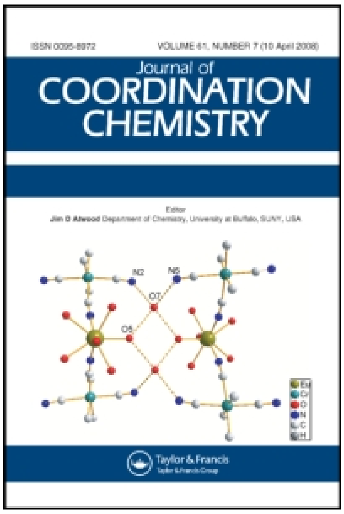

**Journal of Coordination Chemistry**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

# Synthesis, spectral studies of copper(II)tetrathiocyanato dithallate(I) complexes with some acylhydrazones and their antimicrobial activity

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**To cite this Article** Singh, Vinod P. and Singh, Archana(2008) 'Synthesis, spectral studies of copper(II)tetrathiocyanato dithallate(I) complexes with some acylhydrazones and their antimicrobial activity', Journal of Coordination Chemistry, 61: 17, 2767 — 2780

**To link to this Article: DOI:** 10.1080/00958970801975075

**URL:** http://dx.doi.org/10.1080/00958970801975075

*Journal of Coordination Chemistry*
Vol. 61, No. 17, 10 September 2008, 2767–2780

# Synthesis, spectral studies of copper(II)tetrathiocyanato dithallate(I) complexes with some acylhydrazones and their antimicrobial activity

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(*Received 1 July 2007; in final form 18 August 2007*)

Heterobimetallic complexes of $Cu[Tl(SCN)_2]_2 \cdot L$ (where L = acetophenone benzoylhydrazone(abh), acetophenone isonicotinoyl hydrazone(ainh), acetophenone salicyloylhydrazone(ash), acetophenone anthraniloyl hydrazone(aah), *p*-hydroxy acetophenone benzoylhydrazone (phabh), *p*-hydroxy acetophenone isonicotinoyl hydrazone (phainh), *p*-hydroxy acetophenone salicyloylhydrazone(phash) and *p*-hydroxy acetophenone anthraniloyl hydrazone(phaah) were synthesized and characterized. Electronic spectra and $\mu_{\text{eff}}$ values suggest a distorted octahedral environment around copper(II). SCN groups bridge between two metal centers and the ligands are coordinated through >C=O and >C=N– groups. Thermal studies (TGA and DTA) on $Cu[Tl(SCN)_2]_2 \cdot$ ainh indicate multi step decomposition of both endothermic and exothermic nature. ESR data show axial spectra for all the complexes and $d_{x^2-y^2}$ as the ground state. Powder X-ray diffraction parameters for some of the complexes correspond to orthorhombic crystal lattice. The complexes show significant antifungal activity against *Rizoctonia* sp. and *Stemphylium* sp. and moderate antibacterial activity against *Clostridium* sp. and *Pseudomonas* sp. The activity increases at higher concentration of the compound.

*Keywords*: Copper(II); Thallium(I) thiocyanate complexes; Acylhydrazones; Antifungal; Antibacterial activity; Characterization

## 1. Introduction

Thallium(I) compounds show the highest activity against the ascitic form of the Walker-256 carcinosarcoma [1]. $[Tl(C_5H_7N_3O)NO_3]$ and [(nitrato)(1-methylcystosin)thallium(I)] have been considered as model compounds for the interaction of thallium(I) with nucleobases [2]. The thallium(I) ion resembles alkali metal ions or Ag(I) and may replace the $K^+$ in certain enzymes for which it has potential as a probe. Thallium(I) is a soft metal ion and prefers highly polarizable sulfur donor ligands to nitrogen and oxygen donor ligands for bonding [3]. However, copper(II) is a borderline metal ion capable of binding with either end of a SCN group. Infrared spectral studies on $Co[Tl(SCN)_2]_2$

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*Journal of Coordination Chemistry*
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970801975075

indicate that the sulfur is linked to Tl(I) and the NCS–Tl–SCN group is linear [3]. Several Tl(I) compounds, namely Tl(I) alkoxides and acetylacetonates, tend to be polymeric [4, 5].

In continuation of our earlier work on mixed metal complexes of Cu(II) and Tl(I) [6] and our interest in the biological applications of such complexes, we have synthesized and characterized a number of heterobimetallic complexes with some new acylhydrazone ligands using $Cu[Tl(SCN)_2]_2$ as a Lewis acid. The ligands and their complexes have also been screened for antifungal and antibacterial activities.

## 2. Experimental

### 2.1. *Materials*

Metal salts and other chemicals used were of AnalaR (BDH) or equivalent grade. Benzoic acid hydrazide ($C_6H_5CONHNH_2$), salicylic acid hydrazide ($HOC_6H_4CONHNH_2$) and anthranilic acid hydrazide ($H_2NC_6H_4CONHNH_2$) were prepared by the reported methods [7]. Isonicotinic acid hydrazide ($NC_5H_4CONHNH_2$) was obtained from S.D. fine chemicals, Mumbai, whereas thallous nitrate was obtained from Fluka.

### 2.2. *Preparation of ligands*

**2.2.1. (A) Acetophenone acylhydrazones.** Acetophenone benzoyl hydrazone (abh), $C_6H_5C(CH_3)=NNHCOC_6H_5$; acetophenone isonicotinoyl hydrazone (ainh), $C_6H_5C(CH_3)=NNHCOC_5H_4N$; acetophenone salicyloylhydrazone (ash), $C_6H_5C(CH_3)=NNHCOC_6H_4(OH)$ and acetophenone anthraniloylhydrazone (aah), $C_6H_5C(CH_3)=NNHCOC_6H_4(NH_2)$ were synthesized by reacting their corresponding acid hydrazides with acetophenone in 1 : 1 molar ratio in 50 mL ethanol. The reaction mixture was refluxed at 60°C for 2–4 h and then allowed to cool in a beaker and the product collected 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 $CaCl_2$.

