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Synthesis, Spectral Characterization of Polymeric Nickel(II) Tetrathiocyanato Diargentate(I) Complexes with Some Acylhydrazones and Their Bio-activity

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Polymeric heterobimetallic complexes of the type $Ni[Ag(SCN)_2]_2.L$ (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) and *p*-hydroxy acetophenone anthraniloyl hydrazone (phaah) were synthesized and characterized with the help of elemental analyses, electrical conductance, magnetic moment, electronic and IR spectra, thermal and X-ray diffraction studies. Nickel(II) in the complexes has spin-free octahedral geometry. The hydrazone ligands are bi-coordinate bonding through $>C{=}O$ and $>C{=}N$-groups. The complexes form a polymeric structure by bridging SCN groups between two metal centers. Thermal studies (TGA and DTA) on $Ni[Ag(SCN)_2]_2$.ash indicate multi-steps decomposition pattern which are both exothermic and endothermic. X-ray powder diffraction parameters for $Ni[Ag(SCN)_2]_2$.ash and $Ni[Ag(SCN)_2]_2$.phainh correspond to tetragonal and orthorhombic crystal lattices respectively. The ligands, as well as their complexes, show significant antifungal and antibacterial activity. The metal complexes are more active than the parent ligands.

Keywords: Heterobimetallic complexes, thermal studies: antifungal & antibacterial activity, acylhydrazones, electronic and IR spectral studies

1. Introduction

The chemistry of nickel complexes with multi-dentate Schiff base ligands has attracted particular attention because this metal can exhibit several oxidation states (1). Such complexes with different oxidation states have a strong role in bio-inorganic chemistry and redox enzyme systems (2,3) and may provide the basis of models for active sites of biological systems (4,5) or act as catalysts (6,7). Metal complexes of multi-dentate acylhydrazone Schiff bases have been extensively studied (8–12) because such ligands can bind with one, two or more metal centers involving various coordination modes and allow successful synthesis of homo and hetero nuclear metal complexes with interesting stereo-chemistry (13–16). Since the heterobimetallic complexes of acylhydrazones involving nickel(II) and silver(I) metal ions may have their potential use in the biological fields, it is worthwhile to undertake the present study. We have synthesized and characterized a number of polymeric nickel(II) tetrathiocyanato diargentate(I) complexes with acylhydrazone ligands and studied their bio-activity.

2. Experimental

2.1. *Materials*

All the 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 synthesized by the reported methods (17). Isonicotinic acid hydrazide ($NC_5H_4CONHNH_2$) 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 benzoylhydrazone (abh), $C_6H_5C(CH_3){=}NNHCOC_6H_5$; acetophenone isonicotinoyl hydrazone (ainh), $C_6H_5C(CH_3){=}NNHCOC_5H_4N$; acetophenone salicyloyl hydrazone (ash), $C_6H_5C(CH_3){=}NNHCOC_6H_4(OH)$ and acetophenone anthraniloyl

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Table 1. Analytical data of the ligands

Ligands (Color)	*Empirical Formula (Formula wt.)*	*Melting Point (°C)*	*Found (Calculated) %* 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	70.62 (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)	5.57 (5.51)	10.92 (11.02)	70
phainh (Light yellow)	$C_{14}H_{13}N_3O_2$ (255)	260	65.62 (65.88)	5.18 (5.10)	16.38 (16.47)	75
phash (Light yellow)	$C_{15}H_{14}N_2O_3$ (270)	240	66.55 (66.67)	5.24 (5.18)	10.32 (10.37)	85
phaah (Light yellow)	$C_{15}H_{15}N_3O_2$ (269)	225	66.70 (66.91)	5.51 (5.57)	15.51 (15.61)	75

hydrazone (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 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 the product was filtered 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. *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), $C_6H_4(OH)C(CH_3)$= $NNHCOC_6H_4(OH)$; *p*-hydroxy acetophenone anthraniloyl hydrazone (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 RB 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 and IR spectra (Table 1).

