

Thiocyanato bridged bimetallic complexes (M-SCN-Co): Synthesis, characterization and biological studies

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To cite this article:

Mohammad Nasir Uddin, Tania Sultana Rupa. Thiocyanato Bridged Bimetallic Complexes (M-SCN-Co): Synthesis, Characterization and Biological Studies. *Modern Chemistry*. Special Issue: Synthesis and Microbial Screening of Coordination and Organic Compounds. Vol. 3, No. 1-1, 2015, pp. 1-6. doi: 10.11648/j.mc.s.2015030101.11

Abstract: A number of bimetallic thiocyanato-bridged complexes of cations $[M(NH_2X)_6]^{2+}$ and $[M(en)_3]^{2+}$ with anions $[Co(NCS)_4]^{2-}$ are prepared. Their structure has been investigated in terms of FT-IR, ^{13}C NMR and UV-vis spectroscopy, metal analysis, magnetic and conductance studies. The complexes are proposed to have the following compositions, $[M(NH_2X)_5][Co(NCS)_4]$ and $[M(en)_2][Co(NCS)_4]_n$ (where $M=Cu, Ni, Zn, Cd$; $X=H, Ph$; $en=ethylenediamine$). The general feature results from i. a combination of the bridging thiocyanate ligand, ii. the distorted environments of cobalt(II) and iii. regular octahedral geometry of cations. The antibacterial activity of the prepared complexes against the gram positive, *Bacillus cereus* and gram negative *Salmonella typhi*, *Pseudomonas aeruginosa*, *Escherichia coli* pathogens has also been investigated.

Keywords: Bimetallic Thiocyanato-Bridged Complexes, Cobalt(II), Ethylenediamine, Antibacterial Properties

1. Introduction

Binding mode sensitivity of thiocyanate ion has attained great interest in recent years. The linear triatomic pseudohalide, SCN^- , is an ambidentate ligand with two donor atoms, which may coordinate through either S or N atom or both. In coordination polymers, a thiocyanate ion must act as a rigid bridged ligand and link a pair of metal centers [1,2]. The thiocyanate moiety was reported to have an ability to modify the biochemical behaviour when present in mixed ligand coordination complexes [1,3]. The study of complexes which contain bridged dissimilar metal ions, and especially their magnetic studies contribute valuable information about the interaction between metal centres in such complex systems. From the investigation it is evident that these complexes have tremendous character. The literature covering an analogous system, in which the thiocyanate group plays the role of a bridging ligand, is much scarcer.

Bimetallic thiocyanate ligand based single crystals of $MnHg(SCN)_4$ and $CdHg(SCN)_4$ or the complexes of molecular formula $[MM'(SCN)_4(L)]$ [$M = Co^{2+}$, $M' = Cd^{2+}$, Hg^{2+} ; $L=N$, N' -bis(benzylidene)-1,2, phenylenediamine Schiff base] have been reported [1,4]. The heteronuclear $[Hg(SCN)_3Cu(en)_2]NO_3$ complex [$en=1,2$ -ethandiamine and $1,10$ -phen= $1,10$ -phenanthroline] has been synthesized [5].

Based on the bridging function of thiocyanato group two complexes formulated as, $[\{ (Cu(L)_2OH) \} \{ Cr(NCS)_6 \} \cdot H_2O]$, where $L= 2,2$ -bipyridine (bpy) and $1,1,4,7,7$ -pentamethyldiethylenetriamine (PMDT), were reported [6].

Cadmium(II) complexes, $[Cd(\mu-SCN)_2(L^1)_2]$, $[Cd(\mu-SCN)_2(L^2)]$ and $[Cd(NCS)(\mu-SCN)(L^3)]_2$, have been synthesized by reacting cadmium acetate/ NH_4SCN with 4-amino-pyridine (L^1), $C_5H_4N-C(CH_3)=NNH_2$ (L^2), and $C_5H_4N-C(CH_3)=N-CH_2-CH_2-N(C_2H_5)_2$ (L^3), respectively, in methanol [7]. A series of heterobinuclear, thiocyanato-bridged complexes of copper(II) and nickel(II) of macrocyclic ligands having the composition $[ML]_x[M'(NCS)_{4/6}]_y$ [$M=Cu, Ni$, $M'=Ni, Co, Cr, Fe$; $L=5,12$ -dimethyl-[14]-1,4,8,11-tetraazacyclotetradeca-4,11-diene and 5,7,12,14-tetramethyl-[14]-1,4,8,11-tetraazacyclotetradeca-4,11-diene] have been characterized by variable-temperature magnetic susceptibility [2]. A few heterometallic compounds of the type $[CuL]_3[Cr(NCS)_6]_2 \cdot nH_2O$ ($L=2,2$ -bipyridine, $n=0$; $L=o$ -phenanthroline, $n=1$; $L=$ diethylenetriamine, $n=1$); $[CuL_4]_3[Cr(NCS)_6]_2 \cdot nH_2O$; ($L=imidazole$, $n=2$); $[Cu(en)_2Mn(NCS)_4(H_2O)_2]_n$ ($en=$ ethylenediamine) [8-10] have been reported. Bimetallic complexes of the type $[ML_x][M'Ly]$ have been reported by authors where, $M=Cu, Cd, Ni, Co, Zn$ and $M'=Hg$, $L_x=$ ethylenediamine, aniline, NH_3 and $Ly=I^-, SCN^-$ [11]. In continuation of our research

