

Synthesis, Structural Studies, and Antimicrobial Activity of Polymeric Copper(II) Tetrathiocyanato Diargentate(I) Complexes with Some Acylhydrazones

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ABSTRACT: Copper(II) complexes of the type $\text{Cu}[\text{Ag}(\text{SCN})_2]_2\cdot\text{L}$ (where L is acetophenone benzoyl hydrazone, acetophenone isonicotinoyl hydrazone, acetophenone salicyloyl hydrazone, acetophenone anthraniloyl hydrazone, *p*-hydroxyl acetophenone benzoylhydrazone, *p*-hydroxyl acetophenone isonicotinoyl hydrazone, *p*-hydroxyl acetophenone salicyloyl hydrazone, or *p*-hydroxyl acetophenone anthraniloyl hydrazone) were synthesized and characterized. All the complexes were polymeric and insoluble in common organic solvent and were nonelectrolytes. The ligands were coordinated through $>\text{C}=\text{O}$ and $>\text{C}=\text{N}-$ groups. All the SCN groups present in the complexes acted as bridges between two metal centers, resulting in a polymeric structure of the Lewis acid $\text{Cu}[\text{Ag}(\text{SCN})_2]_2$ as well as its complexes. Electronic and electron spin resonance spectra suggested a square planar geometry for the

Lewis acid and an elongated tetragonally distorted octahedral geometry for all the complexes. The powder X-ray diffraction parameters for acetophenone salicyloyl hydrazone and *p*-hydroxyl acetophenone anthraniloyl hydrazone complexes corresponded to orthorhombic and tetragonal crystal lattices, respectively. The complexes showed a fair degree of antifungal activity against *Rizoctonia* sp., *Aspergillus* sp., and *Stemphylium* sp. and moderate antibacterial activity against *Clostridium* sp. (Gram-positive) and *Pseudomonas* sp. (Gram-negative). The complexes were more active than the parent ligands. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1336–1343, 2008

Key words: biological applications of polymers; ESR/EPR; infrared spectroscopy; metal-polymer complexes; UV-vis spectroscopy

INTRODUCTION

Heterobimetallic complexes, particularly thiocyanate complexes, have been used in several fields of physical science, life science, and technology. Despite its stability, $\text{MM}'_2(\text{SCN})_4$ has residual Lewis acidity and coordinates further with Lewis bases to give a variety of monomeric-bridged, polymeric-bridged, or cationic-anionic complexes. A thiocyanate group bridges the two metal centers according to the hard and soft acids and bases (HSAB) principle.¹ Pearson's HSAB principle states that "hard [Lewis] acids prefer to bind to hard [Lewis] bases and soft [Lewis] acids prefer to bind to soft [Lewis] bases". The combination of an electron-deficient or hard metal ion (d^1-d^9) and an electron-rich or soft metal ion (d^{10}) in a single complex leads to the possibility of Lewis acid activation of substrate molecules bound to the electron-rich metal center. This type of cooperative heterobimetallic activation makes the complex useful in catalysis.^{2,3} Many heterobimetallic complexes

have been found to be biologically active against several fungi, bacteria,⁴ and insects.⁵ Interest in copper(II) complexes has grown recently^{6,7} because of their clinical usefulness.⁸

Because copper(II) is easily reducible to copper(I), its heterobimetallic complexes, particularly with acylhydrazone ligands, are still rarely reported. We have synthesized a number of $\text{Cu}[\text{Ag}(\text{SCN})_2]_2\cdot\text{L}$ complexes with a variety of acylhydrazone ligands, and we discuss them here.

EXPERIMENTAL

Materials

All chemicals were BDH or an equivalent grade. Isonicotinic acid hydrazide ($\text{NC}_5\text{H}_4\text{CONHNH}_2$) was obtained from S.D. Fine Chemicals (Mumbai, India) and used after recrystallization in ethanol. Benzoic acid hydrazide ($\text{C}_6\text{H}_5\text{CONHNH}_2$), salicylic acid hydrazide ($\text{HOC}_6\text{H}_4\text{CONHNH}_2$), and anthranilic acid hydrazide ($\text{H}_2\text{NC}_6\text{H}_4\text{CONHNH}_2$) were synthesized by reported methods⁹ through the reaction of hydrazine hydrate ($\text{NH}_2\text{NH}_2\cdot\text{H}_2\text{O}$) with the corresponding esters in a 1 : 1 molar ratio. The obtained hydrazides

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TABLE I
Analytical Data for the Ligands