2.3. *Preparation of metal thiocyanates*

AgSCN was prepared by dissolving $AgNO_3$ (10 mmol, 1.66 g) in a 50 mL water. The solution was treated with NH_4SCN (10 mmol, 0.76 g) dissolved in 25 mL water with constant stirring at room temp. AgSCN thus formed as a white precipitate, was filtered, washed with water, ethanol and finally with diethyl ether and dried in a desiccator.

For the preparation of nickel(II) thiocyanate, $Ni(NO_3)_2.6H_2O$ (10 mmol, 2.91 g) dissolved in 50 mL

Table 2. Analytical data of the complexes

Complex (Color)	*Empirical Formula (Unit Formula wt.)*	*Decomposition Temp. (°C)*	*Found (Calculated) %* Ag	Ni	C	H	N	*Yield (%)*	Λ_M (Ω^{-1} cm^2mol^{-1}) *in DMSO*
$Ni[Ag(SCN)_2]_2$·2diox	$C_{12}H_{16}O_4N_4S_4NiAg_2$	269	31.50	8.55	20.89	2.36	8.12	90	-
(Green)	(683)		(31.62)	(8.64)	(21.08)	(2.34)	(8.20)		
$Ni[Ag(SCN)_2]_2$·abh	$C_{19}H_{14}N_6S_4ONiAg_2$	248	29.10	8.00	30.48	1.90	11.15	85	10.4
(Light blue)	(745)		(28.99)	(7.92)	(30.60)	(1.88)	(11.27)		
$Ni[Ag(SCN)_2]_2$·ainh	$C_{18}H_{13}N_7S_4ONiAg_2$	236	29.20	8.00	28.85	1.81	13.10	82	8.6
(Green)	(746)		(28.95)	(7.91)	(28.95)	(1.74)	(13.14)		
$Ni[Ag(SCN)_2]_2$·ash	$C_{19}H_{14}N_6S_4O_2NiAg_2$	250	28.15	7.80	29.76	1.92	10.92	80	9.2
(Greenish white)	(761)		(28.38)	(7.75)	(29.96)	(1.84)	(11.04)		
$Ni[Ag(SCN)_2]_2$·aah	$C_{19}H_{15}N_7S_4ONiAg_2$	242	28.30	7.62	29.88	1.89	12.75	80	12.6
(Light green)	(760)		(28.42)	(7.76)	(30.00)	(1.97)	(12.89)		
$Ni[Ag(SCN)_2]_2$·phabh	$C_{19}H_{14}N_6S_4O_2NiAg_2$	234	28.25	7.85	29.78	1.90	10.92	87	9.8
(Light blue)	(761)		(28.38)	(7.75)	(29.96)	(1.84)	(11.04)		
$Ni[Ag(SCN)_2]_2$·phainh	$C_{18}H_{13}N_7S_4O_2NiAg_2$	231	28.20	7.88	28.15	1.82	12.78	82	11.2
(Light green)	(762)		(28.35)	(7.74)	(28.35)	(1.71)	(12.86)		
$Ni[Ag(SCN)_2]_2$·phash	$C_{19}H_{14}N_6S_4O_3NiAg_2$	227	27.60	7.70	29.16	1.91	10.76	85	11.7
(Light blue)	(777)		(27.80)	(7.59)	(29.34)	(1.80)	(10.81)		
$Ni[Ag(SCN)_2]_2$·phaah	$C_{19}H_{15}N_7S_4O_2NiAg_2$	210	27.60	7.50	29.28	2.02	12.61	80	10.6
(Light green)	(776)		(27.83)	(7.60)	(29.38)	(1.93)	(12.63)		

Table 3. Magnetic moments, electronic spectra and ligand field parameters of the complexes

