporated to dryness to obtain a blue colored solid product. It was redissolved and purified from dry ethanol to ensure removal of water soluble  $\text{KNO}_3$ .

$\text{AgSCN}$  was prepared by dissolving  $\text{AgNO}_3$  (10 m mol, 1.70 g) in 50 mL water. The solution was treated with  $\text{NH}_4\text{SCN}$  (10 m mol, 0.76 g) dissolved in 25 mL water with constant stirring at room temperature.  $\text{AgSCN}$  thus formed as a white precipitate, was filtered, washed with water, ethanol and finally with diethyl ether and dried in a desiccator.

### 2.4 Synthesis of $\text{Co}[\text{Ag}(\text{SCN})_2]_2$

$\text{Co}(\text{NCS})_2$  (10 mmol, 1.74 g) and  $\text{AgSCN}$  (20 mmol, 3.32 g) were reacted in a round bottom flask containing 50 mL ethyl acetate and fitted with anhydrous  $\text{CaCl}_2$  guard tube. The reaction mixture was stirred continuously for 48 h on a magnetic stirrer at room temperature to complete the reaction. Blue colored Lewis acid thus formed was filtered through a closed assembly, washed with ethylacetate and dried in a desiccator at room temperature.

### 2.5 Synthesis of $\text{Co}[\text{Ag}(\text{SCN})_2]_2 \cdot \text{L}$

$\text{Co}[\text{Ag}(\text{SCN})_2]_2 \cdot \text{L}$  complexes were prepared by reacting the Lewis acid  $\text{Co}[\text{Ag}(\text{SCN})_2]_2$  (5 mmol, 2.54 g) separately with 5 mmol of each of the ligands abh (1.19 g), ainh (1.20 g), ash (1.27 g), aah (1.26 g), phabh (1.27 g), phainh (1.28 g), phash (1.35 g) and phaah (1.35 g) in a round bottom flask containing 50 mL ethylacetate. The reaction mixture was well stirred on a magnetic stirrer for 12–48 h at room temperature until a visible color change (from blue to pink) of the product takes place. The product was filtered, washed with ethyl acetate followed by diethyl ether and then dried in a desiccator over anhydrous  $\text{CaCl}_2$  at room temperature.

**Table 1.** Analytical data of the ligands

Ligands (color)	Empirical formula (formula wt.)	Melting point ( $^\circ\text{C}$ )	Found (calculated) %			Yield (%)
			C	H	N	
abh (White)	$\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}$ (238)	145	75.89 (75.63)	5.92 (5.88)	11.66 (11.76)	75
ainh (White)	$\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}$ (239)	162	70.10 (70.29)	5.50 (5.44)	17.42 (17.57)	70
ash (White)	$\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_2$ (254)	205	70.52 (70.86)	5.61 (5.51)	10.85 (11.02)	75
aah (Cream yellow)	$\text{C}_{15}\text{H}_{15}\text{N}_3\text{O}$ (253)	175	70.92 (71.15)	5.81 (5.93)	16.51 (16.60)	60
phabh (Light yellow)	$\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_2$ (254)	210	70.60 (70.86)	5.67 (5.51)	10.92 (11.02)	70
phainh (Light yellow)	$\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_2$ (255)	260	65.72 (65.88)	5.18 (5.10)	16.38 (16.47)	65
phash (Light yellow)	$\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_3$ (270)	240	66.55 (66.67)	5.16 (5.18)	10.32 (10.37)	75
phaah (Light yellow)	$\text{C}_{15}\text{H}_{15}\text{N}_3\text{O}_2$ (269)	225	66.70 (66.91)	5.48 (5.57)	15.51 (15.61)	65