Ligand (color)	Empirical formula (formula weight)	Melting point (°C)	Found (calcd)			Yield (%)
			C (%)	H (%)	N (%)	
abh (white)	C ₁₅ H ₁₄ N ₂ O (238)	145	75.39 (75.63)	5.92 (5.88)	11.66 (11.76)	75
ainh (white)	C ₁₄ H ₁₃ N ₃ O (239)	162	70.10 (70.29)	5.50 (5.44)	17.42 (17.57)	70
ash (white)	C ₁₅ H ₁₄ N ₂ O ₂ (254)	205	70.62 (70.86)	5.61 (5.51)	10.85 (11.02)	80
aah (cream yellow)	C ₁₅ H ₁₅ N ₃ O (253)	175	70.92 (71.15)	5.81 (5.93)	16.51 (16.60)	70
phabh (light yellow)	C ₁₅ H ₁₄ N ₂ O ₂ (254)	210	70.60 (70.86)	5.67 (5.51)	10.90 (11.02)	75
phainh (light yellow)	C ₁₄ H ₁₃ N ₃ O ₂ (255)	260	65.62 (65.88)	5.18 (5.10)	16.38 (16.47)	70
phash (light yellow)	C ₁₅ H ₁₄ N ₂ O ₃ (270)	240	66.85 (66.67)	5.26 (5.18)	10.32 (10.37)	78
phaah (light yellow)	C ₁₅ H ₁₅ N ₃ O ₂ (269)	225	66.70 (66.91)	5.48 (5.57)	15.52 (15.61)	70

were recrystallized from the appropriate solvent, that is, benzene or ethanol.

Preparation of the ligands

Acetophenone acylhydrazones

Acetophenone benzoyl hydrazone [abh or C₆H₅-C(CH₃)=NNHCOC₆H₅], acetophenone isonicotinoyl hydrazone [ainh or C₆H₅C(CH₃)=NNHCOC₅H₄N], acetophenone salicyloyl hydrazone [ash or C₆H₅-C(CH₃)=NNHCOC₆H₄(OH)], and acetophenone anthraniloyl hydrazone [aah or C₆H₅C(CH₃)=NNHCOC₆H₄(NH₂)] were synthesized through the reaction of their corresponding acid hydrazides with acetophenone in a 1 : 1 molar ratio in 50 mL of ethanol in a round-bottom flask. The reaction mixture was refluxed at 60°C for 2–4 h and then allowed to cool in a beaker, and the product was filtered by suction on a Buckner funnel. The abh and aah ligands were recrystallized from hot benzene, whereas ash and ainh were recrystallized from hot ethanol and dried in a desiccator over anhydrous CaCl₂.

p-Hydroxyl acetophenone acylhydrazones

p-Hydroxyl acetophenone benzoylhydrazone [phabh or C₆H₄(OH)C(CH₃)=NNHCOC₆H₅], *p*-hydroxyl acetophenone isonicotinoyl hydrazone [phainh or C₆H₄(OH)C(CH₃)=NNHCOC₅H₄N], *p*-hydroxyl acetophenone salicyloyl hydrazone [phash or C₆H₄(OH)C(CH₃)=NNHCOC₆H₄(OH)], and *p*-hydroxyl acetophenone anthraniloyl hydrazone [phaah or C₆H₄(OH)C(CH₃)=NNHCOC₆H₄(NH₂)] were synthesized through the reaction of their corresponding acid hydrazide with *p*-hydroxyl acetophenone in a 1 : 1 molar ratio in 50 mL of ethanol. The reactants were refluxed for 4–6 h in a round-bottom flask at 60°C. The crude product was filtered after cooling, recrystallized from hot ethanol, and dried in a desiccator. The ligands were characterized by their melt-

ing points, CHN analyses, and infrared (IR) spectra (Table I).

Preparation of metal thiocyanates

AgSCN was prepared through the dissolution of AgNO₃ (10 mmol, 1.70 g) in 50 mL of water. The solution was treated with NH₄SCN (10 mmol, 0.76 g) dissolved in 25 mL of water with constant stirring at room temperature. AgSCN thus formed as a white precipitate, was filtered, washed with water, ethanol, and finally diethyl ether, and dried in a desiccator.

Cu(NCS)₂ was prepared through the mixing of aqueous solutions of CuSO₄·5H₂O (10 mmol, 2.50 g) with an aqueous solution of NH₄SCN (20 mmol, 1.52 g) and stirring for approximately 15 min with a magnetic stirrer at room temperature (25°C). Black Cu(NCS)₂ was filtered immediately and dried in a desiccator at room temperature.¹⁰

Synthesis of Cu[Ag(SCN)₂]₂

The Lewis acid Cu[Ag(SCN)₂]₂ was prepared through the reaction of Cu(NCS)₂ (10 mmol, 1.80 g) with AgSCN (20 mmol, 3.30 g) in a round-bottom flask containing 50 mL of dioxane. The mixture was stirred with a magnetic stirrer at room temperature for approximately 48 h until there was a visible change in color from black-white to violet. The compound was filtered in a glass crucible, washed with dioxane, and dried in a desiccator at room temperature.