		Band Maxima (cm^{-1})							
Complexes	*μ_{eff} (B.M.)*	*ν_1*	*ν_2*	*ν_3*	*10 Dq (cm^{-1})*	*B (cm^{-1})*	*β*	*B^0(%)*	*LFSE (kcal/mol)*
Ni[Ag(SCN)$_2$]$_2$·2diox	2.95	10380	16825	27560	10380	883	0.848	15.20	35.49
Ni[Ag(SCN)$_2$]$_2$·abh	2.91	10630	16520	26850	10630	765	0.735	26.50	36.34
Ni[Ag(SCN)$_2$]$_2$·ainh	2.98	10205	15625	28570	10205	905	0.869	13.10	34.89
Ni[Ag(SCN)$_2$]$_2$·ash	3.06	10750	16680	27770	10750	813	0.781	21.90	36.75
Ni[Ag(SCN)$_2$]$_2$·aah	2.88	10570	16345	28285	10570	861	0.827	17.30	36.14
Ni[Ag(SCN)$_2$]$_2$·phabh	3.10	10645	16610	27520	10645	813	0.781	21.90	36.39
Ni[Ag(SCN)$_2$]$_2$·phainh	2.90	10720	15890	26630	10720	691	0.664	33.60	36.65
Ni[Ag(SCN)$_2$]$_2$·phash	2.96	10660	16740	28100	10660	857	0.823	17.70	36.44
Ni[Ag(SCN)$_2$]$_2$·phaah	3.12	10825	16255	27520	10825	753	0.723	27.70	37.01

absolute ethanol was reacted with KSCN (20 mmol, 1.94 g) dissolved in 25 mL absolute ethanol in a beaker at room temperature. KNO$_3$ was thus formed as a white solid and removed by filtration. The filtrate containing Ni(SCN)$_2$ was slowly evaporated to dryness to obtain green solid Ni(NCS)$_2$. It was redissolved and purified from dry ethanol to ensure removal of water soluble KNO$_3$.

2.4. *Synthesis of Ni[Ag(SCN)$_2$]$_2$·2diox*

Ni(NCS)$_2$ (10 mmol, 1.75 g) and AgSCN (20 mmol, 3.32 g) were reacted in 1:2 molar ratio in a round bottom flask containing 50 mL dioxane and fitted with a anhydrous CaCl$_2$ guard tube. The reaction mixture was stirred continuously for 24 to 48 h on a magnetic stirrer at room temperature to complete the reaction. Lewis acid thus formed was filtered through a closed assembly, washed with dioxane solvent and dried in a desiccator at room temperature.

2.5. *Synthesis of Ni[Ag(SCN)$_2$]$_2$·L*

Ni[Ag(SCN)$_2$]$_2$·L complexes were prepared by reacting Ni[Ag(SCN)$_2$]$_2$·2diox (5 mmol, 3.41 g) separately with 5 mmol 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 (1.34 g) in a round bottom flask containing 50 mL dioxane. The mixture was stirred well on the magnetic stirrer for 30–50 h at room temperature until a visible color change of the product takes place. The product was filtered, washed with dioxane, followed by diethyl ether and then dried in a desiccator at room temperature.

The complexes were also synthesized directly by stirring the constituents, Ni(NCS)$_2$, AgSCN and the ligands in 1:2:1 molar ratio in dioxane for 40–50 h. Both the methods gave products of similar composition.

2.6. *Analyses and physico-chemical studies*

For determination of the silver content, the weighed amounts of the complexes were heated (80°C) with an excess of dilute HCl (0.01 N). The solution was cooled to deposit AgSCN (18), which was filtered in a crucible, washed first with hot water and then with ethanol and dried at 110°C. For determination of nickel contents, the above filtrate was evaporated to dryness using conc. HNO$_3$ followed by conc. H$_2$SO$_4$. The solid was dissolved in distilled water. From the solution, nickel was estimated gravimetrically as nickel dimethyl glyoxime (18). 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 Hg[Co(SCN)$_4$] as calibrant and corrected for diamagnetism (19). IR spectra were recorded in KBr medium

