

Bimetallic Heteronuclear Complexes Bridged With Ferrichexathiocyanate: Synthesis, characterization and antibacterial properties

Mohammad Nasir Uddin*, D A Chowdhury, Jashmin Akter

Department of Chemistry, University of Chittagong, Chittagong-4331, Bangladesh

*Corresponding email: nasircu72@gmail.com

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ABSTRACT

A number of heterobinuclear thiocyanato-bridged complexes of cations, $[M(NH_2X)_6]^{2+}$ and $[M(en)_3]^{2+}$ (where en= Ethylenediamine, X = H, Ph; M= Ni, Cu, Cd, Zn), with ferrichexathiocyanate have been prepared. The complexes have been characterized by FT-IR, ^{13}C NMR and UV-vis spectroscopy, metal analysis, magnetic and conductance studies. The composition complexes has been proposed on the basis of experimental and literature evidences. The antibacterial activity of the prepared complexes has also been investigated against the gram positive-*Bacillus cereus* and gram negative- *Salmonella typhi* and *Escherichia coli* pathogens.

Keywords: Bimetallic thiocyanato-bridged complexes, ferrichexathiocyanate ethylenediamine, antibacterial properties.

INTRODUCTION

Bimetallic species occupy an important position in modern inorganic chemistry. They play an important role in biological processes like activation of enzymes by metals [1]. Such complexes are useful in the storage and transport of active substances through membranes [2].

The linear triatomic pseudohalide thiocyanate ion, SCN⁻, an ambidentate ligand with two donor atoms, may act as a rigid bridged ligand and link a pair of metal centers through 1,1- μ -SCN, 1,1- μ -NCS or 1,3- μ -SCN configuration to satisfy the coordination number of the metal ion [3,4]. Based on the bridging function of the thiocyanato group, two novel complexes formulated as $[\{(Cu(bpy)_2)OH\}(Cr(NCS)_6)].H_2O$, (bpy= 2,2'-bipyridine) and $[\{(Cu(PMDT))_2OH\}(Cr(NCS)_6)].H_2O$ (PMDT = 1, 1, 4, 7, 7-pentamethyl diethylenetriamine) have been synthesized [5]. Francese *et al.* [6] used a macrocyclic copper(II) complex $Cu(cyclam)^{2+}$ (cyclam=1,4,8,11-tetraazacyclotetradecane) to obtain a heterometallic system bridged by a thiocyanate group. Xiang *et al.* [7] prepared the $[Zn(bipy)_3][Zn(SCN)_4]$ complex and characterized by X-ray diffraction analysis. A series of heterobinuclear thiocyanato-bridged complexes including $(CuL_1)_3[Fe(NCS)_6]_2 \cdot 3H_2O$ and $(NiL_2)_3[Fe(NCS)_6]_2 \cdot 2H_2O$ (where $L_1 = 5, 12$ -dimethyl-[14]-1,4,8,11-tetraazacyclotetradeca-4,11-diene; $L_2 = 5,7,12,14$ -tetramethyl-[14]-1,4,8,11-tetraazacyclotetradeca-4,11-diene) have been characterized by Tomkiewics *et al.* [8] where copper(II) and nickel(II) are connected with two different thiocyanate groups.

The literature survey reveals that very little work has been done on the coordination

chemistry of heteronuclear complexes though such complexes show some exceptional structural behavior especially when one of the metals is iron. In our laboratory different aspects are attempted to synthesize and characterize the heteronuclear complexes having $[\text{Co}(\text{NCS})_4]^{2-}$, $[\text{Ni}(\text{NCS})_4]^{2-}$ and $[\text{Hg}(\text{NCS})_4]^{2-}$ anionic units [9-11]. In continuation of our research the synthesis of thiocyanato-bridged heteronuclear complexes with $[\text{Fe}(\text{NCS})_6]^{3-}$ unit have been reported herein. The antibacterial activities of some of the prepared complexes also have been investigated.

MATERIALS AND METHODS

Chemicals

Ethylenediamine, aniline, methanol, chloroform and N, N-dimethylformamide (DMF) were obtained from Aldrich Chemical Company Ltd. Ammonium nitrate and potassium ferric hexathiocyanate were obtained from M|S Merak (Germany). 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. Using N, N-dimethylformamide (DMF) as the solvent, solutions of the complexes (of the order of 10^{-3} M) were used for conductivity measurements.

Analytical Methods

The analyses of the metal contents of the prepared complexes were done 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 $400\text{-}4000\text{ cm}^{-1}$ 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. Conductivity measurement was performed on a Philips Conductivity Meter (Model-HI 9255). Determination of conductivity of an electrolytic solution involves measuring of the electrical resistance of that solution at a particular temperature, usually 25°C . Magnetic susceptibility values of the prepared complexes were determined using the Magnetic Susceptibility Balance, (Sherwood Scientific) from the Laboratory of Inorganic Chemistry, Chittagong University, Bangladesh.