**2.2.2. (B) p-hydroxy acetophenone acylhydrazones.** *p*-Hydroxy acetophenone benzoylhydrazone (phabh), $C_6H_4(OH)C(CH_3)=NNHCOC_6H_5$; *p*-hydroxy acetophenone isonicotinoyl hydrazone (phainh), $C_6H_4(OH)C(CH_3)=NNHCOC_5H_4N$; *p*-hydroxy acetophenone salicyloylhydrazone (phash), $C_6H_4(OH)C(CH_3)=NNHCO\ C_6H_4(OH)$; *p*-hydroxy acetophenone anthraniloylhydrazone (phaah), $C_6H_4(OH)C(CH_3)=NNHCOC_6H_4(NH_2)$ 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 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 melting points, CHN analyses (table 1) and IR spectra (table 5).

Table 1. Analytical data of the ligands.

| Ligands (Color) | Empirical formula (Formula wt.) | Melting point (°C) | Found (Calcd)% C | H | N | Yield (%) |
|---|---|---|---|---|---|---|
| Abh (White) | $C_{15}H_{14}N_2O$ (238) | 145 | 75.80 (75.63) | 5.92 (5.88) | 11.66 (11.76) | 75 |
| Ainh (White) | $C_{14}H_{13}N_3O$ (239) | 162 | 70.10 (70.29) | 5.50 (5.44) | 17.42 (17.57) | 70 |
| Ash (White) | $C_{15}H_{14}N_2O_2$ (254) | 205 | 70.72 (70.86) | 5.61 (5.51) | 10.95 (11.02) | 80 |
| Aah (Cream yellow) | $C_{15}H_{15}N_3O$ (253) | 175 | 70.92 (71.15) | 5.81 (5.93) | 16.41 (16.60) | 70 |
| Phabh (Light yellow) | $C_{15}H_{14}N_2O_2$ (254) | 210 | 70.70 (70.86) | 5.67 (5.51) | 10.92 (11.02) | 80 |
| Phainh (Light yellow) | $C_{14}H_{13}N_3O_2$ (255) | 260 | 65.72 (65.88) | 5.18 (5.10) | 16.38 (16.47) | 75 |
| Phash (Light yellow) | $C_{15}H_{14}N_2O_3$ (270) | 240 | 66.45 (66.67) | 5.26 (5.18) | 10.32 (10.37) | 85 |
| Phaah (Light yellow) | $C_{15}H_{15}N_3O_2$ (269) | 225 | 66.70 (66.91) | 5.48 (5.57) | 15.41 (15.61) | 75 |

### 2.3. *Preparation of metal thiocyanates*

$Cu(NCS)_2$ was prepared by mixing aqueous solutions of $CuSO_4 \cdot 5H_2O$, (10 mmol, 2.50 g) with an aqueous solution of $NH_4SCN$ (20 mmol, 1.52 g) and stirring for 15 minutes on a magnetic stirrer at room temperature (25°C). Black $Cu(NCS)_2$ was filtered immediately and dried in a desiccator at room temperature [8].

Thallium(I) thiocyanate was prepared by dissolving 10 mmol (2.66g) of $TlNO_3$ in 50 mL water. The solution was treated with 10 mmol (0.76g) $NH_4SCN$ dissolved in 25 mL of water with constant stirring. White TlSCN, thus formed, was filtered and washed with ice cold water followed by absolute ethanol and finally with diethyl ether.

### 2.4. *Synthesis of $Cu[Tl(SCN)_2]_2$*

The Lewis acid $Cu[Tl(SCN)_2]_2$ was prepared by the reported procedure [6] reacting $Cu(NCS)_2$ (10 mmol, 1.80 g) with TlSCN (20 mmol, 5.24 g) in a round bottom flask containing 50 mL dioxane and using an anhydrous $CaCl_2$ guard tube. The reaction mixture was stirred for 75 h on a magnetic stirrer at room temperature to complete the reaction. The violet complex was filtered, washed with dioxane and dried in a desiccator at room temperature.

### 2.5. *Synthesis of $Cu[Tl(SCN)_2]_2 \cdot L$*

The $Cu[Tl(SCN)_2]_2$ (5 mmol, 3.51 g) was suspended in 50 mL hexane and reacted separately with 5 mmol solution of each of the ligands viz. 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 50 mL dioxane in a round bottom flask. The reaction mixture was well stirred on a magnetic stirrer at room temperature for ~48 h under anhydrous conditions until a visible color change of the product was observed. The products thus formed were filtered, washed with dioxane followed by hexane and dried in a desiccator over anhydrous calcium chloride at room temperature.

### 2.6. *Analyses and physico-chemical studies*

The thallium content was determined gravimetrically as TlSCN by treating the complexes with warm (~60°C) 0.2N HCl. After cooling the solution to ~15°C, TlSCN deposited, was filtered, washed with cold water followed by ethanol, dried at 110°C and then weighed as thallium(I) thiocyanate. For determination of copper content, the above filtrate was evaporated to dryness using conc. $HNO_3$ followed by conc. $H_2SO_4$ to destroy the organic content. Copper(II) was treated with sufficient $H_2SO_3$ to reduce it to copper(I) and then estimated gravimetrically as copper(I) thiocyanate [8]. Carbon, hydrogen and nitrogen contents were determined by using a Elemental Vario EL III Carlo Erba 1108 model microanalyzer. The molar conductance of $10^{-3}$M solutions of the complexes in DMSO was measured at room temperature on a Systronic Conductivity meter model-306. Room temperature magnetic susceptibilities were determined on a Faraday balance using $Co[Hg(SCN)_4]$ as calibrant and corrected for diamagnetism [9]. Thermal studies (TGA and DTA) were carried out on a Perkin-Elmer Thermal Analyser between 25–800°C. IR spectra were recorded in KBr on a Vector-22 spectrophotometer. Electronic spectra were recorded in DMSO solution on a Perkin-Elmer Lambda-2 spectrophotometer. The X-band ESR spectra of the complexes were recorded on a EMX 1444 EPR spectrometer at room temperature (298 K) in the solid state using DPPH as $g$ marker ($g = 2.0023$). Powder X-ray diffraction patterns of a few complexes were recorded on an Iso Debye Flex 2002 apparatus using Cu-Kα radiations. The analytical and physico chemical data are given in tables 1–7.