Table 4. Thermal decomposition of Ni[Ag(SCN)$_2$]$_2$·ash complex

			% Wt loss			
Sl. No	*Temp. (°C)*	*Proposed decomposition pattern*	*Obs.*	*Calc.*	*Energy change*	*Remarks*
1.	30–250	Ni[Ag(SCN)$_2$]$_2$·ash ↓	0.0	0.0	Endothermic	No decomposition
2.	250–330	Ni[Ag(SCN)$_2$]$_2$ ↓	34.0	33.4	Exothermic	Loss of ligand molecule
3.	330–370	Ni(NCS)$_2$ + Ag$_2$S ↓	44.0	44.4	Endothermic	Decomposition of AgSCN
4.	370–505	NiS + 2Ag	60.0	60.0	Exothermic	Decomposition of Ni(NCS)$_2$ and Ag$_2$S

Table 5. IR spectral data and assignment of important bands

							SCN bands	
Compound	$\nu(NH{+}OH)$	*Amide I* $\nu(C{=}O)$	$\nu(C{=}N)$	*Amide II*	*Amide III*	$\nu(N{-}N)$	$\nu(CN)$	$\nu(CS)$
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, 189b	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		
$\mathrm{Ni[Ag(SCN)_2]_2}$·abh	3430b, 3278b, 3212w	1635m	1608s	1523s	1385s	990w	2147s, 2092s	731s
$\mathrm{Ni[Ag(SCN)_2]_2}$·ainh	3490b, 3382b, 3258w	1642s	1612s	1540m	1388s	1000w	2152s, 2085s	745s
$\mathrm{Ni[Ag(SCN)_2]_2}$·ash	3500b, 3280b,	1640m	1611s	1528s	1392s	1002w	2140b, 2080s	754s
$\mathrm{Ni[Ag(SCN)_2]_2}$·aah	3460b, 3358m, 3190b	1629m	1606s	1560s	1390s	1004w	2148s, 2082s,	742s
$\mathrm{Ni[Ag(SCN)_2]_2}$·phabh	3562b, 3442b, 3245m	1628m	1600s	1551m	1382s	1005w	2136s, 2090s	745w
$\mathrm{Ni[Ag(SCN)_2]_2}$·phainh	3450b, 3283b	1632s	1604s	1537m	1390s	1007w	2142s, 2092s	740s
$\mathrm{Ni[Ag(SCN)_2]_2}$·phash	3400b, 3272b,	1638s	1612s	1525s	1380s	992w	2140s, 2088s	735s
$\mathrm{Ni[Ag(SCN)_2]_2}$·phaah	3468b, 3358b,	1629m	1610s	1532m	1385s	1002w	2126s, 2085s	756s

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

on Vector-22 spectrophotometer. Electronic spectra were recorded in DMSO solution on a Perkin-Elmer Lambada-2 spectrophotometer. Thermal analyses (TGA and DTA) were carried out on a Perkin-Elmer Thermal Analyzer from room temperature to 800°C. Powder X-ray diffraction patterns of a few complexes were recorded on Iso Debye Flex 2002 apparatus using CuKα radiations. The analytical and physico chemical data are given in Tables 1–6.

2.7. *Bio-activity*

2.7.1. *Antifungal activity*

The ligands as well as their complexes were screened for their antifungal activity against various fungi viz. *Rizoctonia sp., Aspergillus 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 technique.

The solution in different concentrations 0.5, 1 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 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 percent germination was finally calculated.