## 2.6 Analyses and Physico-Chemical Studies

For determination of the silver content, the weighed amount of the complexes were heated (80°C) with an excess of dilute HCl (0.01 N). The solution was cooled to deposit SCN (6), which was filtered in a crucible, washed first with hot water and then with ethanol and dried at 110°C. For determination of cobalt contents, the filtrate was evaporated to dryness using conc. HNO<sub>3</sub>, followed by conc. H<sub>2</sub>SO<sub>4</sub> to destroy the SCN groups and the organic content. The solid was dissolved in distilled water. From the solution, cobalt was estimated gravimetrically as cobalt anthranilate by the literature procedure (6). Carbon, hydrogen and nitrogen contents were determined by using a Elemental Vario EL III Carlo Erba 1108 model microanalyzer. The molar conductance of 10<sup>-3</sup> M solutions of the complexes in DMSO were measured at room temperature on a Systronic Conductivity meter model-306. Room temperature magnetic susceptibilities were determined on a Faraday balance using Hg[Co(SCN)<sub>4</sub>] as calibrant and corrected for diamagnetism (7). IR spectra were recorded in KBr medium on Vector-22 spectrophotometer. Electronic spectra were recorded in DMSO solution on a Perkin-Elmer Lambda-2 spectrophotometer. Thermal analysis (TGA and DTA of Co[Ag(SCN)<sub>2</sub>]<sub>2</sub> · ash complex was recorded on a Perkin-Elmer Thermal Analyzer between room temperature to 550°C. Powder X-ray diffraction patterns of a few complexes were recorded on a Iso Debye Flex 2002 apparatus using Cu Kα radiations. The analytical and physico chemical data are given in Tables 1–6.

## 2.7 Antimicrobial Activity

### 2.7.1 Antifungal Activity

The ligands, as well as their complexes, were screened for antifungal activity against various fungi viz. *Rizoctonia sp.*, and *Stemphylium sp.* These species were isolated from the infected organs of the host plants on potato dextrose agar (potato 250 g + dextrose 20 g + agar 20 g) medium. The cultures of the fungi were purified by a single spore isolation technique.

The solution in different concentrations 0.5, 1.0 and 1.5 mg/mL of each compound in DMSO were prepared for testing against spore germination. A drop of the solution of each concentration was kept separately on glass slides. The conidia, fungal reproducing spores (approx. 200) lifted with the help of an inoculating needle, were mixed in every drop of each compound separately. Each treatment was replicated thrice and a parallel DMSO solvent control set was run concurrently on separate glass slides. All the slides were incubated in humid chambers at 25 ± 2°C for 24 h. Each slide was observed under the microscope for spore germination and percent germination was finally calculated.

Table 2. Analytical data of the complexes

Complex (color)	Empirical formula (formula wt.)	Decomposition temp. (°C)	Found (calculated) %					Yield (%)	Λ <sub>M</sub> (Ω <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> ) in DMSO
			Ag	Co	C	H	N		
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> (Dark blue)	C <sub>4</sub> N <sub>4</sub> S <sub>4</sub> CoAg <sub>2</sub> (507)	268	42.50 (42.60)	11.55 (11.64)	9.36 (9.47)	—	10.89 (11.04)	95	—
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> · abh (Pink)	C <sub>19</sub> H <sub>14</sub> N <sub>6</sub> S <sub>4</sub> OCoAg <sub>2</sub> (745)	210	28.75 (28.99)	7.80 (7.92)	30.41 (30.60)	1.82 (1.88)	11.11 (11.27)	90	10.2
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> · ainh (Violet)	C <sub>18</sub> H <sub>13</sub> N <sub>7</sub> S <sub>4</sub> OCoAg <sub>2</sub> (746)	233	28.80 (28.95)	7.85 (7.91)	28.76 (28.95)	1.76 (1.74)	13.22 (13.14)	88	9.9
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> · ash (Light pink)	C <sub>19</sub> H <sub>14</sub> N <sub>6</sub> S <sub>4</sub> O <sub>2</sub> CoAg <sub>2</sub> (761)	180	28.24 (28.38)	7.70 (7.75)	29.82 (29.96)	1.88 (1.84)	10.86 (11.04)	86	8.5
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> · aah (Pink)	C <sub>19</sub> H <sub>15</sub> N <sub>7</sub> S <sub>4</sub> OCoAg <sub>2</sub> (760)	222	28.30 (28.42)	7.80 (7.76)	30.12 (30.00)	1.87 (1.97)	12.96 (12.89)	92	11.4
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> · phabh (Pink)	C <sub>19</sub> H <sub>14</sub> N <sub>6</sub> S <sub>4</sub> O <sub>2</sub> CoAg <sub>2</sub> (761)	226	28.40 (28.38)	7.65 (7.75)	29.78 (29.96)	1.82 (1.84)	10.92 (11.04)	90	11.6
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> · phainh (Light violet)	C <sub>18</sub> H <sub>13</sub> N <sub>7</sub> S <sub>4</sub> O <sub>2</sub> CoAg <sub>2</sub> (762)	238	28.25 (28.35)	7.70 (7.74)	28.30 (28.35)	1.76 (1.71)	12.73 (12.86)	85	9.5
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> · phash (Pink)	C <sub>19</sub> H <sub>14</sub> N <sub>6</sub> S <sub>4</sub> O <sub>3</sub> CoAg <sub>2</sub> (777)	245	27.60 (27.80)	7.50 (7.59)	29.25 (29.34)	1.72 (1.80)	10.69 (10.81)	88	10.6