Synthesis of Cu[Ag(SCN)₂]₂·L complexes

The Lewis acid Cu[Ag(SCN)₂]₂ (5 mmol, 2.55 g) was suspended in 50 mL of dioxane. It was reacted with a 5-mmol solution of each of the ligands, that is, 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), dissolved in 100 mL of dioxane in a round-bottom flask. The mixture was well stirred with a magnetic stirrer for 24–48 h until the color

change was perceptible. The product was filtered, washed thoroughly with dioxane, and dried in a desiccator.

Analyses and physicochemical studies

For the determination of the silver content, the weighed amount of the complexes was heated (80°C) with an excess of dilute HCl (0.01N). The solution was cooled to deposit AgSCN,¹⁰ which was filtered in a crucible, washed first with hot water and then with ethanol, and dried at 110°C. For the determination of the copper contents, the filtrate was evaporated to dryness with concentrated HNO₃ followed by concentrated H₂SO₄ to destroy their organic content. Copper(II) was first reduced to copper(I) and then estimated gravimetrically as copper(I) thiocyanate. Carbon, hydrogen, and nitrogen contents were determined with an Elementar's Vario EL III microanalyzer (Elementar Analysensysteme GmbH, Hanau, Germany).

The molar conductance of 10⁻³ M solutions of the complexes in dimethyl sulfoxide (DMSO) was measured at room temperature on a Systronic model 306 conductivity meter (Systronic, New Delhi, India). Room-temperature magnetic susceptibilities were determined on a Faraday balance with Hg[Co(SCN)₄] as a standard. The values of the effective magnetic moment (μ_{eff}) were calculated from the experimentally observed molar susceptibilities after the incorporation of diamagnetic corrections.¹¹ IR spectra of the ligands and their complexes were recorded in a KBr medium on a Vector-22 spectrophotometer (Bruker Inc., Ettlingen, Germany). Electronic spectra were recorded in DMSO solutions on a PerkinElmer Lambda-2 spectrophotometer between 4000 and 600 cm⁻¹. The X-band electron spin resonance (ESR) spectra of the complexes were recorded on an EMX 1444 EPR spectrometer at room temperature (298 K) in the solid state with a 100-kHz field modulation. The magnetic field calibration was checked with diphenyl picryl hydrazyl (DPPH) used as a *g* marker (*g* = 2.0023). Powder X-ray diffraction patterns of a few complexes were recorded on an Iso Debye Flex 2002 apparatus using Cu K α radiation. The analytical and physicochemical data are given in Tables I–IV.

Antimicrobial activity

Antifungal activity

The ligands, Lewis acid Cu[Ag(SCN)₂]₂, and their complexes were screened for antifungal activity against various fungi: *Rizoctonia* sp., *Aspergillus* sp., and *Stemphylium* sp. These species were isolated from the infected organs of the host plants on a potato dextrose agar medium (250 g of potato + 20

g of dextrose + 20 g of agar). The cultures of the fungi were purified by the single spore isolation technique.

Solutions with different concentrations (0.5, 1.0, and 1.5 mg/mL) of each compound in DMSO were prepared for testing against spore germination. Drops of the solutions of each concentration were kept separately on glass slides. The conidia, fungal reproducing spores (approximately 200) lifted with the help of an inoculating needle, were mixed in every drop of each compound separately. Each treatment was replicated three times, 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 the germination percentage was finally calculated.

Antibacterial activity

The antibacterial activity of the Lewis acid, ligands, and their complexes was studied against *Clostridium* sp. (Gram-positive) and *Pseudomonas* sp. (Gram-negative) bacteria. Each of the compounds was dissolved in DMSO, and solutions with concentrations of 2 and 1 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 Petri dishes containing a nutrient agar medium (20 g of agar + 3 g of beef extract + 5 g of peptone) 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 nine times.