on heteronuclear bimetallic complexes, the synthesis of thiocyanato-bridged heteronuclear complexes containing $[\text{Ni}(\text{NCS})_4]^{2-}$ anionic group has been reported. The elemental analyses, FT-IR, NMR, electronic spectra, magnetic and conductivity studies indicate that the reaction between $[\text{Ni}(\text{NCS})_4]^{2-}$ and metal(II) complex cations showed bridging properties of thiocyanato ions. Antibacterial activities of the prepared complexes were investigated.

2. Experimental

2.1. Chemicals

Ethylenediamine, aniline, methanol, chloroform and N, N-dimethylformamide (DMF) were obtained from Aldrich Chemical Company Ltd. Ammonium nitrate and Nickel chloride (crystal), Ammonium thiocyanate, Cobalt(II) sulphate were obtained from M/S Merck (Germany). Perchloric acid, nitric acid, sulphuric acid and ammonia were obtained from BDH Chemicals Ltd. All chemicals except solvent were used as received. Solvents were dried by standard methods and distilled under an inert atmosphere.

2.2. Analytical Methods

The analyses of the metal contents of the prepared complexes were obtained by Atomic Absorption Spectrophotometer (model Thermo Scientific ICE-3000) from Biological Laboratory of Chittagong University, Chittagong. The Infrared spectra of the prepared complexes were obtained by FTIR spectrophotometer (Model- 8900, Shimadzu, Japan) using KBr as the matrix in the range 400-4000 cm^{-1} from research laboratory of the Department of Chemistry, C.U. Chittagong. Polystyrene was used as the standard to calibrate the spectrophotometer. Electronic absorption spectra were run on Shimadzu UV-Visible

Recording Spectrophotometer (Model-1800) using 1 cm cells. An electro thermal melting point apparatus was used for the determination of the melting or decomposition points of the complexes. Using N, N-dimethylformamide (DMF) as the solvent, the solutions of the complexes (of the order of 10^{-3} M) were used for conductivity measurements. Conductivity measurement was performed on a Philips Conductivity Meter (Model-HI 9255). Conductivity measurement of an electrolytic solution involves measuring of the electrical resistance of that solution at 25°C. Magnetic susceptibility values of some of the prepared complexes were determined using the Magnetic Susceptibility Balance, (Sherwood Scientific).

2.3. Preparation of Bimetallic Complexes

$[\text{Co}(\text{SCN})_4]^{2-}$: 3 mmol (0.81 g) of cobalt (II) sulphate was dissolved in about 60 mL of water in a beaker. A slight excess of NH_4SCN was added drop wise. A violet solution of $[\text{Co}(\text{SCN})_4]^{2-}$ was formed.

$[\text{M}(\text{NH}_2\text{X})_6]^{2+}$ or $[\text{M}(\text{en})_3]^{2+}$: In another beaker, 3 mmol of metal chloride was dissolved in about 50 mL of water. An excess amount of concentrated ammonia, aniline or ethylenediamine was added to it drop wise. The mixture was heated to boil for about 12-15 minutes.

Bimetallic Complexes: Two solutions were mixed together in their hot states. The mixture was stirred for some time and allowed to cool with frequent stirring to complete the reaction. The precipitate was formed almost immediately and the solid product formed was filtered off and washed with water and dried over calcium chloride. Complexes given in table 1 were prepared following the procedure mentioned above. Their melting point, colour, yield, metal content, magnetic and conductance values of complexes in table 1.

Table 1. Physical properties, metal content, magnetic and conductance values of complexes.

Complexes	Color	Yield	m. p. °C	% of Co (Calc.)	μ_{eff} B.M.	λ_m ohm ⁻¹ cm ² mol ⁻¹
$[\text{Cu}(\text{NH}_3)_5][\text{Co}(\text{SCN})_4]$	Blue	90%	146	13.32 (13.54)	0.98	123
$[\text{Cu}(\text{en})_2][\text{Co}(\text{SCN})_4]$	Black	95%	200	12.42 (12.11)	1.83	114
$[\text{Ni}(\text{en})_2][\text{Co}(\text{SCN})_4]$	Radish	95%	>202	12.55 (12.05)	1.25	48
$[\text{Zn}(\text{en})_2][\text{Co}(\text{SCN})_4]$	Yellowish	95%	186	12.37 (11.89)	1.59	127
$[\text{Ni}(\text{anil})_5][\text{Co}(\text{SCN})_4]$	Blue	95%	> 210	6.98 (7.52)	0.83	22
$[\text{Cu}(\text{anil})_5][\text{Co}(\text{SCN})_4]$	Green	95%	150	6.94 (6.48)	2.68	35
$[\text{Zn}(\text{anil})_5][\text{Co}(\text{SCN})_4]$	Violet	90%	206	6.92 (7.45)	2.56	71
$[\text{Cd}(\text{anil})_5][\text{Co}(\text{SCN})_4]$	Pink	95%	> 210	6.56 (7.05)	1.46	53