Preparation of Bimetallic Complexes, $[\text{M}(\text{L})_x]_3[\text{Fe}(\text{NCS})_6]_2$

Preparation of $[\text{Fe}(\text{NCS})_6]^{3-}$

A 3 mmol (0.81 g) ferric chloride (FeCl_3) was dissolved in about 60 mL water in a beaker. Then a slight excess NH_4SCN was added dropwise. A clear solution of $[\text{Fe}(\text{NCS})_6]^{3-}$ was formed.

$[\text{M}(\text{L})_x]^{2+}$ solution

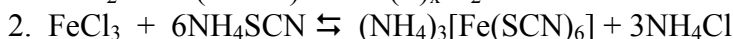
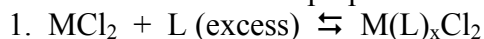
In another beaker, 2 mmol (0.589 g) of water soluble metal salts, chloride, nitrate or sulphate was dissolved in 50 mL water. An excess amount of conc. ammonia, aniline or ethylenediamine (en) was added to it drop wise. The mixture was heated to boil for about 12-15 minutes.

$[\text{M}(\text{L})_x]_3[\text{Fe}(\text{NCS})_6]_2$

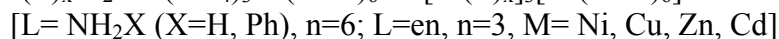
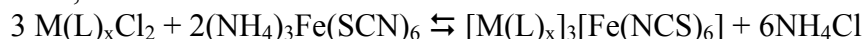
Both the solutions were mixed together in their hot states. The mixture was stirred for

sometimes and allowed to cool with frequent stirring. The precipitate was formed almost immediately and the solid product formed was filtered off and washed with water and dried over calcium chloride.

A possible reaction for the preparation of mixed metal complexes



Then from 1 and 2,



The bimetallic complexes prepared by the procedure as stated above are given in Table 1.

Test For of Antimicrobial Evaluation

Some of the synthesized complexes were screened for their antibacterial activity against different types of bacteria, gram positive- *Bacillus cereus* and gram negative- *Salmonella typhi*, *Escherichia coli* regarded as pathogen to man, by the agar well diffusion method [12]. All media and bacteria suspension were prepared using a suitable method. 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 dimethyl formamide (DMF) and their bimetallic complexes at concentration of 50 µg cm⁻³ and placed in the nutrient agar. The plates were then incubated for 24 hours. The results were recorded by measuring the growth inhibition (% zones of inhibition) surrounding the disc.

Table 1. Physical properties of prepared complexes.

| Sl. No. | Complexes | Color | Yield % | m. p. °C (d) | % Metal content (cal.) | μ _{eff} (B.M.) | λ _m ^o ohm ⁻¹ cm ² .mol ⁻¹ |
|---------|----------------------------------------------------------------------------------------|------------|---------|--------------|------------------------|-------------------------|----------------------------------------------------------------------------------|
| 1 | [Ni(NH ₃) ₆] ₃ [Fe(SCN) ₆] ₂ | Drak green | 95 | >200 | | 2.83 | 8 |
| 2 | [Cu(NH ₃) ₆] ₃ [Fe(SCN) ₆] ₂ | Purple | 95 | >200 | 14.41 (14.59) | 2.38 | 215 |
| 3 | [Zn(NH ₃) ₆] ₃ [Fe(SCN) ₆] ₂ | White | 95 | >200 | | 2.99 | 73 |
| 4 | [Cd(NH ₃) ₆] ₃ [Fe(SCN) ₆] ₂ | White | 95 | 210 | | 1.33 | 292 |
| 5 | [Ni(en) ₃] ₃ [Fe(SCN) ₆] ₂ | Violet | 95 | >200 | 7.27 (7.12) | 2.56 | 57 |
| 6 | [Cu(en) ₃] ₃ [Fe(SCN) ₆] ₂ | Blue | 90 | 200 | 8.1 (7.12) | 2.68 | 98 |
| 7 | [Zn(en) ₃] ₃ [Fe(SCN) ₆] ₂ | White | 95 | 200 | 7.4 (7.31) | 2.58 | 106 |
| 8 | [Cd(en) ₃] ₃ [Fe(SCN) ₆] ₂ | White | 95 | >200 | | 1.53 | 48 |
| 9 | [Ni(en) ₃] ₃ [Fe(SCN) ₆] ₂ | Purple | 95 | >200 | 13.27 (13.09) | 2.69 | 28 |
| 10 | [Cu(en) ₂] ₃ [Fe(CN) ₆] ₂ | Violet | 95 | >200 | | 2.22 | 15 |
| 11 | [Zn(en) ₃] ₃ [Fe(CN) ₆] ₂ | White | 95 | >200 | | 2.29 | 3 |
| 12 | [Cd(en) ₃] ₃ [Fe(CN) ₆] ₂ | White | 95 | >200 | | 1.44 | 3 |

RESULTS AND DISCUSSION

Discussion on Preparation

Bimetallic heteronuclear complexes were prepared by using water as the solvent. Bimetallic heteronuclear complexes were prepared by the reaction of one metal complex with

a different metal complex in the molar ratio 2:3. All the complexes were obtained almost immediately after mixing of the component metal complex solutions. During preparation of $\{[\text{Cd}(\text{aniline})_6]_3[\text{Fe}(\text{SCN})_6]_2\}$ complex mixture was heated to dissolve the oily layer formed due to the presence of aniline. All the complexes are insoluble in chloroform. Some of them are moderately soluble in methanol. All complexes are highly soluble in DMF and stable at air. The metal analysis data indicate formation of the desired complexes with 3:2 molar ratio of the complex cation and the complex anion. Some physical properties of prepared complexes and spectral properties (FTIR, electronic) of prepared complexes are given in Table 1 and Table 2, respectively.