The antibacterial activity of a common standard antibiotic (ampicillin) was also recorded with the same procedure at the same concentrations and with the same solvent. The activity index (%) for the complex was calculated as follows:

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

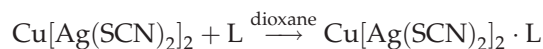
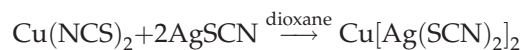
RESULTS AND DISCUSSION

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

TABLE II
Analytical Data for the Complexes

Complex (color)	Empirical formula (formula weight)	Decomposition temperature (°C)	Found (calcd)					Yield (%)	Λ_M ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) in DMSO
			Ag (%)	Cu (%)	C (%)	H (%)	N (%)		
Cu[Ag(SCN) ₂] ₂ (violet)	C ₄ N ₄ S ₄ CuAg ₂ (511.5)	270	42.00 (42.23)	12.25 (12.41)	9.32 (9.38)	—	10.86 (10.95)	91	—
Cu[Ag(SCN) ₂] ₂ :abh (light yellow)	C ₁₉ H ₁₄ N ₆ S ₄ OCuAg ₂ (749.5)	240	28.60 (28.82)	8.50 (8.47)	30.29 (30.42)	1.99 (1.88)	11.16 (11.21)	70	10.6
Cu[Ag(SCN) ₂] ₂ :ainh (light green)	C ₁₈ H ₁₃ N ₇ S ₄ OCuAg ₂ (750.5)	210	28.60 (28.78)	8.50 (8.46)	28.58 (28.78)	1.77 (1.73)	13.10 (13.06)	70	14.2
Cu[Ag(SCN) ₂] ₂ :ash (blue)	C ₁₉ H ₁₄ N ₆ S ₄ O ₂ CuAg ₂ (765.5)	236	28.10 (28.21)	8.32 (8.29)	29.62 (29.78)	1.88 (1.83)	10.79 (10.97)	85	12.4
Cu[Ag(SCN) ₂] ₂ :aah (greenish yellow)	C ₁₉ H ₁₅ N ₇ S ₄ OCuAg ₂ (764.5)	232	28.20 (28.25)	8.30 (8.30)	29.67 (29.82)	1.90 (1.96)	12.75 (12.82)	75	8.9
Cu[Ag(SCN) ₂] ₂ :phabh (greenish yellow)	C ₁₉ H ₁₄ N ₆ S ₄ O ₂ CuAg ₂ (765.5)	228	28.00 (28.21)	8.20 (8.29)	29.62 (29.78)	1.76 (1.83)	10.88 (10.97)	70	11.5
Cu[Ag(SCN) ₂] ₂ :phainh (light green)	C ₁₈ H ₁₃ N ₇ S ₄ O ₂ CuAg ₂ (766.5)	215	28.00 (28.18)	8.20 (8.28)	28.31 (28.18)	1.72 (1.69)	12.81 (12.78)	70	10.2
Cu[Ag(SCN) ₂] ₂ :phaash (greenish yellow)	C ₁₉ H ₁₄ N ₆ S ₄ O ₃ CuAg ₂ (781.5)	245	27.50 (27.64)	8.10 (8.12)	28.96 (29.17)	1.71 (1.79)	10.65 (10.75)	80	13.7
Cu[Ag(SCN) ₂] ₂ :phaah (greenish yellow)	C ₁₉ H ₁₅ N ₇ S ₄ O ₂ CuAg ₂ (780.5)	225	27.50 (27.67)	8.10 (8.13)	29.14 (29.21)	2.01 (1.92)	12.43 (12.55)	75	12.8

Λ_M , conductivity value of 0.001 Molar solution.



The acylhydrazone complexes are light yellow, light green, and blue in color in contrast to the parent Lewis acid, which is violet. They are generally insoluble in water and common organic solvents such as benzene, carbon tetrachloride, chloroform, ethylene chloride, and diethyl ether. However, they are fairly soluble in dimethylformamide and DMSO. The free Lewis acid decomposes at 270°C, whereas the complexes decompose in the range of 210–242°C. The high decomposition point, together with the low solubilities, suggests that these complexes are polymeric. The low molar conductance values of 10^{-3} M solutions of the complexes in DMSO at room temperature suggest that all the complexes are nonelectrolytes.¹²

Magnetic moments and electronic spectra

Where spin–spin coupling between unpaired electrons belonging to different copper ions is absent, μ_{eff} varies between 1.75 and 2.20 BM, depending on the geometries of the complexes due to differences in the orbital contribution.¹³ The Lewis acid Cu[Ag(SCN)₂]₂ shows a normal μ_{eff} value of 2.0 BM, which corresponds to one unpaired electron, suggesting a square planar geometry.⁹ The μ_{eff} values for the complexes in this study have been observed between 1.60 and 1.78 BM, indicating a pseudo-octahedral geometry for all the complexes.¹⁴ The slightly low magnetic moment values below 1.73 BM observed in a few complexes may be due to minor spin–spin interactions between copper ions^{11,13} present in the polymeric structure.