2.4. Test for of Antimicrobial Evaluation

Synthesized complexes were screened by the agar well diffusion method for the test of their antibacterial activity against different types of bacteria, gram positive- *Bacillus cereus* and gram negative- *Salmonella typhi*, *pseudomonas aeruginosa*, *Escherichia coli* regarded as pathogen to man. All media and bacteria suspension were prepared using a suitable method [11]. The in-vitro evaluation of antimicrobial activities was performed according to the diffusion technique. The bacteria were grown in nutrient broth at 37°C for 24 hours. The complexes were tested using diffusion on solid

media. Sterile (5 mm) diameter sensitivity paper disc were impregnated with concentration of dimethylformamide (DMF) and their bimetallic complexes at concentration of 50 $\mu\text{g cm}^{-3}$ and placed in the nutrient agar. The plates were then incubated for 24 hours. Additionally antibiotic discs for cephalosporin were tested as positive control. The results were recorded by measuring the growth inhibition (% zones of inhibition) surrounding the disc.

3. Results and Discussion

Bimetallic mixed-ligand complexes were prepared by

using water as the solvent. Complexes were prepared by the reaction of cationic metal complex with an anionic metal complex in the molar ratio 1:1. All the complexes were obtained almost immediately after mixing of the component metal complex solutions. Due to the presence of aniline oily layer was formed during preparation of $[M(\text{aniline})_6]^{2+}$ complex, hence mixture was heated to dissolve the oily layer. After that, $[(\text{Co}(\text{SCN})_4)^{2-}]$ solution was added. Then the mixture was heated again for about one hour at low temperature. The precipitate formed was separated out by filtration and preserved in desiccators. All the complexes are insoluble in chloroform. All complexes are highly soluble in DMSO and DMF though some of them are moderately soluble in methanol. The metal analysis data indicate formation of the desired complexes with 1:1 molar ratio of the complex cation and the complex anion. Complex, $[\text{Hg}(\text{SCN})_3\text{Cu}(\text{en})_2]\text{NO}_3$ ($\text{en}=1,2$ -ethandiamine) was synthesized by the reaction of $[\text{Cu}(\text{en})_2(\text{NO}_3)_2]$ and $[\text{Hg}(\text{SCN})_4]^{2-}$ in aqueous media [5]. The slow dissociation of $[\text{Ni}(\text{en})_3]^{2+}$ into $[\text{Ni}(\text{en})_2]^{2+}$ or $[\text{Hg}(\text{SCN})_4]^{2-}$ into $[\text{Hg}(\text{SCN})_3]^-$ leads to the growth of crystals¹². The present complexes having the composition, $[\text{M}(\text{NH}_2\text{X})_5][\text{Co}(\text{NCS})_4]$ or $[\{\text{M}(\text{en})_2\}\{\text{Co}(\text{NCS})_4\}]_n$ (where $\text{M}=\text{Cu}, \text{Ni}, \text{Zn}, \text{Cd}$; $\text{X}=\text{H}, \text{Ph}$) were prepared by the reaction of $[\text{M}(\text{NH}_2\text{X})_6]^{2+}$ or $[\text{M}(\text{en})_3]^{2+}$ with anions $[\text{Co}(\text{NCS})_4]^{2-}$. When $[\text{M}(\text{NH}_2\text{X})_6]^{2+}$ or $[\text{M}(\text{en})_3]^{2+}$ has slowly been dissociated into $[\text{M}(\text{NH}_2\text{X})_5]^{2+}$ or $[\text{M}(\text{en})_2]^{2+}$ during the bimetallic complex formation.