Qualitative Characterization

A little amount of the prepared complexes was taken in a test tube. Then concentrated nitric acid (HNO_3) was added to the sample and gently warmed on a water bath for the decomposition. The solution was used for the qualitative characterization of metal ions.

Greenish white precipitate or coloration confirms Cd^{2+} ion with the addition of a few drops of potassium ferrocyanide, $[\text{K}_4\text{Fe}(\text{CN})_6]$ to the acidic sample. If copper is present, a maroon precipitate of $\text{Cu}_2\text{Fe}(\text{CN})_6$ will appear and the coloration confirms Cu^{2+} ion.

The appearance of a dark red color due to the formation of $\text{Fe}(\text{SCN})_3$ complex ion confirms the presence of Fe^{3+} iron when a few drops of KSCN , 1 mL of HCl (conc.) and 2 mL of H_2O are added to a test tube.

Acidifying with CH_3COOH and the solution was made slightly alkaline with NH_4OH . a red solution of nickel(II) dimethylglyoxime should appear with the addition of a few drops of alcoholic dimethylglyoxime confirming the presence of nickel.

In the solution, NaOH is carefully added in a drop wise, white $\text{Zn}(\text{OH})_2$ will precipitate and if excess NaOH is added it is dissolved that confirms the presence of Zinc ion.

The Ni^{2+} and Fe^{3+} ions can be separated by adding ammonia. The Ni^{2+} ion is converted to the deep-blue complex ion, $\text{Ni}(\text{NH}_3)_6^{2+}$, which stays in solution. While the Fe^{3+} ion, which does not readily form a complex ion with ammonia, is re-precipitated as iron(III) hydroxide.

Infrared spectra

In the bimetallic complexes which are the subject of this project, the main stretching modes are for $\nu_{\text{N-H}}$, $\nu_{\text{C-N}}$, $\nu_{\text{C-C}}$, $\nu_{\text{C=C}}$, $\nu_{\text{C-S}}$, $\nu_{\text{S-C}\equiv\text{N}}$ and $\nu_{\text{M-N}}$. The infrared spectra for the present compounds taken in the range $400\text{-}4000\text{ cm}^{-1}$ help to indicate regions of absorption due to the above mentioned vibrations. The peaks at 3442 and 3255 cm^{-1} were assigned to the stretching vibrations of amine group [13,14]. 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 ranges. The N-bonded thiocyanate group exhibits $\nu_{\text{C-N}}$ in the regions of $2020\text{-}2096\text{ cm}^{-1}$ and the S-bonded thiocyanate group exhibits $\nu_{\text{C-N}}$ above 2100 cm^{-1} [8]. Appearance of strong $\nu_{\text{C-N}}$ bands in the regions $2020\text{-}2096$ 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, what proves the presence of thiocyanato ions in bridging and terminal positions [5]. The presence of two bands in between $2105\text{-}2160\text{ cm}^{-1}$ clearly indicates the presence of thiocyanate as bridging unit [15]. For the present complexes bridging unit was confirmed indicating the peaks at the region $2040\text{-}2164\text{ cm}^{-1}$. The weak band corresponding to $\nu(\text{C-S})$ vibration appears at $720\text{-}820\text{ cm}^{-1}$, and the ν_{NCS} bending mode is observed at $640\text{-}696\text{ cm}^{-1}$ [8]. FTIR spectra also show the very broad band at 360 cm^{-1} with shoulders due to superposition of bands arising from $\nu_{\text{C-F-N}}$ and $\nu_{\text{Cu-N}}$ vibrations. The

assignment of $\nu_{\text{Cu-S}}$ vibrations is only tentative because of low intensity of these bands [4]. For all the complexes, the presence of $\nu_{\text{M-N}}$ and $\nu_{\text{M-S}}$ vibration in the same region $407\text{-}558\text{ cm}^{-1}$ confirms coordination and N-, S-donor character of the ligands to the metal ion. Furthermore, the presence of bands in $\delta(\text{NCS})$, $\nu(\text{C-S})$, $\nu(\text{M-N})$ and $\nu(\text{M-S})$ regions are diagnostic for the nature of thiocyanate bonding [15]. A representative IR Spectrum of $\{[\text{Cd}(\text{en})_2][\text{Ni}(\text{SCN})_4]\}$ has been given in Figure 1.