Electronic absorption spectra arise from the electronic transitions within a molecule or ion from a lower electronic energy level to a higher electronic energy level. The transition-metal ions generally show a number of *d–d* transition bands depending on their electronic configuration from *d*¹ to *d*⁹ in ultraviolet–visible (UV–vis) regions. The free Lewis acid Cu[Ag(SCN)₂]₂ shows a broad band, centered at 16,600 cm⁻¹, indicating a square planar geometry for the complex, which is similar to [Cu(NH₃)₄]²⁺ (16,660 cm⁻¹).¹⁵ The other complexes in this study show two bands in the ranges of 12,500–15,380 and 9750–11,100 cm⁻¹, which may be assigned to ²B_{1g} → ²A_{1g} and → ²B_{2g}, suggesting a tetragonally distorted octahedral geometry¹⁵ for the complexes.

ESR spectra

ESR spectra of aah, ainh, phainh, and phaah complexes in the solid state exhibit axial signals with

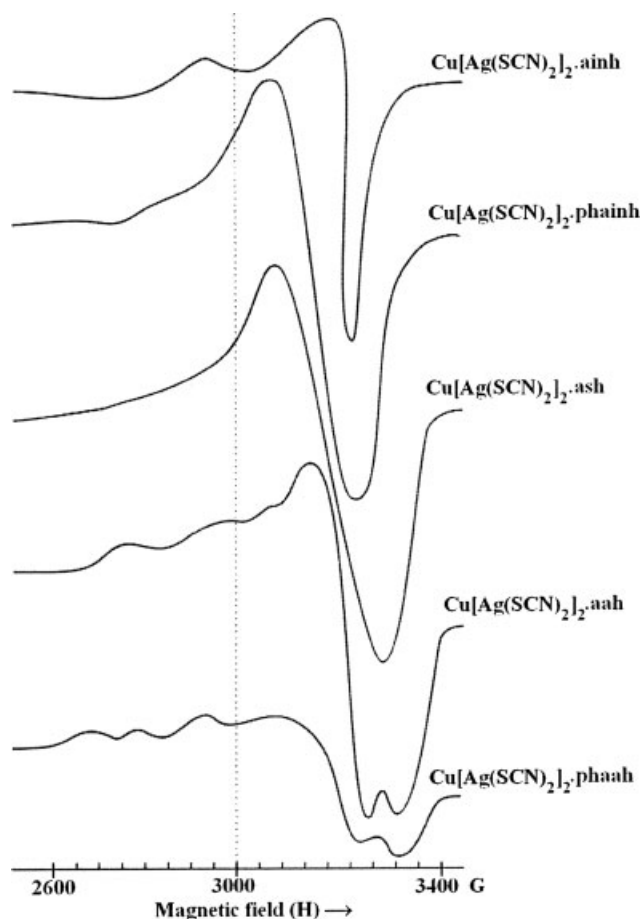


Figure 1 ESR spectra of the complexes in the solid state at 298 K.

separate g_{\parallel} and g_{\perp} values at 298 K (Fig. 1); where g_{\parallel} is g_z (g value along z -axes), g_{\perp} is g value ($g_x = g_y$) perpendicular to z -axes in tetragonal symmetry. The axial signals were analyzed with the procedure reported by Hathaway and Billing.¹⁶ The g_{\parallel} and g_{\perp} values are >2.04 (Table III). This indicates that the copper(II) ion is in axial symmetry, with all the principle axes aligned parallel. This would be consistent with an elongated tetragonally distorted octahedral geometry for the complexes.¹⁶ The trend $g_{\parallel} > g_{\perp} > g_e$ (where g_e is g value for free electron = 2.0023) suggests the presence of an unpaired electron in the $d_{x^2-y^2}$ orbital of the copper(II) ion.^{17,18} The G factor

[defined as $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$] is in the range of 5.2674–7.3433, and this suggests that the local tetragonal axes are only slightly misaligned and the exchange interactions between copper(II) centers in the solid state are negligible.¹⁶ The g_{av} and A_{av} values were calculated with the equations $g_{av} = (g_{\parallel} + 2g_{\perp})/3$ and $A_{av} = (A_{\parallel} + 2A_{\perp})/3$; where g_{av} is $g_{average}$ (average value of all g values), A_{av} is $A_{average}$ (average value of all A values), A_{\parallel} is A_z (Hyperfine Coupling Constant along z -axes); A_{\perp} is A value ($A_x = A_y$) perpendicular to z -axes in tetragonal symmetry. The spectra of aah and phaah complexes show a well-defined hyperfine structure of four lines due to coupling of the electron with the nuclear spin ($I = 3/2$) of the copper atom (Fig. 1).¹⁹ The high-field region of the spectra of the same complexes is partially resolved into its g_x and g_y (where g_x is g value along x -axes and g_y is g value along y -axes) components, where $g_{\perp} = 1/2(g_x + g_y)$ in the g_{\perp} region. This may result from the nonequivalence of the Cu–O and Cu–N bonds formed in the xy plane.²⁰ The ash complex exhibits isotropic spectra with intense broad signals with no hyperfine structure.¹⁴ This may be due to dipolar exchange and unresolved hyperfine interactions. The g_{iso} [where g_{iso} is $g_{isotropic}$ (when g value is independent of the orientation)] value of 2.0836 suggests a geometry involving grossly misaligned axes.¹⁶