2.7.2. *Antibacterial activity*

The antibacterial activity of the ligands and their complexes were studied against *Clostridium sp.* (Gram +ve) and *Pseudomonas sp.* (Gram –ve) bacteria. Each of the compounds was dissolved in DMSO and solutions of the concentration 2 mg/mL 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 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 37°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:

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

3. Results and discussion

The analytical data of the complexes (Table 2) show that $\mathrm{Ni(NCS)_2}$ and AgSCN react in 1:2 molar ratio in dioxane to form a more stable $\mathrm{Ni[Ag(SCN)_2]_2}$.2diox complex. It further reacts with the ligands in 1:1 (M:L) molar ratio as

Table 6. Observed and calculated Q and hkl values

Powder pattern	*2θ*	*Intensity*	*d(A°)*	$Q_{obs}(^1/_{d}^{2})$	$Q_{calc.}$	*hkl*
$Ni[Ag(SCN)_2]_2 \cdot ash$						
1	14.93	78.31	5.9320	0.0284	0.0284	100
2	16.61	70.81	5.3365	0.0351	0.0351	001
3	20.71	81.25	4.2893	0.0544	0.0568	110
4	22.98	79.58	3.8705	0.0668	0.0635	101
5	26.88	72.68	3.3173	0.0909	0.0919	111
6	30.72	66.66	2.9100	0.1181	0.1136	200
7	35.07	55.23	2.5589	0.1527	0.1487	201
8	37.04	45.86	2.4270	0.1698	0.1688	102
9	37.19	46.25	2.4177	0.1711	0.1771	211
10	40.00	42.81	2.2539	0.1968	0.1972	112
11	42.96	43.25	2.1052	0.2256	0.2272	220
12	48.34	41.88	1.8828	0.2821	0.2824	212
$Ni[Ag(SCN)_2]_2 \cdot phainh$						
1	11.69	87.41	7.5678	0.0175	0.0175	100
2	13.29	72.19	6.6634	0.0225	0.0225	010
3	13.98	70.30	6.3327	0.0249	0.0249	001
4	17.77	67.82	4.9913	0.0401	0.0400	110
5	18.67	73.70	4.7535	0.0443	0.0424	101
6	19.36	73.91	4.5839	0.0476	0.0474	011
7	21.75	100.00	4.0853	0.0599	0.0649	111
8	23.80	76.22	3.7391	0.0715	0.0700	200
9	26.19	59.92	3.4029	0.0864	0.0900	020
10	27.43	76.75	3.2512	0.0946	0.0949	201
11	28.78	61.26	3.1023	0.1039	0.1075	120
12	30.37	57.30	2.9430	0.1155	0.1149	021
13	30.87	54.54	2.8966	0.1192	0.1174	211
14	32.71	62.39	2.7375	0.1334	0.1324	121
15	33.41	68.26	2.6819	0.1390	0.1394	112
16	35.20	59.25	2.5494	0.1539	0.1575	300
17	37.20	45.45	2.4173	0.1711	0.1696	200
18	38.04	48.39	2.3654	0.1787	0.1800	310
19	41.23	44.46	2.1896	0.0286	0.2071	122
20	43.12	46.98	2.0978	0.2272	0.2274	031
21	46.26	48.50	1.9625	0.2596	0.2596	222
22	46.81	45.51	1.9408	0.2655	0.2641	113
23	48.25	43.80	1.8860	0.2811	0.2725	230

follows:

$$Ni(NCS)_2 + 2AgSCN \xrightarrow{\text{dioxane}} Ni[Ag(SCN)_2]_2 \cdot 2diox$$
$$Ni[Ag(SCN)_2]_2{\cdot}2diox + L \xrightarrow{\text{dioxane}} Ni[Ag(SCN)_2]_2 \cdot L + 2dioxane$$

The $Ni[Ag(SCN)_2]_2{\cdot}L$ complexes are colored varying from light blue, green to light green in color. They all are insoluble in water and common organic solvents viz. ethanol, methanol, benzene, hexane, chloroform, carbon tetrachloride, and diethyl ether but are soluble in DMF and DMSO. The complexes decompose in the range 210–269°C and are non-electrolytes (20) as indicated by their low molar conductance values of 10^{-3} M solutions of the complexes in DMSO at room temperature.