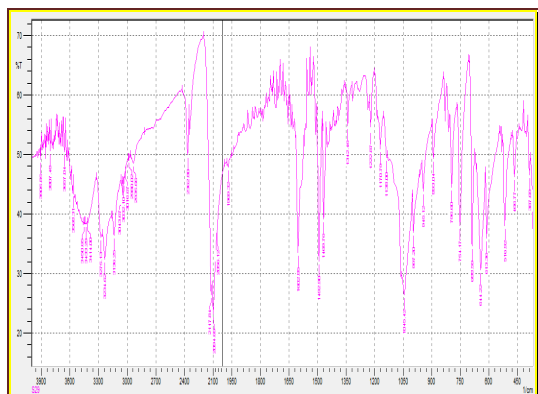


Figure 1. IR spectrum of complex $\{[\text{Zn}(\text{Aniline})_6]_3[\text{Fe}(\text{SCN})_6]_2\}$

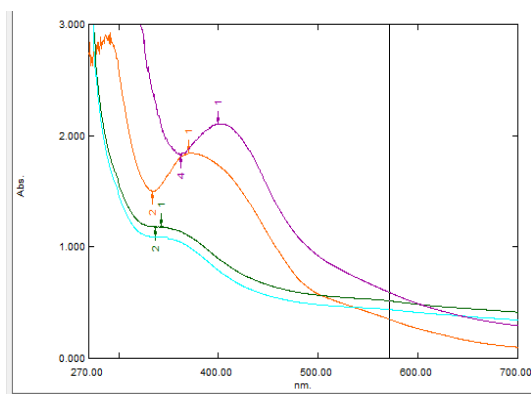


Figure 2. Representative electronic spectra of some prepared complexes.

The Electronic Spectra

The visible ultraviolet spectroscopy is a simple but powerful tool for the interpretation of chemical bonds and structure of most chelates. Because of the insolubility of the presently prepared complexes in common organic solvents, the spectra of the prepared complexes were run in dimethylformamide. The bands at around 530 nm in the visible region for the prepared complexes can be assigned to $d-d$ transition. 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 420 nm may be assumed as due to the presence of ferrichexathiocyanate. Figure 2 shows the representative electronic spectra of some prepared complexes.

^{13}C NMR Spectra

Splitting of the ^{13}C NMR signal approximately at $132.5\text{ }(\delta)$ for the complex, $[\text{Zn}(\text{Anil})_6]_3[\text{Fe}(\text{NCS})_6]_2$ indicates the presence of both nonbridged and bridging thiocyanate. In addition multiplet at $135\text{ }(\delta)$ complies with phenyl group of aniline.

Magnetic Measurements

From the experimental values of magnetic measurements of the prepared complexes, it is revealed that $\{[\text{Zn}(\text{en})_3]_3[\text{Fe}(\text{NCS})_6]_2\}$ and $\{[\text{Cd}(\text{en})_3]_3[\text{Fe}(\text{NCS})_6]_2\}$ complexes are diamagnetic thus indicating the d^{10} electronic configuration in such complexes. The effective magnetic moment for remaining complexes at room temperature was above 2.00 B.M. and it is higher than expected the spin-only value but similar to the value of 2.25 B.M. obtained for $\text{K}_3[\text{Fe}(\text{NCS})_6]$. From the experimental values of magnetic measurements of the prepared complexes, it is found that magnetic moments are lower than the expected theoretical spin only values. The possible reason of such lower magnetic moment may be due to some antiferromagnetic interactions in the bimetallic complex. The exchange interactions seem to be super exchange type and most likely through the thiocyanato groups. However,

weak bonds and longer bond lengths may hide or prevent possibility of exchange interactions.

Table 2. Spectral properties of prepared complexes.