3.1. Infrared Spectra

The infrared spectra for the present compounds taken in the range 400-4000 cm^{-1} help to indicate regions, $\nu_{\text{N-H}}$, $\nu_{\text{C-N}}$, $\nu_{\text{C-C}}$, $\nu_{\text{C-S}}$, $\nu_{\text{S-C=N}}$ and $\nu_{\text{M-N}}$, of absorption. The

characteristic band assignments for the prepared complexes are presented in Table 2. Figure 1 shows a representative IR Spectrum of complex, $\{[\text{Zn}(\text{An})_5][\text{Co}(\text{SCN})_4]\}$. The interest in the IR spectrum of the compound lies mainly in the bands due to the NCS groups. The thiocyanate ion has three fundamental modes of vibration: the C-N stretch, ν_1 ; the doubly degenerated ν_2 and the C-S stretch, ν_3 . These vibrational modes occur at different frequency range. The N-bonded thiocyanate group exhibits $\nu_{\text{C-N}}$ in the regions of 2020-2096 cm^{-1} and the S-bonded thiocyanate group exhibits $\nu_{\text{C-N}}$ above 2100 cm^{-1} [2]. Appearance of strong $\nu_{\text{C-N}}$ bands in the regions 2020-2096 and 2100 cm^{-1} in the present complexes is a good indication of M-SCN-M coordination of the thiocyanate group. This band gives a clear split, which proves the presence of thiocyanato ions in bridging and terminal positions [6]. The complex having the formula, $(\text{CuL}_1)[\text{Co}(\text{NCS})_4].3\text{H}_2\text{O}$, [where L_1 is 5, 12-dimethyl-[14]-1,4,8,11-tetraazacyclo tetradeca-4,11-diene] exhibits two bands near 2000 cm^{-1} corresponding to the $\nu(\text{NCS})$ stretching mode. Additionally, bands above 2100 cm^{-1} are observed indicating the presence of a bridging thiocyanate group [2]. The presence of two bands in between 2105-2160 cm^{-1} clearly indicates the coordination of SCN- anion with bridging modes [1]. The weak band corresponding to $\nu(\text{C-S})$ vibration appears at 771 cm^{-1} , and the ν_{NCS} bending mode is observed at 480 cm^{-1} as a shoulder [2]. The peaks at 3442 and 3255 cm^{-1} were assigned to the stretching vibrations of amine group [5,7]. FTIR spectra also show the very broad band at 360 cm^{-1} with shoulders due to superposition of bands arising from $\nu_{\text{C-N}}$ and $\nu_{\text{Cu-N}}$ vibrations. The assignment of $\nu_{\text{Cu-S}}$ vibrations is only tentative because of low intensity of these bands [6].

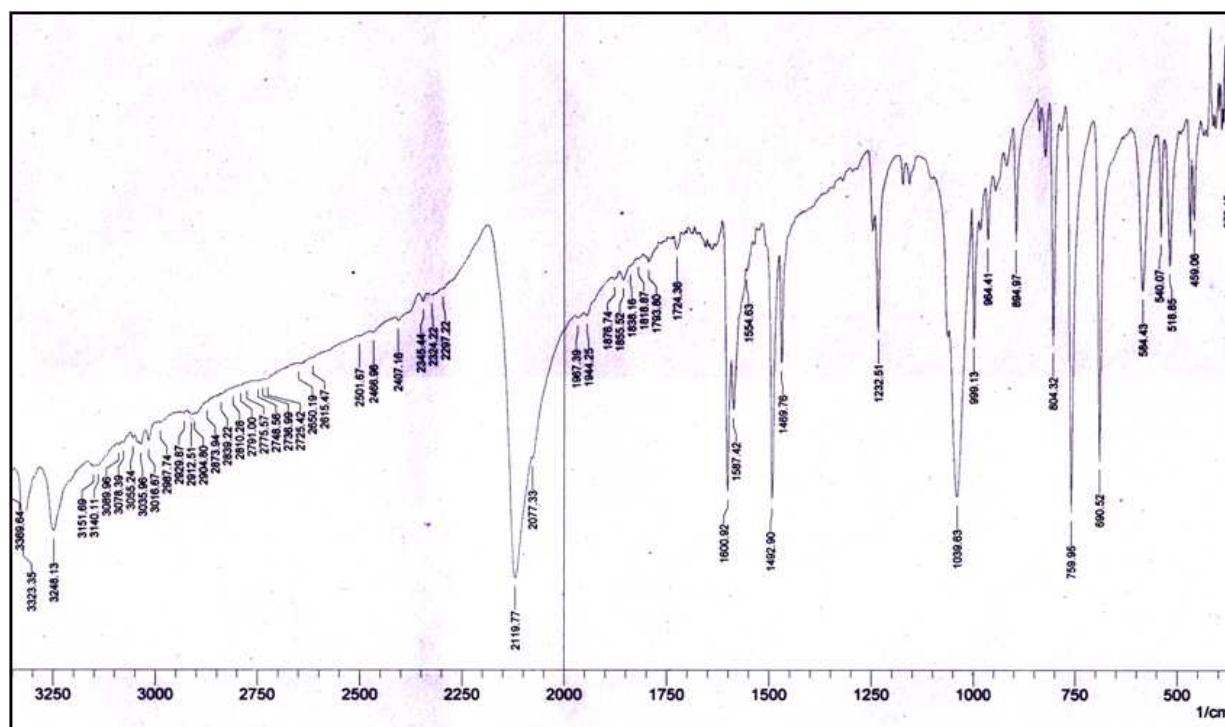


Figure 1. Representative IR Spectrum of complex, $\{[\text{Zn}(\text{An})_5][\text{Co}(\text{SCN})_4]\}$

Table 2. Spectral (IR, UV-vis) data of the prepared complexes.