## 3. Antimicrobial activity

### 3.1. *Antifungal activity*

The ligands, $Cu[Tl(SCN)_2]_2$ and their complexes were screened for antifungal activity against *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 single spore isolation.

Solutions 0.5, 1.0 and 1.5 $mg\,mL^{-1}$ 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 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 calculated.

### 3.2. *Antibacterial activity*

The antibacterial activity of the Lewis acid, ligands and their complexes was studied against *Clostridium* sp. (Gram +ve) and *Pseudomonas* sp. (Gram −ve) bacteria. Each compound was dissolved in DMSO and solutions of 2 $mg\,mL^{-1}$ and 1 $mg\,mL^{-1}$ 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

Table 2. Analytical data of the complexes.

| Complex (Color) | Empirical formula (Formula wt.) | Decomposition temp. (°C) | Found (Calcd)% | | | | | Yield (%) | $\Lambda$ ($\Omega^{-1}$cm$^2$mol$^{-1}$) in DMSO |
|---|---|---|---|---|---|---|---|---|---|
| | | | Tl | Cu | C | H | N | | |
| $Cu[Tl(SCN)_2]_2$ (Violet) | $C_4N_4S_4CuTl_2$ (703.5) | 264 | 57.80 (58.00) | 9.00 (9.02) | 6.76 (6.82) | – | 7.88 (7.96) | 80 | – |
| $Cu[Tl(SCN)_2]_2 \cdot$ abh (Dirty white) | $C_{19}H_{14}N_6S_4OCuTl_2$ (941.5) | 207 | 43.10 (43.33) | 6.62 (6.74) | 24.08 (24.22) | 1.52 (1.48) | 8.74 (8.92) | 70 | 9.6 |
| $Cu[Tl(SCN)_2]_2 \cdot$ ainh (Light green) | $C_{18}H_{13}N_7S_4OCuTl_2$ (942.5) | 182 | 43.15 (43.29) | 6.60 (6.73) | 22.82 (22.92) | 1.44 (1.38) | 10.33 (10.40) | 75 | 11.5 |
| $Cu[Tl(SCN)_2]_2 \cdot$ ash (Dark yellow) | $C_{19}H_{14}N_6S_4O_2CuTl_2$ (957.5) | 165 | 42.50 (42.61) | 6.55 (6.63) | 23.66 (23.81) | 1.54 (1.46) | 8.69 (8.77) | 82 | 10.1 |
| $Cu[Tl(SCN)_2]_2 \cdot$ aah (Yellow) | $C_{19}H_{15}N_7S_4OCuTl_2$ (956.5) | 178 | 42.55 (42.65) | 6.58 (6.64) | 23.71 (23.83) | 1.51 (1.57) | 10.11 (10.24) | 75 | 12.5 |
| $Cu[Tl(SCN)_2]_2 \cdot$ phabh (Light yellow) | $C_{19}H_{14}N_6S_4O_2CuTl_2$ (957.5) | 190 | 42.50 (42.61) | 6.48 (6.63) | 23.69 (23.81) | 1.40 (1.46) | 8.65 (8.77) | 78 | 11.2 |
| $Cu[Tl(SCN)_2]_2 \cdot$ phainh (Yellowish green) | $C_{18}H_{13}N_7S_4O_2CuTl_2$ (958.5) | 219 | 42.60 (42.57) | 6.60 (6.62) | 22.44 (22.53) | 1.32 (1.35) | 10.30 (10.22) | 70 | 14.5 |
| $Cu[Tl(SCN)_2]_2 \cdot$phash (Yellow) | $C_{19}H_{14}N_6S_4O_3CuTl_2$ (973.5) | 160 | 41.70 (41.91) | 6.45 (6.52) | 23.38 (23.42) | 1.41 (1.44) | 8.52 (8.63) | 80 | 10.4 |
| $Cu[Tl(SCN)_2]_2 \cdot$phaah (Light yellow) | $C_{19}H_{15}N_7S_4O_2CuTl_2$ (972.5) | 171 | 41.75 (41.95) | 6.50 (6.53) | 23.36 (23.44) | 1.48 (1.54) | 9.97 (10.08) | 72 | 11.6 |

Table 3. Magnetic moments and electronic spectral bands.

| Complex | $\mu_{eff}$ (B.M.) | $\lambda_{max}$ (cm$^{-1}$)<br>$^2B_{1g} \rightarrow {}^2B_{2g}$ | $^2B_{1g} \rightarrow {}^2A_{1g}$ |
|---|---|---|---|
| $Cu[Tl(SCN)_2]_2$ | 1.70 | | 16390 |
| $Cu[Tl(SCN)_2]_2 \cdot$ abh | 1.82 | 11235 | 14700 |
| $Cu[Tl(SCN)_2]_2 \cdot$ ainh | 1.85 | 10640 | 13790 |
| $Cu[Tl(SCN)_2]_2 \cdot$ ash | 1.74 | 11100 | 14925 |
| $Cu[Tl(SCN)_2]_2 \cdot$ aah | 1.80 | 10870 | 14490 |
| $Cu[Tl(SCN)_2]_2 \cdot$ phabh | 1.86 | 10750 | 15150 |
| $Cu[Tl(SCN)_2]_2 \cdot$ phainh | 1.75 | 11300 | 14285 |
| $Cu[Tl(SCN)_2]_2 \cdot$ phash | 1.83 | 11560 | 15870 |
| $Cu[Tl(SCN)_2]_2 \cdot$ phaah | 1.78 | 11360 | 14815 |