| Sl No. | Complexes | ν_{N-H} | $\nu_{C=C}$ | ν_{C-N} | $\nu_{C\equiv N}$ (cyanide) | ν_{C-S} | $\nu_{S-C\equiv N}$ | ν_{M-N} | ν_{M-S} | Spectral bands | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
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| 1 | [Ni(NH ₃) ₆] ₃ | 3300(s) | 1180(s) | 1332(m) | 2100(vs) | 820(w) | 696(s) | 507(m) | 447(m) | 570, 465, 405, 294 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | [Fe(SCN) ₆] ₂ | 3240(w) | 1080(m) | 1411(s) | 2164(s) | | | | | | 2 | [Cu(NH ₃) ₆] ₃ | 3420(w) | 1222(s) | 1400(m) | 2100(vs) | 742(s) | 669(m) | 546(s) | 466(s) | 530, 353, 342 | [Fe(SCN) ₆] ₂ | 3200(m) | 1156(m) | 1440(m) | 2100(vs) | 3 | [Zn(NH ₃) ₆] ₃ | 3275(m) | 1230(s) | 1406(m) | 2040(s) | 810(w) | 690(vs) | 558(m) | 478(m) | 520, 293, 289 | [Fe(SCN) ₆] ₂ | 3334(w) | 1260(m) | 1380(w) | 2100(vs) | 4 | [Cd(NH ₃) ₆] ₃ | 3061(m) | 1052(m) | 1366(w) | 2040(vs) | 720(s) | 648(s) | 528(w) | 468(w) | 530, 370, 286 | [Fe(SCN) ₆] ₂ | 3150(w) | 1112(s) | 1410(s) | 2100(sh) | 5 | [Ni(An) ₆] ₃ | 3296(m) | 1047(vs) | 1482(vs) | 2130(vs) | 806(s) | 640(s) | 520(s) | 441(m) | 530, 428, 415, 289 | [Fe(SCN) ₆] ₂ | 3327(s) | 1234(m) | 1460(s) | 2100(sh) | 6 | [Cu(An) ₆] ₃ | 3215(m) | 1076(s) | 1407(m) | 2105(sh) | 761(s) | 690(s) | 520(m) | 420(m) | 528, 400, 311, 297 | [Fe(SCN) ₆] ₂ | 3315(m) | 1230(m) | 1482(s) | 2130(vs) | 7 | [Zn(An) ₆] ₃ | 3136(s) | 1045(s) | 1342(m) | 2094(vs) | 796(s) | 644(s) | 516(m) | 416(m) | 400, 297 | [Fe(SCN) ₆] ₂ | 3234(m) | 1138(m) | 1488(s) | 2117(m) | 8 | [Cd(An) ₆] ₃ | 3290(w) | 1037(s) | 1407(m) | 2076(sh) | 760(s) | 660(m) | 514(m) | 423(m) | 530, 370, 286 | [Fe(SCN) ₆] ₂ | 3323(m) | 997(m) | 1490(s) | 2130(vs) | 9 | [Ni(en) ₃] ₃ | 3360(m) | 1091(vs) | 1460(m) | 2106(s) | 870(w) | 669(s) | 522(m) | 407(m) | 530, 450, 425, 287 | [Fe(SCN) ₆] ₂ | 3390(m) | 1274(m) | 1410(m) | 2160(m) | 10 | [Cu(en) ₂] ₃ | 3280(s) | 1040(m) | 1380(w) | 2100(s) | 802(s) | 615(m) | 520(m) | 493(m) | 530, 350 | [Fe(CN) ₂] ₃ | 3350(m) | 1106(m) | 1468(m) | 2115(m) | 11 | [Zn(en) ₃] ₃ | 3161(m) | 1033(m) | 1460(ms) | 2092(vs) | 804(w) | 666(s) | 516(m) | 486(m) | 571, 290 | [Fe(CN) ₆] ₂ | 3300(s) | 1096(s) | 1360(w) | 2138(m) | 12 | [Cd(en) ₃] ₃ | 3275(m) | 1023(s) | 1448(m) | 2100(sh) | 761(s) | 690(s) | 524(m) | 466(m) |
| 2 | [Cu(NH ₃) ₆] ₃ | 3420(w) | 1222(s) | 1400(m) | 2100(vs) | 742(s) | 669(m) | 546(s) | 466(s) | 530, 353, 342 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | [Fe(SCN) ₆] ₂ | 3200(m) | 1156(m) | 1440(m) | 2100(vs) | | | | | | 3 | [Zn(NH ₃) ₆] ₃ | 3275(m) | 1230(s) | 1406(m) | 2040(s) | 810(w) | 690(vs) | 558(m) | 478(m) | 520, 293, 289 | [Fe(SCN) ₆] ₂ | 3334(w) | 1260(m) | 1380(w) | 2100(vs) | 4 | [Cd(NH ₃) ₆] ₃ | 3061(m) | 1052(m) | 1366(w) | 2040(vs) | 720(s) | 648(s) | 528(w) | 468(w) | 530, 370, 286 | [Fe(SCN) ₆] ₂ | 3150(w) | 1112(s) | 1410(s) | 2100(sh) | 5 | [Ni(An) ₆] ₃ | 3296(m) | 1047(vs) | 1482(vs) | 2130(vs) | 806(s) | 640(s) | 520(s) | 441(m) | 530, 428, 415, 289 | [Fe(SCN) ₆] ₂ | 3327(s) | 1234(m) | 1460(s) | 2100(sh) | 