Code No.	Complexes	ν_{N-H}	ν_{C-C}	ν_{C-N}	$\nu_{C\equiv N}$ (cyanide)	ν_{C-S}	$\nu_{S-C\equiv N}$	ν_{M-N}	electronic spectral data (DMSO)
R ₉	[Cu(NH ₃) ₅][Co(SCN) ₄]	3232w 3307w			2077w	669s 730sh	669s	445w	737, 385,283
R ₁₀	[Cu(en) ₂][Co(CNS) ₄]	3282w 3292w	1055w 1093w	1458m	2065 vs 2113sh	761w 775w	580 ms	441w	688, 477,274
R ₁₁	[Ni(en) ₂][Co(SCN) ₄]	3246w 3271w	1056ms 1080sh	1361w 1465w	2077s 2117s	770sh 792ms	592ms	486w	517,323,261
R ₁₂	[Zn(en) ₂][Co(SCN) ₄]	3261ms 3311ms	1008s 1070s	1327w	2100ms 2112ms	763ms	567vs	459ms	514,329,264
R ₁₃	[Ni(anil) ₅][Co(SCN) ₄]	3255ms 3325w	1047s 1234w	1469w	2123sh 2133s	775sh 804w	690s	397s	909,297,261
R _{6,14}	[Cu(anil) ₅][Co(SCN) ₄]	3253ms 3325ms	999w 1047ms	1469w 1492s	2121s 2131s	780sh 804w	690ms	520w	500,395,305
R ₁₅	[Zn(anil) ₅][Co(SCN) ₄]	3248ms	999w 1039s	1232w 1260sh	2077sh 2119s	759s 804ms	690vs	518ms	908,540,295,264
R ₁₆	[Cd(anil) ₅][Co(SCN) ₄]	3253w	989w 1006w	1232w 1260sh	2071sh 2198vs	690s 758vs	690s	513ms	908,298,264

* vs = very strong; s = strong; ms = medium strong; m = medium; w = weak; vw = very weak; sh = shoulder

For all the complexes, the presence of ν_{M-N} and ν_{M-S} vibration in the same region confirms coordination and N-donor character of the ligands to the metal ion. Furthermore, the presence of bands in $\delta(NCS)$, $\nu(C-S)$, $\nu(M-N)$ and $\nu(M'-S)$ regions are diagnostic for the nature of thiocyanate bonding [1].

3.2. ¹³C NMR

¹³C nmr of the complex [Zn(aniline)₅][Co(NCS)₄] was obtained. A splitting peak at (δ) 123.5 indicates the bridging thiocyanate and that multiplet at (δ) 135 comply with phenyl group of aniline [12].

3.3. UV-Vis Spectra

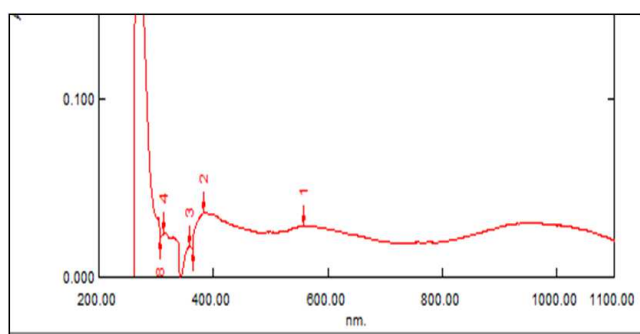


Figure 2. A representative electronics spectra of complex, {[Cd(en)₂][Ni(SCN)₄]}

The UV-Vis spectra of all complexes were obtained in DMSO solution. In the UV-Vis spectrum of complex the first electronic absorption band observed at around 260 nm is due to the metal to ligand charge transfer (MLCT). The band at around 500 nm assigned to the *d-d* transition of metal ion indicates some distortion from the perfect symmetry. The broad band at around 400 nm can be assigned to the *d-d* transition of metal ion and the broadness of the peak reveals the inherent distortion of this type of complexes from perfect symmetry [2,5]. The peaks observed below 350 nm are

assumed as due to $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ transitions. And the peaks observed at 983 nm may be assumed as due to the presence of metal tetrathiocyanate¹¹ as shown in Figure 2. UV-vis spectral data of the prepared complexes have been given in Table 2.