**Table 3.** Magnetic moments, electronic spectral data and ligand field parameters of the complexes

Complexes	$\mu_{\text{eff}}$ (B.M.)	Band maxima ( $\text{cm}^{-1}$ )		10 Dq ( $\text{cm}^{-1}$ )	B ( $\text{cm}^{-1}$ )	$\beta$	$\beta'$ (%)	LFSE (kcal/mol)
		$\nu_1$	$\nu_3$					
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub>	3.98		16025					
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> · abh	4.71	9260	19880	10415	785	0.808	19.20	23.74
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> · ainh	4.69	9325	20250	10535	809	0.833	16.70	24.01
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> · ash	4.83	9190	20425	10385	828	0.853	14.70	23.67
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> · aah	4.87	9340	20120	10555	799	0.823	17.70	24.06
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> · phabh	4.79	9280	20180	10440	804	0.828	17.20	23.79
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> · phainh	4.73	9295	19930	10460	787	0.810	19.00	23.84
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> · phash	4.70	9315	20475	10525	825	0.850	15.00	23.99
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> · phaah	4.81	9280	20650	10485	838	0.863	13.70	23.90

### 2.7.2 Antibacterial Activity

The antibacterial activity of the ligands and their complexes was studied against *Clostridium sp.* (gram + ve) and *Pseudomonas sp.* (gram - ve) bacteria. Each of the compound was dissolved in DMSO and solutions of the concentration 1 mg/mL and 2 mg/mL were prepared separately. Paper discs of Whatman filter paper (No. 42) of uniform diameter (2 cm) were cut and sterilized in an autoclave. The paper discs soaked in the desired concentration of the complex solutions were placed aseptically in the Petri-dishes containing nutrient agar media (agar 20 g + beef extract 3 g + peptone 5 g) seeded with *Clostridium* and *Pseudomonas sp.* bacteria separately. The petri dishes were incubated at 32°C and the inhibition zones were recorded after 24 h of incubation. Each treatment was replicated 9 times.

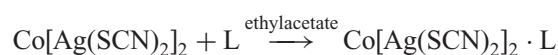
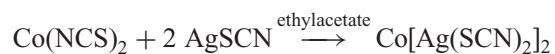
The antibacterial activity of a common standard antibiotic Ampicillin was also recorded using the same procedure as above at the same concentrations and solvent. The % Activity Index for the complex was calculated by the formula as under:

% Activity Index

$$= \frac{\text{Zone of inhibition by test compound (diameter)}}{\text{Zone of inhibition by standard (diameter)}} \times 100$$