Table 4. ESR parameters of the complexes in solid state at room temperature (298 K).

| Complex | $A_{\parallel}$ (G) | $A_{\perp}$ (G) | $A_{av}$ (G) | $g_{\parallel}$ | $g_{\perp}$ | $g_{av}$ | $G$ |
|---|---|---|---|---|---|---|---|
| $Cu[Tl(SCN)_2]_2 \cdot$ ainh | 136 | 47 | 76.6 | 2.2702 | 2.0561 | 2.1275 | 4.8164 |
| $Cu[Tl(SCN)_2]_2 \cdot$ ash | 126 | 77 | 93.3 | 2.2957 | 2.0436 | 2.1143 | 6.7821 |
| $Cu[Tl(SCN)_2]_2 \cdot$ aah | 145 | 47 | 79.4 | 2.2736 | 2.0529 | 2.1264 | 5.1720 |
| $Cu[Tl(SCN)_2]_2 \cdot$ phainh | 133 | 50 | 77.6 | 2.2800 | 2.0548 | 2.1299 | 5.1095 |
| $Cu[Tl(SCN)_2]_2 \cdot$ phash | 176 | 69 | 104.4 | 2.3082 | 2.0454 | 2.1330 | 6.7885 |

Table 5. IR spectral data and assignment of important bands.

| Compound | $\nu$(NH+OH) | Amide I $\nu$(C=O) | $\nu$(C=N) | Amide II | Amide III | $\nu$(N–N) | SCN bands<br>$\nu$(CN) | $\nu$(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 | | |
| $Cu[Tl(SCN)_2]_2 \cdot$ abh | 3440b, 3280b, 3190m | 1632m | 1605s | 1527s | 1383s | 1000w | 2155s, 2060s | 752w |
| $Cu[Tl(SCN)_2]_2 \cdot$ ainh | 3554b, 3445b, 3190m | 1643s | 1610m | 1550s | 1380s | 1005s | 2150w, 2096s | 764s |
| $Cu[Tl(SCN)_2]_2 \cdot$ ash | 3532b, 3427b, 3280w | 1635m | 1602s | 1537s | 1395m | 1010w | 2156s, 2050s | 747s |
| $Cu[Tl(SCN)_2]_2 \cdot$ aah | 3465w, 3380b, 3187m | 1632s | 1615s | 1558m | 1385m | 1005w | 2162s, 2070s | 755w |
| $Cu[Tl(SCN)_2]_2 \cdot$ phabh | 3550b, 3400b, 3257b | 1627m | 1600s | 1555m | 1382m | 1002w | 2152s, 2065s | 740m |
| $Cu[Tl(SCN)_2]_2 \cdot$ phainh | 3560b, 3442m, 3287b | 1640s | 1603s | 1545s | 1386s | 1005s | 2160w, 2082s | 745s |
| $Cu[Tl(SCN)_2]_2 \cdot$ phash | 3557b, 3455b, 3280w | 1642m | 1606m | 1516 | 1382m | 990w | 2160s, 2077s | 752w |
| $Cu[Tl(SCN)_2]_2 \cdot$ phaah | 3470b, 3360m, 3140b | 1630s | 1615s | 1528m | 1380s | 1007w | 2158s, 2072s | 760w |

s = strong, b = broad, m = medium, w = weak.

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 37°C and the inhibition zones were recorded after 24 h of incubation. Each treatment was replicated nine times.

Table 6. Thermal decomposition of $Cu[Tl(SCN)_2]_2 \cdot$ ainh.

| S.No. | Temp (°C) | Proposed decomposition pattern | % Loss of wt. Obs. | % Loss of wt. Calcd | Energy change | Remarks |
|---|---|---|---|---|---|---|
| 1. | 25–182 | $Cu[Tl(SCN)_2]_2 \cdot$ ainh | 0.00 | 0.00 | Endothermic | No decomposition |
| | | ↓ | | | | |
| 2. | 182–245 | $Cu(SCN)_2 \cdot$ ainh + $Tl_2S$ | 9.00 | 8.9 | Endothermic | TlSCN decomposed |
| | | ↓ | | | | |
| 3. | 245–460 | $Cu(SCN)_2$ +v $Tl_2$ S | 34.00 | 34.27 | Endothermic | Loss of organic ligand ainh |
| | | ↓ | | | | |
| 4. | 460–750 | CuS + $Tl_2S$ | 43.40 | 43.18 | Endothermic | $Cu(SCN)_2$ decomposed |

The antibacterial activity of a common standard antibiotic Ampicilln 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:

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

## 4. Results and discussion

The analytical data (table 2) show that $Cu(NCS)_2$ and TlSCN react in 1 : 2 molar ratio in dioxane resulting in $Cu[Tl(SCN)_2]_2$ which further reacts with the acylhydrazone (RCONHN=C<) bases to form $Cu[Tl(SCN)_2]_2 \cdot L$ complexes.