3.4. Magnetic Measurements

From the experimental values of magnetic measurements of some of the prepared complexes, it is found that magnetic moments of some of the mixed metal complexes are lower than the expected theoretical spin only values. The possible reason of such lower magnetic moment may be due to weak antiferromagnetic interactions in the mixed metal complex transmitted by the thiocyanato group [2]. The exchange interactions seem to be super exchange type and most likely through the thiocyanato or the thio groups. However, weak bonds and longer bond lengths may hide or prevent possibility of exchange interactions [1,2,6,10].

3.5. Conductance

The conductance values 0-60 ohm⁻¹cm²mol⁻¹ of the prepared complexes in DMSO solution corresponding to non electrolytes. The low conductance values of 60-120 ohm⁻¹cm²mol⁻¹ for the prepared complexes in DMSO solution were obtained. This suggests +2 oxidation states of the metal ions present in such complexes. The high conductance values 150> ohm⁻¹cm²mol⁻¹ of the complexes in DMSO solutions are reported having their electrolytic nature corresponding to 1:2 electrolytes¹⁴. The low conductance values corresponding to 1:1 electrolytes strongly support proposed formulation of the prepared complexes.

Magnetic, conductivity data and metal content of the prepared complexes have been given in Table 1.

4. Geometry

The crystal structure of [NiL]₃[Fe(NCS)₆]₂ (where L =

5,6,12,13-Me4-[14]-4,11-dieneN4) has established the exchange interaction between NiII and FeIII ions that is transmitted by the thiocyanate groups [15]. The environment of the FeIII ion is octahedral, while the thiocyanate groups are nearly linear. Each FeIII ion is bound to two Ni(II) ions when thiocyanate groups coordinate to the nickel(II) ions by their sulphur atom [2]. The environment of the NiII ion in $[\text{CuL}_1][\text{Ni}(\text{NCS})_6] \cdot 2\text{H}_2\text{O}$ complex is square-pyramidal, while the thiocyanate groups are nearly linear [2]. A distorted square-pyramidal structure was proposed for the complex, $(\text{CuL})[\text{Co}(\text{NCS})_4]$, ($\text{L}=\text{N-rac-(5,12-Me}_2\text{-7,14-Et}_2\text{-[14]-4,11-diene N4)}$) with four equatorial nitrogen atoms of macrocyclic ligand and one sulfur atom from the thiocyanato bridging group in an axial position. The cobalt(II) centre possesses one bridging and three non-bridging thiocyanate ligands [16]. The structure of $[\text{Cu}(\text{en})_2\text{Mn}(\text{NCS})_4(\text{H}_2\text{O})_2]_n$ (en = ethylenediamine) consists of chains in which alternating $\text{Cu}(\text{en})_2^{2+}$ and $\text{Mn}(\text{NCS})_4(\text{H}_2\text{O})_2^{2-}$ entities are bridged by thiocyanate ligands. The coordination environment is octahedral for Mn(II) and elongated octahedral for Cu(II) [9].

On the basis of the above discussion and the experimental evidences, metal analysis, spectral, magnetic and conductivity studies following geometry for the present prepared bimetallic complexes can be proposed. Bimetallic complexes are prepared by the reaction of cations $[\text{M}(\text{NH}_2\text{X})_6]^{2+}$ and $[\text{M}(\text{en})_3]^{2+}$ with anions $[\text{Co}(\text{NCS})_4]^{2-}$. The coordination geometry around the Co^{2+} ion in $[\text{Co}(\text{NCS})_4]^{2-}$ anion is distorted tetrahedral. The metal centre possesses three non-bridging and one bridging thiocyanate ligands, while the thiocyanate groups are nearly linear. The environment of the cations in $[\text{M}(\text{NH}_2\text{X})_5]^{2+}$ are octahedral when sixth coordination site is occupied by one bridging thiocyanate ligands from anion. The proposed schematic structure of the complex is presented in Figure 3.

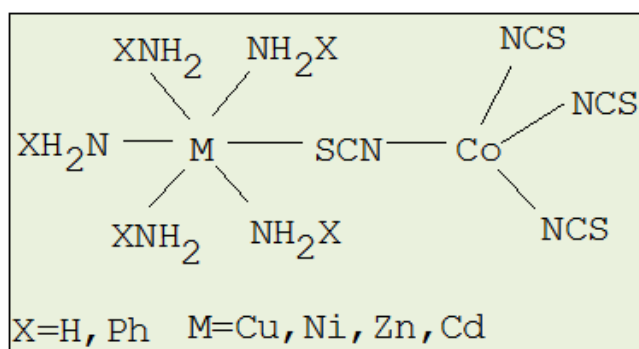


Figure 3. The proposed schematic structure of the complex, $[\text{M}(\text{NH}_2\text{X})_6][\text{Co}(\text{NCS})_4]$.