6 | [Cu(An) ₆] ₃ | 3215(m) | 1076(s) | 1407(m) | 2105(sh) | 761(s) | 690(s) | 520(m) | 420(m) | 528, 400, 311, 297 | [Fe(SCN) ₆] ₂ | 3315(m) | 1230(m) | 1482(s) | 2130(vs) | 7 | [Zn(An) ₆] ₃ | 3136(s) | 1045(s) | 1342(m) | 2094(vs) | 796(s) | 644(s) | 516(m) | 416(m) | 400, 297 | [Fe(SCN) ₆] ₂ | 3234(m) | 1138(m) | 1488(s) | 2117(m) | 8 | [Cd(An) ₆] ₃ | 3290(w) | 1037(s) | 1407(m) | 2076(sh) | 760(s) | 660(m) | 514(m) | 423(m) | 530, 370, 286 | [Fe(SCN) ₆] ₂ | 3323(m) | 997(m) | 1490(s) | 2130(vs) | 9 | [Ni(en) ₃] ₃ | 3360(m) | 1091(vs) | 1460(m) | 2106(s) | 870(w) | 669(s) | 522(m) | 407(m) | 530, 450, 425, 287 | [Fe(SCN) ₆] ₂ | 3390(m) | 1274(m) | 1410(m) | 2160(m) | 10 | [Cu(en) ₂] ₃ | 3280(s) | 1040(m) | 1380(w) | 2100(s) | 802(s) | 615(m) | 520(m) | 493(m) | 530, 350 | [Fe(CN) ₂] ₃ | 3350(m) | 1106(m) | 1468(m) | 2115(m) | 11 | [Zn(en) ₃] ₃ | 3161(m) | 1033(m) | 1460(ms) | 2092(vs) | 804(w) | 666(s) | 516(m) | 486(m) | 571, 290 | [Fe(CN) ₆] ₂ | 3300(s) | 1096(s) | 1360(w) | 2138(m) | 12 | [Cd(en) ₃] ₃ | 3275(m) | 1023(s) | 1448(m) | 2100(sh) | 761(s) | 690(s) | 524(m) | 466(m) | 435, 430, 297, 264 | [Fe(CN) ₆] ₂ | 3325(s) | 1124(s) | 1348(w) | 2050(w) | | | | | | | | | | |
| 3 | [Zn(NH ₃) ₆] ₃ | 3275(m) | 1230(s) | 1406(m) | 2040(s) | 810(w) | 690(vs) | 558(m) | 478(m) | 520, 293, 289 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | [Fe(SCN) ₆] ₂ | 3334(w) | 1260(m) | 1380(w) | 2100(vs) | | | | | | 4 | [Cd(NH ₃) ₆] ₃ | 3061(m) | 1052(m) | 1366(w) | 2040(vs) | 720(s) | 648(s) | 528(w) | 468(w) | 530, 370, 286 | [Fe(SCN) ₆] ₂ | 3150(w) | 1112(s) | 1410(s) | 2100(sh) | 5 | [Ni(An) ₆] ₃ | 3296(m) | 1047(vs) | 1482(vs) | 2130(vs) | 806(s) | 640(s) | 520(s) | 441(m) | 530, 428, 415, 289 | [Fe(SCN) ₆] ₂ | 3327(s) | 1234(m) | 1460(s) | 2100(sh) | 6 | [Cu(An) ₆] ₃ | 3215(m) | 1076(s) | 1407(m) | 2105(sh) | 761(s) | 690(s) | 520(m) | 420(m) | 528, 400, 311, 297 | [Fe(SCN) ₆] ₂ | 3315(m) | 1230(m) | 1482(s) | 2130(vs) | 7 | [Zn(An) ₆] ₃ | 3136(s) | 1045(s) | 1342(m) | 2094(vs) | 796(s) | 644(s) | 516(m) | 416(m) | 400, 297 | [Fe(SCN) ₆] ₂ | 3234(m) | 1138(m) | 1488(s) | 2117(m) | 8 | [Cd(An) ₆] ₃ | 3290(w) | 1037(s) | 1407(m) | 2076(sh) | 760(s) | 660(m) | 514(m) | 423(m) | 530, 370, 286 | [Fe(SCN) ₆] ₂ | 3323(m) | 997(m) | 1490(s) | 2130(vs) | 9 | [Ni(en) ₃] ₃ | 3360(m) | 1091(vs) | 1460(m) | 2106(s) | 870(w) | 669(s) | 522(m) | 407(m) | 530, 450, 425, 287 | [Fe(SCN) ₆] ₂ | 3390(m) | 1274(m) | 1410(m) | 2160(m) | 10 | [Cu(en) ₂] ₃ | 3280(s) | 1040(m) | 1380(w) | 2100(s) | 802(s) | 615(m) | 520(m) | 493(m) | 530, 350 | [Fe(CN) ₂] ₃ | 3350(m) | 1106(m) | 1468(m) | 2115(m) | 11 | [Zn(en) ₃] ₃ | 3161(m) | 1033(m) | 1460(ms) | 2092(vs) | 804(w) | 666(s) | 516(m) | 486(m) | 571, 290 | [Fe(CN) ₆] ₂ | 3300(s) | 1096(s) | 1360(w) | 2138(m) | 12 | [Cd(en) ₃] ₃ | 3275(m) | 1023(s) | 1448(m) | 2100(sh) | 761(s) | 690(s) | 524(m) | 466(m) | 435, 430, 297, 264 | [Fe(CN) ₆] ₂ | 3325(s) | 1124(s) | 1348(w) | 2050(w) | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 4 | [Cd(NH ₃) ₆] ₃ | 3061(m) | 