The complexes vary from light green to yellow to light yellow to yellowish green, in contrast to the Lewis acid which is violet. They are generally insoluble in water, benzene, ethanol, chloroform, carbon tetrachloride, ethylene dichloride and ether but are fairly soluble in DMF and DMSO. They decompose in water into $Cu(NCS)_2$ and TlSCN. On heating the Lewis acid decomposes at 264°C, whereas its complexes decompose in the range 160–219°C. All the metal complexes show very low molar conductance values for $10^{-3}$ M solutions in DMSO at room temperature (between 9.6–14.5 $\Omega^{-1}\,cm^2\,mol^{-1}$) indicating that they are non electrolytes [10].

### 4.1. *Magnetic moments and electronic spectra*

In Cu(II) complexes, $\mu_{eff}$ values are generally between 1.75–2.20 B.M [11], higher than the spin only $\mu_{eff}$ value of 1.73 B.M. corresponding to one unpaired electron. In tetrahedral Cu(II) complexes, the high $\mu_{eff}$ values are due to an orbital contribution while in octahedral complexes to mixing of excited T term into the E ground term [12]. The $\mu_{eff}$ values in this study have been observed between 1.70–1.86 B.M, indicating a distorted octahedral geometry around Cu(II). A slightly low magnetic moment value (1.70 B.M.) for $Cu[Tl(SCN)_2]_2$ may be due to spin-spin interaction between copper ions [11] in a polymeric structure.

Table 7. Observed and calculated $Q$ and $hkl$ values.

| Powder pattern | $2\theta$ | Intensity | $d$ (Å) | $Q_{\mathrm{obs}}$ $(1/d^2)$ | $Q_{\mathrm{Calcd}}$ | $hkl$ |
|---|---|---|---|---|---|---|
| $Cu[Tl(SCN)_2]_2 \cdot$ ainh | | | | | | |
| 1 | 18.71 | 68.30 | 4.7437 | 0.0444 | 0.0444 | 100 |
| 2 | 19.55 | 56.76 | 4.5404 | 0.0485 | 0.0485 | 010 |
| 3 | 21.44 | 42.41 | 4.1441 | 0.0582 | 0.0582 | 001 |
| 4 | 26.42 | 75.83 | 3.3739 | 0.0878 | 0.0929 | 110 |
| 5 | 28.56 | 44.41 | 3.1259 | 0.1023 | 0.1026 | 101 |
| 6 | 30.20 | 99.35 | 2.9596 | 0.1142 | 0.1067 | 011 |
| 7 | 35.62 | 62.10 | 2.5205 | 0.1574 | 0.1511 | 111 |
| 8 | 37.71 | 39.49 | 2.3855 | 0.1757 | 0.1776 | 200 |
| 9 | 42.24 | 45.98 | 2.1397 | 0.2184 | 0.2261 | 210 |
| 10 | 44.82 | 39.77 | 2.0220 | 0.2446 | 0.2384 | 120 |
| 11 | 46.96 | 31.04 | 1.9348 | 0.2671 | 0.2522 | 021 |
| 12 | 47.26 | 31.20 | 1.9233 | 0.2703 | 0.2772 | 102 |
| 13 | 48.01 | 36.63 | 1.8951 | 0.2784 | 0.2813 | 012 |
| 14 | 48.85 | 49.15 | 1.8643 | 0.2877 | 0.2843 | 211 |
| 15 | 51.84 | 33.47 | 1.7637 | 0.3215 | 0.3257 | 112 |
| 16 | 56.41 | 32.76 | 1.6310 | 0.3759 | 0.3996 | 300 |
| 17 | 59.95 | 32.18 | 1.5431 | 0.4199 | 0.4298 | 221 |
| 18 | 61.29 | 37.84 | 1.5125 | 0.4371 | 0.4365 | 030 |
| 19 | 62.33 | 35.77 | 1.4896 | 0.4507 | 0.4481 | 310 |
| 20 | 62.98 | 37.78 | 1.4758 | 0.4591 | 0.4589 | 212 |
| 21 | 65.72 | 38.09 | 1.4209 | 0.4953 | 0.4947 | 031 |
| 22 | 70.64 | 31.31 | 1.3334 | 0.5624 | 0.5682 | 103 |
| 23 | 78.01 | 33.59 | 1.2249 | 0.6665 | 0.6693 | 032 |
| $Cu[Tl(SCN)_2]_2 \cdot$ phash | | | | | | |
| 1 | 17.85 | 29.85 | 5.0155 | 0.0397 | 0.0397 | 100 |
| 2 | 18.58 | 53.11 | 4.7760 | 0.0438 | 0.0438 | 010 |
| 3 | 19.47 | 53.26 | 4.5586 | 0.0481 | 0.0481 | 001 |
| 4 | 26.33 | 53.97 | 3.3848 | 0.0873 | 0.0878 | 101 |
| 5 | 28.42 | 36.15 | 3.1408 | 0.1014 | 0.0919 | 011 |
| 6 | 32.00 | 100.00 | 2.7972 | 0.1278 | 0.1316 | 111 |
| 7 | 35.62 | 58.07 | 2.5203 | 0.1574 | 0.1588 | 200 |
| 8 | 37.51 | 33.23 | 2.3976 | 0.1739 | 0.1752 | 020 |
| 9 | 40.19 | 24.92 | 2.2435 | 0.1987 | 0.1924 | 002 |
| 10 | 40.74 | 24.66 | 2.2147 | 0.2039 | 0.2026 | 210 |
| 11 | 42.18 | 39.32 | 2.1423 | 0.2179 | 0.2149 | 120 |
| 12 | 43.97 | 21.06 | 2.0592 | 0.2358 | 0.2321 | 102 |
| 13 | 44.77 | 29.33 | 2.0244 | 0.2440 | 0.2405 | 012 |
| 14 | 46.80 | 28.81 | 1.9410 | 0.2654 | 0.2630 | 121 |
| 15 | 47.90 | 34.55 | 1.8992 | 0.2772 | 0.2759 | 112 |
| 16 | 50.18 | 26.77 | 1.8179 | 0.3026 | 0.3092 | 211 |
| 17 | 55.35 | 26.38 | 1.6598 | 0.3630 | 0.3573 | 300 |
| 18 | 57.19 | 23.65 | 1.6107 | 0.3854 | 0.3942 | 030 |
| 19 | 61.12 | 27.57 | 1.5163 | 0.4349 | 0.4339 | 130 |
| 20 | 61.61 | 29.08 | 1.5053 | 0.4413 | 0.4423 | 031 |
| 21 | 63.00 | 26.06 | 1.4753 | 0.4594 | 0.4492 | 311 |
| 22 | 63.70 | 22.90 | 1.4609 | 0.4685 | 0.4726 | 103 |
| 23 | 65.74 | 29.31 | 1.4205 | 0.4956 | 0.5164 | 113 |
| 24 | 69.37 | 20.75 | 1.3548 | 0.5448 | 0.5497 | 302 |
| 25 | 70.41 | 20.49 | 1.3372 | 0.5592 | 0.5530 | 230 |
| 26 | 74.33 | 20.85 | 1.2760 | 0.6142 | 0.6081 | 023 |
| 27 | 75.43 | 22.42 | 1.2602 | 0.6297 | 0.6263 | 132 |