3.1. *Magnetic moments and electronic spectra*

The effective magnetic moments reported for high spin octahedral complexes of nickel(II) are in the range 2.9–3.4 B.M., while for the tetrahedral nickel(II) complexes, the values range from 3.5 to 4.0 B.M. (19). Nickel(II) complexes, in this paper, (Table 3) show μ_{eff} values between 2.88–3.12 B.M. corresponding to two unpaired electrons in octahedral Nickel(II) complexes generally show three bands in octahedral environment corresponding to the transitions $^3A_{2g}(F) \rightarrow {}^3T_{2g}\ (F)\ (\nu_1), \rightarrow {}^3T_{1g}\ (F)\ (\nu_2)$ and $^3T_{1g}(P)\ (\nu_3)$ (21). In the spectra of $[Ni(NH_3)_6]^{2+}$, these bands have been reported at 10700, 17540 and 28170 cm^{-1}, respectively (22). The present complexes also show above three transitions in the region 10205–10825 $cm^{-1}(\nu_1)$, 15625–16825 $cm^{-1}(\nu_2)$ and 26630–28570 $cm^{-1}(\nu_3)$ suggesting octahedral geometry for all the complexes. Ligand field parameters (10Dq, B, β, β° and LFSE) have also been calculated by the procedure laid down by Lever (22). Energy of the first absorption band is taken to be equal to 10 Dq. The low values of Racah parameter, B (691–905 cm^{-1}) compared to the free ion value of 1041 cm^{-1} indicate significant covalent character in the complexes. The nephelauxetic ratio β (0.664–0.869) and other parameters also support some covalent character in the metal ligand bond.

3.2. *IR spectra*

All the ligands (abh, ainh, ash, aah, phabh, phainh, phash and phaah) show broad bands in the region 3200–3500 cm^{-1}due to ν(NH). In the complexes these bands either occur nearly at the same wave number or are slightly shifted from their positions to a higher wave number. This indicates that the >NH group does not participate in bonding (23). A broad band in the same region may also indicate ν(OH) due to the presence of OH group in some of the complexes.

A shift to lower wave number in amide I (12–23 cm^{-1}) and amide II (13–30 cm^{-1}) and a shift to higher wave numbers in the amide III band (6–14 cm^{-1}) in the spectra of all the complexes (Table 4) compared to those of the ligands indicates coordination through carbonyl oxygen (24). In the complexes, ν(C=N) bands appear at a lower frequency (10–25 cm^{-1}) than those observed in the ligands, indicating the coordination through nitrogen atom of the azomethine (>C=N=) group to the metal (9). ν(N=N) observed between 975 and 990 cm^{-1} in the ligands shifts to higher frequency by 15–35 cm^{-1} in the complexes, indicating the coordination of one of the nitrogen atom of the N=N group (25). In the thiocyanate complexes ν(CN), ν(CS) and δNCS are diagnostic of the nature of SCN bonding. The strong bands in the ranges 2126–2152 cm^{-1} and 2080–2092 cm^{-1} in all the complexes can be assigned to ν(CN) of a bidentate bridged SCN group. ν(CS) modes appearing at 731–756 cm^{-1} also support the above type of thiocyanate bonding (26).