In case of $[\text{M}(\text{en})_2]^{2+}$ the environment of the metal ion is octahedral, while the thiocyanate groups are nearly linear. Each central metal ion is bound to two thiocyanate groups from neighbor anions forming a long chain polymeric structure, $[\{\text{M}(\text{en})_2\}\{\text{Co}(\text{NCS})_4\}]_n$. The thiocyanate groups coordinate to the metal ions of cations by their sulphur atom. A proposed schematic view of complex, $[\{\text{M}(\text{en})_2\}\{\text{Co}(\text{NCS})_4\}]_n$ is presented in Figure 4. The general

feature results from a combination of the presence of a bridging thiocyanate ligand and the distorted environments of the metals cobalt (II) of anions and regular octahedral geometry of cations.

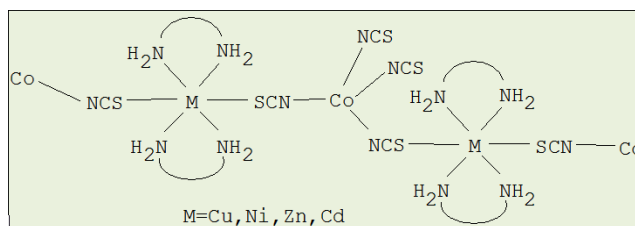


Figure 4. A proposed schematic view of complex, $[\{\text{M}(\text{en})_2\}\{\text{Co}(\text{NCS})_4\}]_n$.

5. Antibacterial Activity



Figure 5a. Zone of inhibition against *Salmonella typhi* by complexes R_9, R_{10}, R_{11} and R_{12} .



Figure 5b. Zone of inhibition against *Escherichia coli* by complexes R_9, R_{10}, R_{11} and R_{12} .

The inhibition zones of the test organisms for different complexes are presented in Figure 5. Results of the inhibition have been graphically shown in Figure 6. Complexes R_{10}, R_{12}, R_{16} are highly effective with all the tested bacteria. It is found that though $R_9, R_{11}, R_{13}, R_{15}$ are most effective against *Salmonella typhi* and *Pseudomonas aeruginosa* but totally ineffective with remaining two organisms. The complex R_{14} shows high inhibition against all tested bacteria except *Bacillus cereus*. In addition to chelation, some important factor such as nature of the metal ion, metal ion coordinating site, hydrophilicity, hypophilicity and binuclear structure may have considerable influence on the antibacterial activity. The chelate complexes may deactivate various cellular enzymes which play vital role in various metabolic pathways of these microorganisms. Other factors such as solubility, conductivity and dipole moment affected by the presence of

metal ions, may be the reasons for the increased biological activities of the metal complexes. Therefore, the antibacterial activity of the complexes can be ascribed to an intricate blend of all of the above contributions.

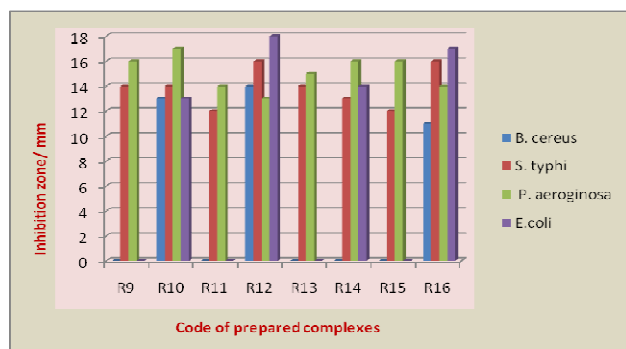


Figure 6. Results of the inhibition of the complexes against human pathogen bacteria.

6. Conclusion

The results of these analyses show that the theoretical and experimental percentages of the metal content are in a close consistence. The prepared complexes were characterized by FT-IR spectroscopy, UV-Vis spectra, magnetic and conductivity measurements. The data indicate the formation of the complexes. Conductivity measurements indicate their electrolytic nature consistence with +2 oxidation state of the metal ions present in such complexes. The magnetic measurement values indicate that some of the complexes showed antiferromagnetic interactions. The high yield of the complexes indicates good possibilities of their analytical uses to determine metal contents of some related compounds. Further works are required to exploit and ascertain such possibilities. From comparative study, the prepared complexes have been found to be quite effective against selected human pathogenic bacteria.