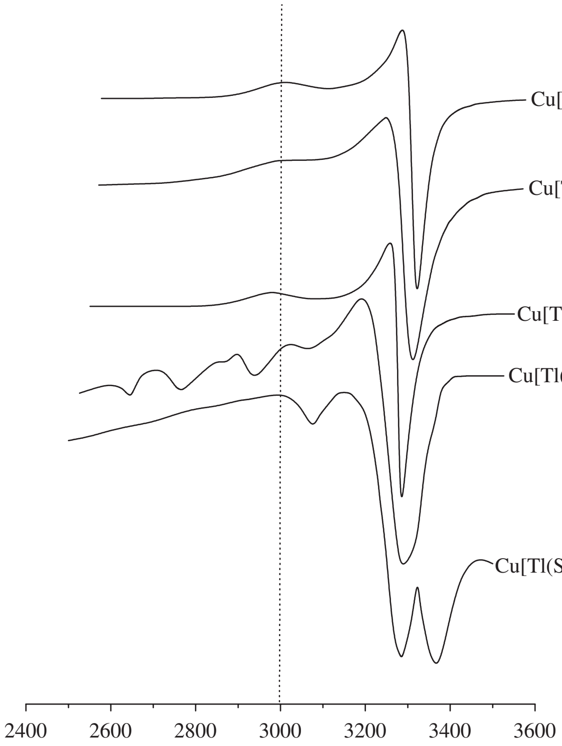
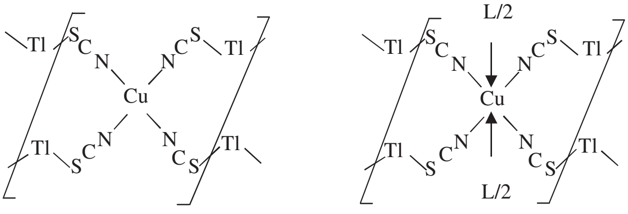


Figure 1. ESR spectra of the complexes in the solid state at 298 K.

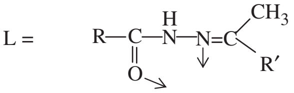
Free Cu[Tl(SCN)$_2$]$_2$ shows a broad band centered at 16,390 cm$^{-1}$ indicating a square planar geometry, similar to [Cu(NH$_3$)$_4$]$^{2+}$ (16 660 cm$^{-1}$) [13]. All other complexes in this study show two bands in the ranges 13,790–15,870 cm$^{-1}$ and 10,640–11,560 cm$^{-1}$, assigned to $^2B_{1g} \rightarrow {}^2A_{1g}$ and $\rightarrow {}^2B_{2g}$, transitions, suggesting a tetragonally distorted octahedral geometry [13] (table 3).

### 4.2. *ESR spectra*

ESR spectra of powdered samples of the complexes with ainh, ash, aah, phainh and phash exhibit an axial signal with two g values at 298 K (figure 1). The axial signals were analyzed by the procedure given by Hathaway and Billing [14]. The $g_{\|}$ and $g_{\perp}$ values (table 4) are >2.04, consistent with copper(II) in axial symmetry with all the principle axes aligned parallel. These $g$ values indicate an elongated tetragonally distorted octahedral stereochemistry. The $G$ factor defined as $G = (g_{\|} - 2)/(g_{\perp} - 2)]$, in the range 4.8164–6.7885, suggests that the local tetragonal axes are only slightly misaligned and the exchange interactions between copper(II) centers are negligible in the solid state [15]. Cu[Tl(SCN)$_2$]$_2$.phash shows 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. The $g_{\mathrm{av}}$ and $A_{\mathrm{av}}$ values were calculated using the equations $g_{\mathrm{av}} = (g_{\|} + 2g_{\perp})/3$; $A_{\mathrm{av}} = (A_{\|} + 2A_{\perp})/3$. However, the observation that $g_{\|} > g_{\perp} > g_e$ shows that the unpaired electron is in the $d_{x^2-y^2}$ orbital of the copper(II) [16, 17].



(a) $Cu[Tl(SCN)_2]_2$ (b) $Cu[Tl(SCN)_2]_2 \cdot L$



Where, R = $C_6H_5$ for abh and phabh
= $NC_5H_4$ for ainh and phainh
= $HOC_6H_4$ for ash and phash
= $H_2NC_6H_4$ for aah and phaah
R′= $C_6H_5$ for abh, phainh, phash and phaah

Figure 2. Representative structures of the complexes.