IR spectra

The bonding of the ligands to copper(II) has been judged by a careful comparison of the IR spectra of the complexes with those of the free ligands. A few significant bands have been selected to observe the effect on ligand vibration in the complexes. In all the ligands (abh, ainh, ash, aah, phabh, phainh, phash, and phaah), $\nu(\text{NH})$ is normally broad and can be observed in the region of 3200–3400 cm^{-1} .²¹ In the metal complexes, $\nu(\text{NH})$ occurs either nearly at the same wave number as that in the parent ligands or in a few complexes at a slightly higher wave number indicating noninvolvement of the $>\text{NH}$ group in bonding.

TABLE III
ESR Parameters for the Complexes in the Solid State at Room Temperature (298 K)

Complex	A_{\parallel} (G)	A_{\perp} (G)	A_{av} (G)	g_{\parallel}	g_{\perp}	g_{av}	G
Cu[Ag(SCN) ₂] ₂ ·ash			$A_{iso} = 156$			$g_{iso} = 2.0836$	
Cu[Ag(SCN) ₂] ₂ ·aah	153	35	74.3	2.2795	2.0416	2.1209	6.7187
Cu[Ag(SCN) ₂] ₂ ·ainh	120	47	71.3	2.2718	2.0516	2.1250	5.2674
Cu[Ag(SCN) ₂] ₂ ·phainh	105	67	79.6	2.2682	2.0466	2.1205	5.7480
Cu[Ag(SCN) ₂] ₂ ·phaah	130	35	66.7	2.2952	2.0402	2.1252	7.3433

g , spectroscopic splitting factor or g factor; g_{iso} , $g_{isotropic}$ (when g value is independent of the orientation); A_{iso} , $A_{isotropic}$ (when Hyperfine coupling constant, A is independent of the direction of the orbital with respect to the applied magnetic field).

TABLE IV
IR Spectral Data and Assignments of Important Bands

Compound	$\nu(\text{NH}+\text{OH})$	Amide I $\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	Amide II	Amide III	$\nu(\text{N}-\text{N})$	SCN band	
							$\nu(\text{CN})$	$\nu(\text{CS})$
abh	3435b, 3280b, 3189s	1650s	1620s	1540s	1378s	975m		
ainh	3380w, 3260b, 3180b	1665s	1630s	1560m	1376s	980s		
ash	3410w, 3275m	1655s	1633m	1548m	1386s	990w		
aah	3469s, 3356m, 3189b	1648m	1631s	1575s	1377m	980m		
phabh	3526s, 3248b, 3399w	1640m	1610m	1573s	1370m	988m		
phainh	3550w, 3285s, 3436b	1653s	1615s	1567m	1384s	979m		
phash	3390w, 8269w	1660w	1633m	1539s	1367s	976m		
phaah	3468s, 3355m, 3136b	1645s	1625s	1545s	1371s	988m		
$\text{Cu}[\text{Ag}(\text{SCN})_2]_2\cdot\text{abh}$	3462b, 3291m, 3190m	1624m	1605m	1520s	1389s	1000w	2155s, 2098s	740m
$\text{Cu}[\text{Ag}(\text{SCN})_2]_2\cdot\text{ainh}$	3390w, 3280b	1630s	1615s	1532s	1380s	1005s	2150s, 2085b	755m
$\text{Cu}[\text{Ag}(\text{SCN})_2]_2\cdot\text{ash}$	3382w, 3272b, 3178w	1630m	1607s	1534s	1382s	1005m	2158s, 2085s	748m
$\text{Cu}[\text{Ag}(\text{SCN})_2]_2\cdot\text{aah}$	3460b, 3345w, 3200w	1630s	1620s	1541s	1401s	1010w	2159s, 2089s	752s
$\text{Cu}[\text{Ag}(\text{SCN})_2]_2\cdot\text{phabh}$	3508b, 3442b, 3247m	1629s	1600s	1527s	1390s	1015w	2157s, 2092s	760w
$\text{Cu}[\text{Ag}(\text{SCN})_2]_2\cdot\text{phainh}$	3550w, 3448b, 3282b	1638m	1595m	1545m	1392s	995b	2152s, 2080w	760b
$\text{Cu}[\text{Ag}(\text{SCN})_2]_2\cdot\text{phash}$	3497, 3360b, 3140w	1630s	1615m	1511s	1400m	1000w	2156s, 2098s	745w
$\text{Cu}[\text{Ag}(\text{SCN})_2]_2\cdot\text{phaah}$	3420w, 3270b, 3170w	1640s	1616m	1530s	1375s	990w	2166s, 2080s	755m