### 3 Results and Discussion

The analytical data of the complexes (Table 2) show that Co(NCS)<sub>2</sub> and AgSCN react in 1:2 molar ratio in ethylacetate to form a more stable Co[Ag(SCN)<sub>2</sub>]<sub>2</sub> complex. The Lewis acid further reacts with the acylhydrazone ligands in 1:1 (M:L) molar ratio in the following manner:



The Lewis acid is dark blue in color, whereas the colors of its complexes vary from violet, pink, light pink to brown. They are generally insoluble in common organic solvent viz. ethanol, benzene, chloroform, carbon tetrachloride, ethylene chloride and diethyl ether, but are soluble in DMF and DMSO. They dissociate in water, acetone and acetonitrile. The free Lewis acid decomposes at 268°C, while the complexes decompose between 180–245°C. All the complexes have very low molar conductance values of 10<sup>-3</sup> M solutions of the complexes in DMSO at room temperature suggest that they are non-electrolytes (8).

**Table 4.** IR spectral data and assignment of important bands

Compounds	$\nu(\text{NH} + \text{OH})$	Amide I $\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	Amide II	Amide III	$\nu(\text{N-N})$	SCN bands $\nu(\text{CN})$ , $\nu(\text{CS})$
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> · abh	3440b, 3282b	1639s	1604s	1529s	1388s	995w	2152s, 2100s, 716 m
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> · ainh	3390w, 3258b, 3180b	1642s	1610s	1541s	1389 m	1002w	2145s, 2080 m, 752 m
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> · ash	3400b, 3280b	1638s	1612s	1529s	1392 m	10015w	2141s, 2092w, 758s
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> · aah	3358b, 3190b	1632 m	1614s	1548s	1385s	1006w	2155, 2106w, 754s
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> · phabh	3540b, 3402b, 3288s	1629 m	1604s	1558s	1385s	1000w	2141s, 2098w, 714 m
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> · phainh	3550w, 3290b	1634 m	1600s	1545 m	1390 m	992w	2150s, 2090w, 748 m
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> · phash	3392w, 3273b	1641 m	1605s	1516s	1383s	1002w	2143s, 2085w, 758s
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> · phaah	3460b, 3356b, 3140b	1630s	1618s	1528 m	1386 m	1005w	2158s, 2088w, 745s

**Table 5.** Thermal analyses of  $\text{Co}(\text{Ag}(\text{SCN})_2)_2 \cdot \text{ash}$ 

Sl. No.	Temp. ( $^{\circ}\text{C}$ )	Proposed decomposition pattern	% Loss of weight		Energy change	Remarks
			obs.	calc.		
1	0–180	$\text{Co}[\text{Ag}(\text{SCN})_2]_2 \cdot \text{ash}$	0.00	0.00	Endothermic	No decomposition
2	180–200	$\text{Co}(\text{SCN})_2 \cdot \text{ash} + \text{Ag}_2\text{S} + \text{S}$	6.90	6.83	Endothermic	Decomposition of $\text{AgSCN}$
3	200–260	$\text{Co}(\text{SCN})_2 \cdot \text{ash} + \text{Ag}_2\text{S}$	11.00	11.04	Endothermic	Removal of S
4	260–335	$\text{Co}(\text{SCN})_2 \cdot [(\text{OH})\text{C}_6\text{H}_4\text{CONHN}=\text{CCH}_3] + \text{Ag}_2\text{S}$	21.00	21.16	Exothermic	Decomposition of $\text{C}_6\text{H}_5$ from ligand
5	335–550	$\text{Co}(\text{SCN})_2 + \text{Ag}_2\text{S}$	44.60	44.42	Exothermic	Decomposition of whole ligand