1052(m) | 1366(w) | 2040(vs) | 720(s) | 648(s) | 528(w) | 468(w) | 530, 370, 286 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | [Fe(SCN) ₆] ₂ | 3150(w) | 1112(s) | 1410(s) | 2100(sh) | | | | | | 5 | [Ni(An) ₆] ₃ | 3296(m) | 1047(vs) | 1482(vs) | 2130(vs) | 806(s) | 640(s) | 520(s) | 441(m) | 530, 428, 415, 289 | [Fe(SCN) ₆] ₂ | 3327(s) | 1234(m) | 1460(s) | 2100(sh) | 6 | [Cu(An) ₆] ₃ | 3215(m) | 1076(s) | 1407(m) | 2105(sh) | 761(s) | 690(s) | 520(m) | 420(m) | 528, 400, 311, 297 | [Fe(SCN) ₆] ₂ | 3315(m) | 1230(m) | 1482(s) | 2130(vs) | 7 | [Zn(An) ₆] ₃ | 3136(s) | 1045(s) | 1342(m) | 2094(vs) | 796(s) | 644(s) | 516(m) | 416(m) | 400, 297 | [Fe(SCN) ₆] ₂ | 3234(m) | 1138(m) | 1488(s) | 2117(m) | 8 | [Cd(An) ₆] ₃ | 3290(w) | 1037(s) | 1407(m) | 2076(sh) | 760(s) | 660(m) | 514(m) | 423(m) | 530, 370, 286 | [Fe(SCN) ₆] ₂ | 3323(m) | 997(m) | 1490(s) | 2130(vs) | 9 | [Ni(en) ₃] ₃ | 3360(m) | 1091(vs) | 1460(m) | 2106(s) | 870(w) | 669(s) | 522(m) | 407(m) | 530, 450, 425, 287 | [Fe(SCN) ₆] ₂ | 3390(m) | 1274(m) | 1410(m) | 2160(m) | 10 | [Cu(en) ₂] ₃ | 3280(s) | 1040(m) | 1380(w) | 2100(s) | 802(s) | 615(m) | 520(m) | 493(m) | 530, 350 | [Fe(CN) ₂] ₃ | 3350(m) | 1106(m) | 1468(m) | 2115(m) | 11 | [Zn(en) ₃] ₃ | 3161(m) | 1033(m) | 1460(ms) | 2092(vs) | 804(w) | 666(s) | 516(m) | 486(m) | 571, 290 | [Fe(CN) ₆] ₂ | 3300(s) | 1096(s) | 1360(w) | 2138(m) | 12 | [Cd(en) ₃] ₃ | 3275(m) | 1023(s) | 1448(m) | 2100(sh) | 761(s) | 690(s) | 524(m) | 466(m) | 435, 430, 297, 264 | [Fe(CN) ₆] ₂ | 3325(s) | 1124(s) | 1348(w) | 2050(w) | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 5 | [Ni(An) ₆] ₃ | 3296(m) | 1047(vs) | 1482(vs) | 2130(vs) | 806(s) | 640(s) | 520(s) | 441(m) | 530, 428, 415, 289 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | [Fe(SCN) ₆] ₂ | 3327(s) | 1234(m) | 1460(s) | 2100(sh) | | | | | | 6 | [Cu(An) ₆] ₃ | 3215(m) | 1076(s) | 1407(m) | 2105(sh) | 761(s) | 690(s) | 520(m) | 420(m) | 528, 400, 311, 297 | [Fe(SCN) ₆] ₂ | 3315(m) | 1230(m) | 1482(s) | 2130(vs) | 7 | [Zn(An) ₆] ₃ | 3136(s) | 1045(s) | 1342(m) | 2094(vs) | 796(s) | 644(s) | 516(m) | 416(m) | 400, 297 | [Fe(SCN) ₆] ₂ | 3234(m) | 1138(m) | 1488(s) | 2117(m) | 8 | [Cd(An) ₆] ₃ | 3290(w) | 1037(s) | 1407(m) | 2076(sh) | 760(s) | 660(m) | 514(m) | 423(m) | 530, 370, 286 | [Fe(SCN) ₆] ₂ | 3323(m) | 997(m) | 1490(s) | 2130(vs) | 9 | [Ni(en) ₃] ₃ | 3360(m) | 1091(vs) | 1460(m) | 2106(s) | 870(w) | 669(s) | 522(m) | 407(m) | 530, 450, 425, 287 | [Fe(SCN) ₆] ₂ | 3390(m) | 1274(m) | 1410(m) | 2160(m) | 10 | [Cu(en) ₂] ₃ | 3280(s) | 1040(m) | 1380(w) | 2100(s) | 802(s) | 615(m) | 520(m) | 493(m) | 530, 350 | [Fe(CN) ₂] ₃ | 3350(m) | 1106(m) | 1468(m) | 2115(m) | 11 | [Zn(en) ₃] ₃ | 3161(m) | 1033(m) | 1460(ms) | 2092(vs) | 804(w) | 666(s) | 516(m) | 486(m) | 571, 290 | [Fe(CN) ₆] ₂ | 3300(s) | 1096(s) | 1360(w) | 2138(m) | 12 | [Cd(en) ₃] ₃ | 3275(m) | 1023(s) | 1448(m) | 2100(sh) | 761(s) | 690(s) | 524(m) | 466(m) | 435, 430, 297, 264 | [Fe(CN) ₆] ₂ | 3325(s) | 1124(s) | 1348(w) | 2050(w) | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 