Table 7A. Antifungal activity of ligands and their complexes

	% Inhibition of spore germination								
	Rizoctonia sp. (mg/mL)			*Aspergillus sp. (mg/mL)*			*Stemphylium sp. (mg/mL)*		
Compounds	*0.5*	*1.0*	*1.5*	*0.5*	*1.0*	*1.5*	*0.5*	*1.0*	*1.5*
abh	46	64	80	23	40	47	78	80	89
ainh	60	94	95	34	36	38	67	73	85
ash	62	69	79	33	39	44	58	64	79
aah	39	77	84	32	40	48	82	84	86
phabh	44	45	78	34	64	71	61	62	64
phainh	76	92	95	35	60	66	71	89	95
phash	67	71	82	36	40	48	75	83	84
phaah	33	61	65	25	27	30	57	75	85
$Ni[Ag(SCN)_2]_2 \cdot$abh	70	82	92	23	42	58	79	84	92
$Ni[Ag(SCN)_2]_2 \cdot$ainh	72	95	96	34	37	41	74	76	88
$Ni[Ag(SCN)_2]_2 \cdot$ash	83	87	96	35	42	48	61	67	86
$Ni[Ag(SCN)_2]_2 \cdot$aah	78	79	86	42	52	67	84	86	87
$Ni[Ag(SCN)_2]_2 \cdot$phabh	61	72	78	48	64	82	61	68	71
$Ni[Ag(SCN)_2]_2 \cdot$phainh	84	92	98	44	72	87	74	92	96
$Ni[Ag(SCN)_2]_2 \cdot$phash	71	83	90	51	62	72	83	86	91
$Ni[Ag(SCN)_2]_2 \cdot$phaah	68	88	90	35	47	58	66	76	90

3.3. *Thermal analyses (TGA and DTA)*

Thermal studies on $Ni[Ag(SCN)_2]_2$.ash complex show that the complex is highly stable and shows no weight loss up to 250°C (Table 5). Between 250–330°C, the complex appreciably loses weight due to the decomposition of ligand molecules. The DTA curve show significant heat liberation during ligand decomposition. The weight of the complex observed between 330–370°C corresponds to $Ni(NCS)_2 + Ag_2S$ as a result of decomposition of AgSCN. Between 370–505°C, it further decomposes exothermically and the final residue obtained at 505°C corresponds to $NiS + 2Ag$.

3.4. *X-ray diffraction studies*

The X-ray powder diffraction patterns for $Ni[Ag(SCN)_2]_2 \cdot$ash and $Ni[Ag(SCN)_2]_2 \cdot$phainh complexes

Table 7B. Antibacterial activity of ligands and their complexes

	Diameter of inhibition zone (in mm)		*%Activity Index*		*Diameter of inhibition zone (in mm)*		*% Activity Index*	
	Clostridium sp. (mg/mL)				*Pseudomonas sp. (mg/mL)*			
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
$Ni[Ag(SCN)_2]_2 \cdot$abh	5	6	35.7	37.5	4	6	22.2	33.3
$Ni[Ag(SCN)_2]_2 \cdot$ainh	6	7	42.8	43.8	5	7	27.8	38.9
$Ni[Ag(SCN)_2]_2 \cdot$ash	5	7	35.7	43.8	3	6	16.7	33.3
$Ni[Ag(SCN)_2]_2 \cdot$aah	7	9	50.0	56.3	7	9	38.9	50.0
$Ni[Ag(SCN)_2]_2 \cdot$phabh	7	8	50.0	50.0	6	8	33.3	44.4
$Ni[Ag(SCN)_2]_2 \cdot$phainh	8	10	57.1	62.5	8	9	44.4	50.0
$Ni[Ag(SCN)_2]_2 \cdot$phash	6	8	42.8	50.0	7	8	38.9	44.4
$Ni[Ag(SCN)_2]_2 \cdot$phaah	10	11	71.4	68.8	9	11	50.0	61.1
Ampicillin (standard)	14	16	100.0	100.0	18	18	100.0	100.0

were recorded and successfully indexed (Table 6) by using Ito's method (27) and the lattice constants calculated as follows:

$$\mathrm{Ni[Ag(SCN)_2]_2} \cdot \mathrm{ash},\ a = 5.93,\ b = 5.93 \text{ and } c = 5.34\text{Å},$$
$$\mathrm{Ni[Ag(SCN)_2]_2} \cdot \mathrm{phainh},\ a = 7.57,\ b = 6.66 \text{ and } c = 6.33\text{Å}$$