**Table 6.** Observed and calculated Q and hkl values

Powder pattern	$2\theta$	d	Relative intensity	Q obs.	Q calc.	hkl
$\text{Co}[\text{Ag}(\text{SCN})_2]_2 \cdot \text{aah}$						
1	12.35	7.1670	73.76	0.0195	0.0195	100
2	13.20	6.7073	64.63	0.0222	0.0222	001
3	17.55	5.0534	56.36	0.0391	0.0390	110
4	19.05	4.6588	100.00	0.0461	0.0417	101
5	22.05	4.0312	60.63	0.0615	0.0612	111
6	24.95	3.5688	81.77	0.0785	0.0780	200
7	26.05	3.4206	60.59	0.0855	0.0888	002
8	27.65	3.2262	48.69	0.0961	0.0975	210
9	29.05	3.0738	77.42	0.1058	0.1002	201
10	29.55	3.0229	54.51	0.1094	0.1083	102
11	30.40	2.9403	56.61	0.1157	0.1197	211
12	31.95	2.8011	62.49	0.1274	0.1275	112
13	35.50	2.5287	48.95	0.1564	0.1560	220
14	36.95	2.4328	44.63	0.1690	0.1668	202
15	38.50	2.3383	41.83	0.1829	0.1863	212
16	39.30	2.2925	36.63	0.1903	0.1950	310
17	40.25	2.2406	51.56	0.1992	0.1977	301
18	41.60	2.1710	42.12	0.2122	0.2172	311
19	44.55	2.0338	41.71	0.2417	0.2448	222
$\text{Co}[\text{Ag}(\text{SCN})_2]_2 \cdot \text{phabh}$						
1	16.58	5.3466	78.93	0.0350	0.0350	100
2	18.08	4.9075	72.77	0.0415	0.0415	010
3	18.92	4.6895	91.33	0.0455	0.0455	001
4	25.16	3.5402	66.32	0.0798	0.0765	110
5	25.65	3.4725	66.25	0.0829	0.0805	101
6	26.40	3.3758	63.90	0.0877	0.0870	011
7	31.09	2.8768	65.29	0.1208	0.1220	111
8	33.93	2.6421	53.32	0.1433	0.1400	200
9	36.47	2.4635	46.26	0.1648	0.1660	020
10	38.27	2.3520	36.68	0.1808	0.1815	210
11	40.16	2.2453	49.16	0.1984	0.2010	120
12	41.41	2.1806	43.48	0.2103	0.2115	021
13	42.85	2.1103	36.76	0.2245	0.2235	012
14	43.90	2.0624	33.47	0.2351	0.2270	211
15	45.60	1.9896	31.36	0.2526	0.2465	121
16	46.24	1.9632	31.43	0.2595	0.2585	112
17	49.78	1.8316	41.78	0.2981	0.3060	220
18	51.18	1.7849	35.26	0.3139	0.3150	300
19	52.62	1.7392	36.57	0.3306	0.3220	202

### 3.1 Magnetic Moments and Electronic Spectra

Cobalt(II) tetrahedral complexes generally show magnetic moments between 4.0–4.6 while the octahedral complexes show between 4.7–5.2 because of the orbital contribution (7). The  $\mu_{\text{eff}}$  values observed between 4.69–4.87 B.M., for the present complexes are fairly close to those reported for three unpaired electrons in an octahedral environment. Moreover, the  $\mu_{\text{eff}}$  values (3.98 B.M.) of Lewis acid  $\text{Co}[\text{Ag}(\text{SCN})_2]_2$  suggests a tetrahedral environment around cobalt(II).

Cobalt(II) complexes give rise to three absorption bands in the visible region under the influence of the octahedral field by the excitation of the electron from the ground state  ${}^4\text{T}_{1g}$  (F) to the excited states  ${}^4\text{T}_{2g}$ ,  ${}^4\text{A}_{2g}$  (F) and  ${}^4\text{T}_{1g}$  (P) (9). In the case of  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ , three transitions are observed at 8130, 17540 and 21980  $\text{cm}^{-1}$ , respectively (10). In the present case, only two bands are observed between 9190–9340  $\text{cm}^{-1}$  ( $\nu_1$ ) and 19880–20650  $\text{cm}^{-1}$  ( $\nu_3$ ) indicating octahedral geometry for the complexes. The  $\nu_2$  transition was not observed due to very weak intensity (9). The various ligand field parameter (10 Dq, B,  $\beta$ ,  $\beta^0$ , and LFSE) were also calculated and indicate a considerable covalent character of the M-L bonds (Table 3). A single band observed at 16025  $\text{cm}^{-1}$  in the electronic spectra of Lewis acid is assigned as  ${}^4\text{A}_2$  (F)  $\rightarrow$   ${}^4\text{T}_{1g}$  (P) transition and suggest a tetrahedral geometry for the complex.