## 4.3. *IR spectra*

The ligands, abh, ainh, ash, aah, phabh, phainh, phash and phaah show broad bands in the region 3150–3550 $cm^{-1}$ due to $\nu NH + \nu OH$. In the metal complexes, these bands either occur nearly at the same positions as in the parent ligands or shifted to higher frequency suggesting the non-involvement of –NH in bonding [18].

In the ligands, the $\nu(C{=}O)$ band occurs between 1640 and 1665 $cm^{-1}$ and is shifted to lower frequency by 13–22 $cm^{-1}$ in their complexes (table 5) suggesting coordination of >C=O group to the metal ion in all the complexes [19]. Similarly, amide II bands also appear to be shifted considerably to lower frequency (10–15 $cm^{-1}$) compared to the parent ligand bands and a shift to higher frequency (5–15 $cm^{-1}$) in the amide III bands in all the complexes, further supports coordination through the >C=O group.

The $\nu(C{=}N)$ in the region 1610–1633 $cm^{-1}$ in the spectra of the ligands shifted to lower frequency by 10–28 $cm^{-1}$ in the metal complexes suggesting coordination through the azomethine [20]. $\nu(N–N)$ observed between 975 and 990 $cm^{-1}$ in the ligands shifts to higher frequency by 15–25 $cm^{-1}$ in the complexes, indicating coordination of one nitrogen of the N–N group [21].

In the thiocyanate complexes, $\nu(CN)$ and $\nu(CS)$ are diagnostic of the nature of SCN bonding [7]. Splitting of $\nu(C{=}N)$ bands into two or three components in reveals the presence of differently bonded SCN groups [18]. In the present study, all the complexes show strong bands in the ranges 2150–2162 $cm^{-1}$ and 2050–2096 $cm^{-1}$ assigned to $\nu(CN)$ of a bidentate, bridged SCN. The $\nu(CS)$ modes at 740–764 $cm^{-1}$ also support this bonding [18].

On the basis of above studies polymeric structures of the Lewis acid and the complexes are proposed (figure 2).

## 5. Thermal studies (TGA and DTA)

Thermal studies of $Cu[Tl(SCN)_2]_2 \cdot$ ainh show the complex is fairly stable to 182°C. Above this temperature it starts decomposition by an endothermic process and the weight of the residue up to 245°C corresponds to $Cu(SCN)_2 \cdot$ ainh + $Tl_2S$. The bonded organic ligand starts gradual decomposition between 245 to 460°C and the weight of residue at 460°C corresponds to $Cu(SCN)_2 + Tl_2S$. The DTA curves show significant heat liberation as a result of ligand decomposition [22] between 245–460°C. The complex shows further weight loss in the temperature range 460–750°C and the final residue at 750°C corresponds to $CuS + Tl_2S$. The proposed decomposition scheme is given in table 6.

### 5.1. *X-ray diffraction studies*

All the complexes are fine powdery solids. X-ray powder diffraction method provides a way of investigating, the crystallography of a crystal in powder form. The diffraction patterns for $Cu[Tl(SCN)_2]_2 \cdot$ ainh and $Cu[Tl(SCN)_2]_2 \cdot$ phash complexes were recorded and d-spacings were calculated from the diffraction lines (table 7). The patterns observed for these complexes have been indexed by Ito's method [23] and the lattice constants ($a$, $b$, $c$) were calculated as:

$$Cu[Tl(SCN)_2]_2 \cdot \text{ainh}\ a = 4.74,\ b = 4.54 \text{ and } c = 4.14\,\text{Å}$$

$$Cu[Tl(SCN)_2]_2 \cdot \text{phash}\ a = 5.02,\ b = 4.78 \text{ and } c = 4.56\,\text{Å}$$

These lattice constants indicate orthorhombic crystal lattice for both complexes.

### 5.2. *Antifungal activity*

From the experimental data (table 8a), it has been observed that the ligands as well as their complexes show antifungal activity against *Rizoctonia* sp., and *Stemphylium* sp. at 0.5, 1.0 and 1.5 $mg\,mL^{-1}$ concentration [24]. The effect is susceptible to the concentration of the compound used for inhibition, greatly enhanced at the higher concentration. Metal complexes show better activity than $Cu[Tl(SCN)_2]_2$ and parent ligands [25]. DMSO control has little activity. The antifungal experimental results of the compounds were compared against DMSO as the control and are expressed as percentage inhibition versus control. Ligand phainh shows the highest activity (90%) among all the ligands at 1.5 $mg\,mL^{-1}$ against both the fungi. Similarly the $Cu[Tl(SCN)_2]_2 \cdot$ phainh complex also show the highest activity (99%) against both fungi at 1.5 $mg\,mL^{-1}$ concentration.

Table 8(a). Antifungal activity of ligands and their complexes.