References

- [1] Upadhayay N., Synthesis, Characterization and Biological Studies of Some Thiocyanato-bridged Bimetallic Complexes Containing Co(II), Cd(II), Hg(II) and *N, N'*-Bis(benzylidene)-1,2-phenylene-diamine Schiff Base, *Chem. Sci. Trans.*, 2013; 2(2): 455-460.
- [2] Tomkiewicz A., Kłak J. and Mroziński J., Bimetallic complexes with macrocyclic ligands. Variation of magnetic exchange interactions in some heteronuclear thiocyanato-bridged compounds, *Materials Science-Poland*, 2004; 22(3): 253.
- [3] Shukla S. N., Nigam H. K., Upadhayay N., Khan S. and Srivastava A., *J Appl. Biosci.*, 2006, 32(1), 68.
- [4] Usha R.J., Mani J.A.M and Joseph V., Impedance analysis of bimetallic thiocyanate ligand based single crystals of $MnHg(SCN)_4$ and $CdHg(SCN)_4$, *Archives of Appl. Sci. Res.* 2012; 4(1): 638-644.
- [5] Kooti M. and Noori Z., Synthesis, characterization and luminescent properties of some of thiocyanato bridged heteronuclear polymeric complexes of mercury. *J. of Appl. Chem. Res.* 2010; 4(14): 47-52.
- [6] Dobrzańska L., Wrzeszcz G., Grodzicki A. and Rozpłoch F., Synthesis and Properties of Thiocyanato-Bridged Chromium(III)-Copper(II) Hydroxo Complexes, *Polish J. Chem.* 2000; 74: 1017-1021.
- [7] Banerjee S., Wu B., Lassahn P., Janiak C. and Ghosh A., Synthesis, structure and bonding of cadmium(II) thiocyanate systems featuring nitrogen based ligands of different denticity, *Inorg. Chim. Acta.* 2005; 358: 535-544.
- [8] Smékal Z., Březina F., Šindelář Z., Klička R. and Nádvorník M., Polynuclear complexes of chromium(III), copper(II) or nickel(II) with thiocyanate as a bridging ligand, *Transition Met. Chem.* 1997; 22: 299-.
- [9] Dobrzańska L., Wrzeszcz G., Grodzicki A. and Rozpłoch F., Synthesis and Characterization of Thiocyanato-Bridged Heteropolynuclear Chromium(III)-Copper(II) Complexes, *Polish J. Chem.* 2000, 14, 199-206.
- [10] Kou H.Z., Liao D.Z., Cheng P., Jiang Z.H., Yan S.P., Wang G.L., Yao X.K. and Wang H.G., A new one-dimensional thiocyanato-bridged bimetallic compound $[Cu(en)_2Mn(NCS)_4(H_2O)_2]_n$. Synthesis, crystal structure, and magnetic properties, *Can. J. Chem.* 1998; 76: 11021107.
- [11] Uddin M.N., Chowdhury D.A. and Islam J., Synthesis, Characterization and Antibacterial Evaluation of Some Mixed-metal Mixed-ligand Complexes, *Chiang Mai J. Sci.* 2013; 40(4): 625-635.
- [12] Uddin M.N., Akter J. and Manchur M.A., Cyano Bridged Bimetallic Compounds of the Type $M^{2+}-NC-Fe^{3+}$ ($M = Co, Ni, Cu, Zn, Cd$) Using the $[Fe(CN)_6]^{3-}$ Building Block and their Antibacterial Evaluation, *Orbital: Electron. J. Chem.* 2013; 5(4): 257-263.
- [13] Clemente-León M., Coronado E., Galán-Mascarós J.R., Gómez-García C.J., Woike Th. and Clemente-Juan J.M., Bimetallic Cyanide-Bridged Complexes Based on the Photochromic Nitroprusside Anion and Paramagnetic Metal Complexes. Syntheses, Structures, and Physical Characterization of the Coordination Compounds $[Ni(en)_2]_4[Fe(CN)_5NO]_2$, $[Fe(CN)_6] \cdot 5H_2O$, $[Ni(en)_2][Fe(CN)_5NO] \cdot 3H_2O$, $[Mn(3-MeOsalen)(H_2O)_2][Fe(CN)_5NO]$, and $[Mn(5-Brsalen)]_2[Fe(CN)_5NO]$, *Inorg. Chem.* 2001: 40: 87-94.
- [14] Raman N., Raja Y.P. and Kulandaisary A., Synthesis and characterisation of Cu(II), Ni(II), Mn(II), Zn(II) and VO(II) Schiff base complexes derived from *o*-phenylenediamine and acetoacetanilide, *Journal of Chem. Sci.* 2001; 113: 183-189.
- [15] Skorupa A., Korybut-Daszkiewicz B. and Mroziński J., Heteronuclear thiocyanate-bridged compounds of the type $(NiL)_3[M(NCS)_6]_2$ ($M=Fe(III), Cr(III)$; $L=5,6,12,13-Me_4-[14]-4,11$ -diene N_4), *Inorg. Chem. Acta.* 2002; 336: 65-70.
- [16] Skorupa A., Korybut-Daszkiewicz B. and Mroziński J., Crystal structure and magnetic properties of two heteronuclear thiocyanate bridged compounds: $(CuL)[Co(NCS)_4]$ ($L=N$ -*meso*-(5,12- Me_2 -7,14- Et_2 -[14]-4,11-diene N_4) and *N-rac*-(5,12- Me_2 -7,14- Et_2 -[14]-4,11-diene N_4)), *Inorg. Chem. Acta.* 2002; 324: 286-292.