### 3.2 IR Spectra

In all the complexes, the  $\nu(\text{N-H})$  bands are normally broad and occur nearly at the same or slightly higher frequencies as in the parent ligands between 3100–3500  $\text{cm}^{-1}$  (Table 4). This signifies that the  $>\text{NH}$  group does not take part in bonding. The amide I band,  $\nu(\text{C}=\text{O})$  in the ligands abh, ainh, ash, aah, phabh, phainh, phash and phaah appears at 1650, 1665, 1655, 1648, 1640, 1653, 1660 and 1645  $\text{cm}^{-1}$ , respectively. In the complexes  $\nu(\text{C}=\text{O})$  is shifted to lower frequency by 11–23  $\text{cm}^{-1}$  indicating coordination of the  $>\text{C}=\text{O}$  group to the metal (11). The amide II bands appear to have shifted considerably to a lower frequency by 11–27  $\text{cm}^{-1}$  upon complex formation compared to the ligand bands, a shift to a higher frequency (6–16  $\text{cm}^{-1}$ ) is observed in amide III bands in all the complexes supporting coordination through the  $>\text{C}=\text{O}$  group.

The  $\nu(\text{C}=\text{N})$  band observed in the 1610–1633  $\text{cm}^{-1}$  region in the spectra of the ligands shifted considerably to lower frequency by 6–28  $\text{cm}^{-1}$  in the metal complexes suggesting coordination through the azomethine group (12). The shift to higher wave number in  $\nu(\text{N-N})$  from the free ligands to the complexes by 13–32  $\text{cm}^{-1}$ , suggests involvement of only one nitrogen of the hydrazone ( $-\text{NHN}=\text{C}<$ ) group (13). In the thiocyanate complexes,  $\nu(\text{CN})$ ,  $\nu(\text{CS})$  and  $\delta\text{NCS}$  are diagnostic of the nature of SCN bonding (5). In the present complexes, two split  $\nu(\text{CN})$  bands occur between 2141–2158  $\text{cm}^{-1}$  and 2085–2106  $\text{cm}^{-1}$  and a  $\nu(\text{CS})$  band in the region 714–758  $\text{cm}^{-1}$ . The position of these bands indicate the presence of bidentate bridging SCN groups (5).

### 3.3 Thermal Analysis (TGA and DTA)

Thermal analysis of the complex,  $\text{Co}[\text{Ag}(\text{SCN})_2]_2 \cdot \text{ash}$  shows no weight loss up to 180°C. Between 180–200°C, the  $\text{AgSCN}$  part of the complex decomposes into  $\text{Ag}_2\text{S}$  and S by an endothermic process. The weight of residue at 260°C corresponds to  $\text{Co}(\text{NCS})_2 \cdot \text{ash} + \text{Ag}_2\text{S}$ . The bonded ligand molecule start decomposition above 260°C through various decomposition stages (Table 5). The DTA curves show significant heat liberation as a result of ligand decomposition (14) between 260–550°C. The final residue obtained at 550°C corresponds to  $\text{Co}(\text{NCS})_2 + \text{Ag}_2\text{S}$ .

### 3.4 X-ray Diffraction Studies

The X-ray powder diffraction method provides a way of investigating, within limits, the crystallography of a crystal in powder form. The diffraction patterns for the complexes were recorded and indexed by Ito's method (15) (Table 6). The following lattice constants were obtained.