| Compounds | % Inhibition of spore germination | | | | | |
|---|---|---|---|---|---|---|
| | *Rizoctonia* sp. ($\mathrm{mg\,mL^{-1}}$) | | | *Stemphylium* sp. ($\mathrm{mg\,mL^{-1}}$) | | |
| | 0.5 | 1.0 | 1.5 | 0.5 | 1.0 | 1.5 |
| Abh | 46 | 64 | 79 | 68 | 80 | 89 |
| Ainh | 60 | 74 | 85 | 67 | 73 | 85 |
| Ash | 62 | 69 | 79 | 58 | 64 | 69 |
| Aah | 39 | 67 | 74 | 72 | 84 | 86 |
| Phabh | 44 | 55 | 78 | 61 | 68 | 74 |
| Phainh | 76 | 82 | 90 | 71 | 79 | 90 |
| Phash | 67 | 71 | 82 | 75 | 80 | 84 |
| Phaah | 33 | 61 | 65 | 57 | 65 | 75 |
| $\mathrm{Cu[Tl(SCN)_2]_2}$ | 70 | 84 | 90 | 68 | 72 | 80 |
| $\mathrm{Cu[Tl(SCN)_2]_2 \cdot abh}$ | 86 | 92 | 94 | 80 | 86 | 90 |
| $\mathrm{Cu[Tl(SCN)_2]_2 \cdot ainh}$ | 90 | 98 | 99 | 73 | 78 | 88 |
| $\mathrm{Cu[Tl(SCN)_2]_2 \cdot ash}$ | 94 | 96 | 97 | 73 | 79 | 91 |
| $\mathrm{Cu[Tl(SCN)_2]_2 \cdot aah}$ | 86 | 96 | 97 | 82 | 86 | 93 |
| $\mathrm{Cu[Tl(SCN)_2]_2 \cdot phabh}$ | 94 | 96 | 98 | 67 | 73 | 95 |
| $\mathrm{Cu[Tl(SCN)_2]_2 \cdot phainh}$ | 96 | 98 | 99 | 78 | 95 | 99 |
| $\mathrm{Cu[Tl(SCN)_2]_2 \cdot phash}$ | 92 | 96 | 98 | 80 | 84 | 88 |
| $\mathrm{Cu[Tl(SCN)_2]_2 \cdot phaah}$ | 88 | 91 | 97 | 68 | 78 | 88 |

The antifungal activity of the complexes varies in the following order for ligands:

For *Rizoctonia* sp.

$$\text{phainh} > \text{ainh} > \text{abh} = \text{phash} > \text{ash} = \text{aah} = \text{phaah} > \text{abh}.$$

For *Stemphylium* sp.

$$\text{phainh} > \text{abh} > \text{phash} = \text{phaah} > \text{aah} = \text{ash} > \text{ainh} > \text{phabh}.$$

From the data it has been observed that these complexes are more effective against *Rizoctonia sp*. compared to *Stemphylium* sp.

### 5.3. *Antibacterial activity*

The metal complexes, Lewis acid, ligands, standard drug Ampicillin and DMSO solvent control were screened separately for their antibacterial activity against *Clostridium* sp. (Gram +ve) and *Pseudomonas* sp. (Gram –ve). The activity increases as the concentration of the compounds increases [26]. Ainh is the most active ligand. The complexes are more active than the Lewis acid and parent ligands. The antibacterial activity of the complexes has been compared with the activity of a common standard antibiotic Ampiciline and % Activity Index for the complexes has been calculated. The antibacterial results suggest that the ligands and their complexes (table 8b) show moderate activity against both the bacteria [27, 28] as compared to Ampicillin. $\mathrm{Cu[Tl(SCN)_2]_2 \cdot phainh}$ shows the highest antibacterial activity (% Activity Index = 62.5) against *Clostridium* sp. at $2\,\mathrm{mg\,mL^{-1}}$, but $\mathrm{Cu[Tl(SCN)_2]_2 \cdot ainh}$ and $\mathrm{Cu[Tl(SCN)_2]_2 \cdot phabh}$ show highest activity (% Activity index = 50) against *Pseudomonas* sp. at $2\,\mathrm{mg\,mL^{-1}}$ concentration. Complexes are more effective against *Clostridium* sp. than *Pseudomonas* sp.

Table 8(b). Antibacterial activity of ligands and their complexes.

| | *Clostridium* sp. ($mg\,mL^{-1}$) | | | | *Pseudomonas* sp. ($mg\,mL^{-1}$) | | | |
|---|---|---|---|---|---|---|---|---|
| | Diameter of inhibition zone (in mm) | | % Activity index | | Diameter of inhibition zone (in mm) | | % Activity index | |
| Compounds | 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 |
| $Cu[Tl(SCN)_2]_2$ | 3 | 4 | 21.4 | 25.0 | 4 | 5 | 22.2 | 27.8 |
| $Cu[Tl(SCN)_2]_2 \cdot$ abh | 3 | 6 | 21.4 | 37.5 | 4 | 5 | 22.2 | 27.8 |
| $Cu[Tl(SCN)_2]_2 \cdot$ ainh | 7 | 8 | 50.0 | 50.0 | 8 | 9 | 44.4 | 50.0 |
| $Cu[Tl(SCN)_2]_2 \cdot$ ash | 4 | 5 | 28.6 | 31.3 | 5 | 6 | 27.8 | 33.3 |
| $Cu[Tl(SCN)_2]_2 \cdot$ aah | 5 | 7 | 35.7 | 43.8 | 4 | 7 | 22.2 | 38.9 |
| $Cu[Tl(SCN)_2]_2 \cdot$ phabh | 6 | 8 | 42.9 | 50.0 | 7 | 9 | 38.9 | 50.0 |
| $Cu[Tl(SCN)_2]_2 \cdot$ phainh | 7 | 10 | 50.0 | 62.5 | 4 | 8 | 22.2 | 44.4 |
| $Cu[Tl(SCN)_2]_2 \cdot$ phash | 4 | 6 | 28.6 | 37.5 | 5 | 8 | 27.8 | 44.4 |
| $Cu[Tl(SCN)_2]_2 \cdot$ phaah | 6 | 7 | 42.9 | 43.8 | 7 | 8 | 38.9 | 44.4 |
| Ampicillin (standard) | 14 | 16 | 100.0 | 100.0 | 18 | 18 | 100.0 | 100.0 |

## Acknowledgements

The authors thank the Director, Institute of Engineering and Technology, C.S.J.M. University Kanpur for providing laboratory facilities, the Head, Chemistry Department, Indian Institute and Technology, Kanpur for recording electronic, IR, ESR spectra, thermal and X-ray diffraction studies. The authors also thank to Dr Nand Lal, Institute of Life Sciences, CSJM University, Kanpur for his help in antimicrobial screening.

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