The above constants 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*

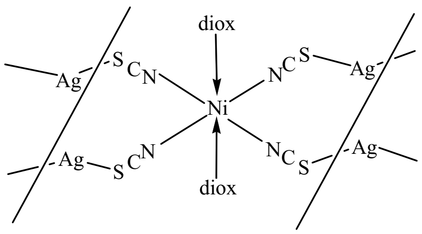
The experimental antifungal data (Table 7A) indicate that the complexes show a fair degree of activity against *Rizoctonia sp.*, *Stemphylium sp.* and *Aspergillus sp.* at 0.5, 1.0 and 1.5 mg/mL concentration. The metal complexes are appreciably more active than the ligands (28,29). Their activity is enhanced at the higher concentration. Among all the ligands, phainh shows the highest activity (95%) against *Rizoctonia sp.*, and *Stemphylium sp.* at 1.5 mg/mL concentration. Similarly, $\mathrm{Ni[Ag(SCN)_2]_2}$.phainh shows the highest activity (98, 87, and 96%) against *Rizoctonia sp.*, *Aspergillus sp.* and *Stemphylium sp.,* respectively among all the complexes at the concentration of 1.5 mg/mL. The complexes generally vary in their antifungal activity in the following order of fungal species.

Rizoctonia sp. > *Stemphylium sp.* > *Aspergillus sp.*

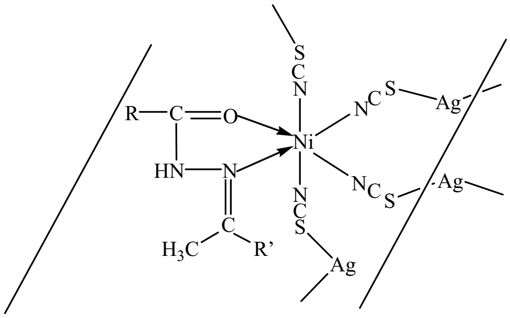
The toxicity of the complexes can be related to the strength of the metal-ligand bond, besides other factors such as size of the cation, receptor sites diffusion and a combined effect of the metal and ligands for inactivation of the biomolecules.

3.5.2. *Antibacterial activity*

The antibacterial activity data of the complexes (Table 7B) show a moderate activity against *Clostridium sp.* (Gram +ve) and *Pseudomonas sp.* (Gram −ve) (30–32). The activity generally increases with increasing the concentration of the complexes (33). The metal complexes are more effective against *Clostridium sp.* than *Pseudomonas sp.* The activity of the complexes has been compared with the activity of a common standard antibiotic Ampicillin and % Activity Index has been calculated for the complexes. The % Activity Index data indicate the highest activity (68.8 and 61.1%) for $\mathrm{Ni[Ag(SCN)_2]_2}$.phaah complex against both the bacteria at the concentration of 2.0 mg/mL among all metal complexes.



(a) Structure of $\mathrm{Ni[Ag(SCN)_2]_2}$.2diox



(b) Structure of $\mathrm{Ni[Ag(SCN)_2]_2}$.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, ainh, ash and aah
= HOC_6H_4 for phabh, phainh, phash and phaah

Fig. 1. Proposed structures of the complexes.

4. Conclusions

Ag(I) is a soft metal ion and prefers highly polarizable sulphur donor ligands to nitrogen and oxygen donor ligands for bonding. However, Ni(II) is a borderline metal ion capable of binding with either ends of a SCN group. The infrared spectral studies on $\mathrm{Ni[Ag(SCN)_2]_2}$.2diox indicate that the sulfur end of the SCN group is linked to Ag(I) and nitrogen end to Ni(II). The above studies suggest a polymeric thiocyanate bridged 6-coordinate octahedral structure (Figure 1) for the precursor complex $\mathrm{Ni[Ag(SCN)_2]_2}$.2diox. In this complex, two solvent molecules (dioxane) are weakly coordinated with the nickel(II) ion. On reaction with comparatively stronger bidentate acylhydrazone ligands, both the dioxane molecules are easily replaced and more stable polymeric complexes are formed. The complexes show exothermic ligand decomposition above 250°C. All the metal complexes exhibit significant and better antifungal and antibacterial activity than the parent ligands.

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