$\text{Co}[\text{Ag}(\text{SCN})_2]_2 \cdot \text{aah}$   $a = 7.17$ ,  $b = 7.17$ , and  $c = 6.71^\circ\text{A}$   
 $\text{Co}[\text{Ag}(\text{SCN})_2]_2 \cdot \text{phash}$   $a = 5.35$ ,  $b = 4.91$ , and  $c = 4.69^\circ\text{A}$

The above values indicate a tetragonal crystal lattice for the former and an orthorhombic crystal lattice for the latter complex.

### 3.5 Bio-Activity

#### 3.5.1 Antifungal Activity

The ligands, as well as their complexes screened individually exhibit varying degree of inhibitory effect on the growth of *Rizoctonia sp.*, and *Stemphylium sp.* at 0.5, 1.0 and 1.5 mg/mL concentrations. The ligands are less effective than their complexes (16). DMSO control has also shown a little activity as compare to the metal complexes and ligands. The antifungal experimental results of the compounds were compared against DMSO as the control and are expressed as percentage inhibition versus control. It is evident from the experimental data (Table 7A) that the antifungal activity is more pronounced against *Rizoctonia sp.* than *Stemphylium sp.* Among the ligands, phainh shows the highest activity (95%) against both the fungi.  $\text{Co}[\text{Ag}(\text{SCN})_2]_2 \cdot \text{aah}$  shows 99% activity against *Rizoctonia sp.* at the concentration of 1.5 mg/mL whereas,  $\text{Co}[\text{Ag}(\text{SCN})_2]_2 \cdot \text{phainh}$  shows 98% activity against *Stemphylium sp.* The effect is susceptible to the concentration of the compound used for inhibition and generally increases at higher concentration.

The complexes generally vary in their antifungal activity in the following order of ligands.

For *Rizoctonia sp.*

aah > phainh = abh > phash > ainh = ash > phabh > phaah

For *Stemphylium sp.*

phainh > abh = aah > phash = phaah > ainh > phabh > ash

**Table 7A.** Antifungal activity of ligands and their complexes

Compounds	% Inhibition of spore germination (mg/ml)					
	<i>Rizoctonia sp.</i> (mg/mL)			<i>Stemphylium sp.</i> (mg/mL)		
	0.5	1.0	1.5	0.5	1.0	1.5
abh	46	64	80	78	80	89
ainh	60	94	95	67	73	85
ash	62	69	79	58	64	79
aah	39	77	84	82	84	86
phabh	44	45	78	61	62	64
phainh	76	92	95	71	89	95
phash	67	71	82	75	83	84
phaah	33	61	65	57	75	85
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> · abh	63	76	98	80	89	93
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> · ainh	78	95	96	68	78	88
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> · ash	80	95	96	62	65	80
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> · aah	75	88	99	84	88	92
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> · phabh	61	83	92	64	65	87
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> · phainh	87	95	98	76	91	98
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> · phash	70	86	97	78	87	89
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> · phaah	51	72	82	70	79	89

The toxicity of the complexes can be related to the strength of the metal–ligand bond, besides other factors such as size of the cation (17), receptor sites, diffusion and a combined effect of the metal and the ligand for inactivation of the biomolecules (18).

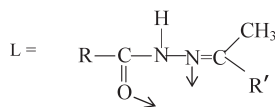
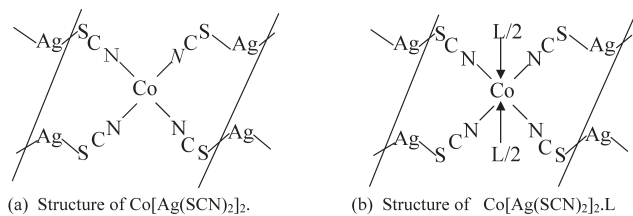
### 3.5.2 Antibacterial Activity

The antibacterial activity data (Table 7B) of the ligands and their complexes show a moderate activity against *Clostridium sp.* (gram +ve) and *Pseudomonas sp.* (gram –ve) at the concentration of 1.0 and 2.0 mg/mL. The metal complexes show