The amide I band [$\nu(\text{C}=\text{O})$] in the ligands occurs between 1640 and 1665 cm^{-1} , and it is shifted to lower wave numbers by 10–40 cm^{-1} in their complexes (Table IV); this indicates the coordination of the $>\text{C}=\text{O}$ group to the metal ion in all the complexes.²² A slight shift to a lower wave number (10–20 cm^{-1}) in the amide II band [$\nu(\text{CN} + \text{NH})$] and to a slightly higher wave number (5–30 cm^{-1}) in the amide III bands in the complexes also confirm the $>\text{C}=\text{O}$ coordination.⁹

$\nu(\text{C}=\text{N})$, observed in the 1610–1633- cm^{-1} region in the spectra of the ligands, shifts to a lower frequency by 10–25 cm^{-1} in their metal complexes, and this suggests coordination through the azomethine group.²³ $\nu(\text{N}-\text{N})$, observed between 975 and 990 cm^{-1} in the ligands, shifts to a higher frequency by 20–30 cm^{-1} in the complexes, and this indicates the coordination of one of the nitrogen atoms of the N–N group.²⁴ The strong bands in the ranges of 2150–2166 and 2080–2098 cm^{-1} in all the complexes can be assigned to $\nu(\text{CN})$ of a bidentate-bridged SCN group. The $\nu(\text{CS})$ modes appearing at 740–760 cm^{-1} also support the aforementioned type of thiocyanate bonding.²¹

Because IR spectra indicate a bidentate bridging nature for all four SCN groups present in the complexes, a polymeric structure for the Lewis acid as well as its complexes is proposed (Fig. 2). The insolubility of the complexes in water and most of the organic solvents, coupled with their high decomposition temperatures,²⁵ also supports the polymeric nature of these compounds.

X-ray diffraction studies

Because the complexes are insoluble in common inert organic solvents suitable for single-crystal

growth for X-ray analysis, X-ray powder diffraction patterns for two complexes were recorded, and the prominent lines were indexed for different hkl values by Ito's method.⁹ The following lattice constants were calculated:

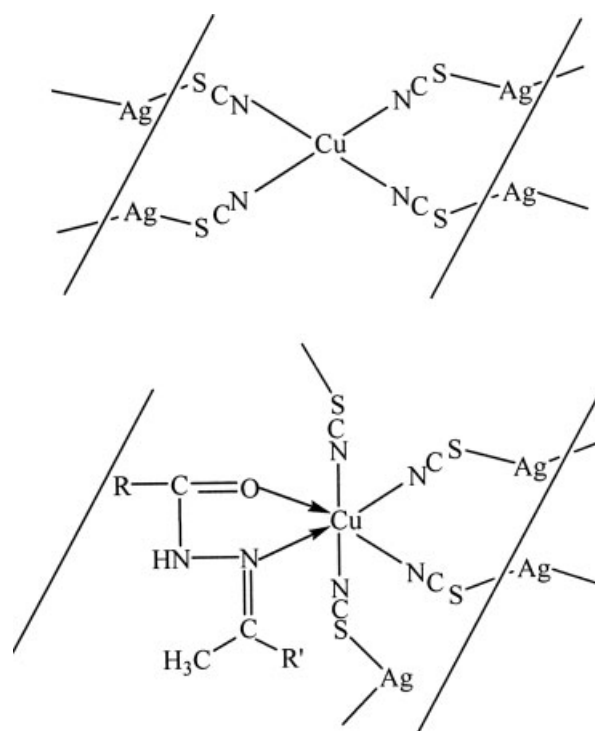


Figure 2 Structure of the Lewis acid $\text{Cu}[\text{Ag}(\text{SCN})_2]_2$ and its complexes $\text{Cu}[\text{Ag}(\text{SCN})_2]_2\cdot\text{L}$. R is C_6H_5 for abh and phabh, NC_5H_4 for ainh and phainh, HOC_6H_4 for ash and phash, and $\text{H}_2\text{NC}_6\text{H}_4$ for aah and phaah; R' is C_6H_5 for abh, ainh, ash, and aah and HOC_6H_4 for phabh, phainh, phash, and phaah.