**Table 7B.** Antibacterial activity of ligands and their complexes

Compounds	Diameter of inhibition zone (in mm)				Diameter of inhibition zone (in mm)			
			% Activity index				% Activity index	
	<i>Clostridium sp.</i> (mg/mL)				<i>Pseudomonas sp.</i> (mg/mL)			
	1.0	2.0	1.0	2.0	1.0	2.0	1.0	2.0
abh	2	4	14.3	25.0	2	3	11.1	16.7
ainh	4	6	28.6	37.5	3	6	16.7	33.3
ash	2	3	14.3	18.8	2	4	11.1	22.2
aah	4	5	28.6	31.2	5	6	27.8	33.3
phabh	3	4	21.4	25.0	2	2	11.1	11.1
phainh	2	4	14.3	25.0	2	2	11.1	11.1
phash	2	2	14.3	12.5	2	3	11.1	16.7
phaah	3	3	21.4	18.8	3	4	16.7	22.2
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> · abh	9	11	64.3	68.7	9	12	50.0	66.7
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> · ainh	8	9	57.1	56.2	7	8	38.9	44.4
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> · ash	6	7	43.8	43.8	10	12	55.5	66.7
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> · aah	7	8	50.0	50.0	8	9	44.4	50.0
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> · phabh	5	7	35.7	43.7	7	8	38.9	44.4
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> · phainh	7	9	50.0	56.2	6	9	33.3	50.0
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> · phash	9	12	64.3	75.0	6	8	33.3	44.4
Co[Ag(SCN) <sub>2</sub> ] <sub>2</sub> · phaah	7	9	50.0	56.2	7	8	38.9	44.4
Ampicillin (standard)	14	16	100.0	100.0	18	18	100.0	100.0





Where,

R	=	$\text{C}_6\text{H}_5$ for abh and phabh
	=	$\text{NC}_5\text{H}_4$ for ainh and phainh
	=	$\text{HOC}_6\text{H}_4$ for ash and phash
	=	$\text{H}_2\text{NC}_6\text{H}_4$ for aah and phaah
R'	=	$\text{C}_6\text{H}_5$ for abh, ainh, ash and aah
	=	$\text{HOC}_6\text{H}_4$ for phabh, phainh, phash and phaah

**Fig. 1.** Representative structures of the complexes.

higher antibacterial activity than the ligands and DMSO control. The DMSO solvent showed very little and insignificant activity. The antibacterial activity increases with increasing concentration of the complexes (19). Ligand ainh is the most active ligand among all the ligands. The activity of the complexes has been compared with the activity of a common standard antibiotic Ampicillin and % Activity Index for the complexes has been calculated. The % Activity Index data show the highest activity (75%) for  $\text{Co}[\text{Ag}(\text{SCN})_2]_2 \cdot \text{phash}$  against *Clostridium sp.* at the concentration of 2 mg/mL. The complexes are more effective against *Clostridium sp.* than *Pseudomonas sp.* The highest activity (66.70%) has been observed against *Pseudomonas sp.* by  $\text{Co}[\text{Ag}(\text{SCN})_2]_2 \cdot \text{abh}$  and  $\text{Co}[\text{Ag}(\text{SCN})_2]_2 \cdot \text{ash}$  complexes.

#### 4 Conclusions

On the basis of above studies, a thiocyanate bridged polymeric structure for the Lewis acid  $\text{Co}[\text{Ag}(\text{SCN})_2]_2$  is suggested. The Lewis acid has four-coordinate tetrahedral geometry around cobalt metal ion. The acylhydrazone ligands are coordinated to the cobalt(II) metal ion of Lewis acid as bidentate ligands to increase its coordination number from four to six and the resulting complexes form octahedral structure (Fig. 1). The metal complexes are fairly stable at room temperature and show multi-step decomposition patterns at higher temperatures. The newly synthesized complexes of acylhydrazones show appreciable

and better antifungal and antibacterial activity than the parent ligands.

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