$\text{Cu}[\text{Ag}(\text{SCN})_2]_2\cdot\text{ash}$: $a = 5.90 \text{ \AA}$, $b = 5.62 \text{ \AA}$, and $c = 5.27 \text{ \AA}$

$\text{Cu}[\text{Ag}(\text{SCN})_2]_2\cdot\text{phaah}$: $a = b = 5.93 \text{ \AA}$ and $c = 14.90 \text{ \AA}$

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

Antifungal activity

The antifungal experimental data indicate that the ligands and their complexes show a fair degree of activity against fungi, that is, *Rizoctonia* sp., *Aspergillus* sp., and *Stemphylium* sp., at 0.5, 1.0, and 1.5 mg/mL doses.²⁶ The effect is susceptible to the concentration of the compound used for inhibition. The activity is enhanced at the higher concentration. A DMSO control has shown negligible activity in comparison with the metal complexes and ligands. The antifungal experimental results of the compounds have been compared against DMSO as the control and are expressed as the inhibition percentage versus the control. The ligand phainh shows the highest activity (95%) against *Rizoctonia* sp. and *Stemphylium* sp. among all the ligands at the 1.5 mg/mL dose. $\text{Cu}[\text{Ag}(\text{SCN})_2]_2\cdot\text{phainh}$ and $\text{Cu}[\text{Ag}(\text{SCN})_2]_2\cdot\text{phaah}$ show 99% activity against *Rizoctonia* sp. at the 1.5 mg/mL dose. The phainh complex also shows 96% activity against *Stemphylium* sp. at 1.5 mg/mL. From the data, it has been observed that the metal complexes of acylhydrazones show greater activity than the ligands and the Lewis acid separately.²⁷ The complexes generally vary in their antifungal activity in the following order of ligands:

phainh > aah > phaah > phabh > aing
> phash > abh > ash

The toxicity of the complexes can be related to the strength of the metal–ligand bond, besides other factors such as the size of the cation,²⁸ receptor sites, diffusion,²⁹ and a combined effect of the metal and ligands³⁰ for the inactivation of the biomolecules.

Antibacterial activity

The metal complexes, Lewis acid, ligands, standard drug ampicillin, and solvent DMSO as a control were screened separately for their antibacterial activity against *Clostridium* sp. (Gram-positive) and *Pseudomonas* sp. (Gram-negative). The activity generally increases with the concentration of the compounds increasing.³¹ Among all the ligands, ainh is the most active ligand. However, $\text{Cu}[\text{Ag}(\text{SCN})_2]_2\cdot\text{phainh}$ and $\text{Cu}[\text{Ag}(\text{SCN})_2]_2\cdot\text{phaah}$ show the highest activity against both bacteria. It has been observed from the

activity data that the complexes are more active than the parent ligands. The activity of the complexes has been compared with the activity of a common standard antibiotic, ampicillin, and the activity index (%) for the complexes has been calculated. The antibacterial results suggest that the ligands and their complexes show moderate activity against both bacteria^{32,33} in comparison with the standard drug (ampicillin). The metal complexes show higher antibacterial activity than the Lewis acid, ligands, and DMSO control. The DMSO control showed no activity against any bacterial strain. The activity index (%) data show the highest activity (77.8%) for $\text{Cu}[\text{Ag}(\text{SCN})_2]_2\cdot\text{phainh}$ against *Pseudomonas* sp. at the dose of 2 mg/mL.

CONCLUSIONS

This study suggests a thiocyanate-bridged, polymeric, four-coordinate square planar structure for the Lewis acid $\text{Cu}[\text{Ag}(\text{SCN})_2]_2$. The acylhydrazone ligands are coordinated to the copper(II) metal ion of the Lewis acid as bidentate ligands through $>\text{C}=\text{O}$ and $>\text{C}=\text{N}-$ groups to increase its coordination number from four to six, and the resulting complexes form a distorted octahedral structure (Fig. 1). IR spectroscopy studies of $\text{Cu}[\text{Ag}(\text{SCN})_2]_2$ indicate that the sulfur end of the SCN group is linked to Ag(I) and the nitrogen end is linked to Cu(II). The ESR spectra of most of the copper(II) complexes are axial and suggest that the unpaired electron is in the $d_{x^2-y^2}$ orbital of the copper(II) ion. The newly synthesized complexes of acylhydrazones show appreciable and better antifungal and antibacterial activity in comparison with the parent ligands.

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