6 | [Cu(An) ₆] ₃ | 3215(m) | 1076(s) | 1407(m) | 2105(sh) | 761(s) | 690(s) | 520(m) | 420(m) | 528, 400, 311, 297 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | [Fe(SCN) ₆] ₂ | 3315(m) | 1230(m) | 1482(s) | 2130(vs) | | | | | | 7 | [Zn(An) ₆] ₃ | 3136(s) | 1045(s) | 1342(m) | 2094(vs) | 796(s) | 644(s) | 516(m) | 416(m) | 400, 297 | [Fe(SCN) ₆] ₂ | 3234(m) | 1138(m) | 1488(s) | 2117(m) | 8 | [Cd(An) ₆] ₃ | 3290(w) | 1037(s) | 1407(m) | 2076(sh) | 760(s) | 660(m) | 514(m) | 423(m) | 530, 370, 286 | [Fe(SCN) ₆] ₂ | 3323(m) | 997(m) | 1490(s) | 2130(vs) | 9 | [Ni(en) ₃] ₃ | 3360(m) | 1091(vs) | 1460(m) | 2106(s) | 870(w) | 669(s) | 522(m) | 407(m) | 530, 450, 425, 287 | [Fe(SCN) ₆] ₂ | 3390(m) | 1274(m) | 1410(m) | 2160(m) | 10 | [Cu(en) ₂] ₃ | 3280(s) | 1040(m) | 1380(w) | 2100(s) | 802(s) | 615(m) | 520(m) | 493(m) | 530, 350 | [Fe(CN) ₂] ₃ | 3350(m) | 1106(m) | 1468(m) | 2115(m) | 11 | [Zn(en) ₃] ₃ | 3161(m) | 1033(m) | 1460(ms) | 2092(vs) | 804(w) | 666(s) | 516(m) | 486(m) | 571, 290 | [Fe(CN) ₆] ₂ | 3300(s) | 1096(s) | 1360(w) | 2138(m) | 12 | [Cd(en) ₃] ₃ | 3275(m) | 1023(s) | 1448(m) | 2100(sh) | 761(s) | 690(s) | 524(m) | 466(m) | 435, 430, 297, 264 | [Fe(CN) ₆] ₂ | 3325(s) | 1124(s) | 1348(w) | 2050(w) | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 7 | [Zn(An) ₆] ₃ | 3136(s) | 1045(s) | 1342(m) | 2094(vs) | 796(s) | 644(s) | 516(m) | 416(m) | 400, 297 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | [Fe(SCN) ₆] ₂ | 3234(m) | 1138(m) | 1488(s) | 2117(m) | | | | | | 8 | [Cd(An) ₆] ₃ | 3290(w) | 1037(s) | 1407(m) | 2076(sh) | 760(s) | 660(m) | 514(m) | 423(m) | 530, 370, 286 | [Fe(SCN) ₆] ₂ | 3323(m) | 997(m) | 1490(s) | 2130(vs) | 9 | [Ni(en) ₃] ₃ | 3360(m) | 1091(vs) | 1460(m) | 2106(s) | 870(w) | 669(s) | 522(m) | 407(m) | 530, 450, 425, 287 | [Fe(SCN) ₆] ₂ | 3390(m) | 1274(m) | 1410(m) | 2160(m) | 10 | [Cu(en) ₂] ₃ | 3280(s) | 1040(m) | 1380(w) | 2100(s) | 802(s) | 615(m) | 520(m) | 493(m) | 530, 350 | [Fe(CN) ₂] ₃ | 3350(m) | 1106(m) | 1468(m) | 2115(m) | 11 | [Zn(en) ₃] ₃ | 3161(m) | 1033(m) | 1460(ms) | 2092(vs) | 804(w) | 666(s) | 516(m) | 486(m) | 571, 290 | [Fe(CN) ₆] ₂ | 3300(s) | 1096(s) | 1360(w) | 2138(m) | 12 | [Cd(en) ₃] ₃ | 3275(m) | 1023(s) | 1448(m) | 2100(sh) | 761(s) | 690(s) | 524(m) | 466(m) | 435, 430, 297, 264 | [Fe(CN) ₆] ₂ | 3325(s) | 1124(s) | 1348(w) | 2050(w) | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 8 | [Cd(An) ₆] ₃ | 3290(w) | 1037(s) | 1407(m) | 2076(sh) | 760(s) | 660(m) | 514(m) | 423(m) | 530, 370, 286 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | [Fe(SCN) ₆] ₂ | 3323(m) | 997(m) | 1490(s) | 2130(vs) | | | | | | 9 | [Ni(en) ₃] ₃ | 3360(m) | 1091(vs) | 1460(m) | 2106(s) | 870(w) | 669(s) | 522(m) | 407(m) | 530, 450, 425, 287 | [Fe(SCN) ₆] ₂ | 3390(m) | 1274(m) | 1410(m) | 2160(m) | 10 | [Cu(en) ₂] ₃ | 3280(s) | 1040(m) | 1380(w) | 2100(s) | 802(s) | 615(m) | 520(m) | 493(m) | 530, 350 | [Fe(CN) ₂] ₃ | 3350(m) | 1106(m) | 1468(m) | 2115(m) | 11 | [Zn(en) ₃] ₃ | 3161(m) | 1033(m) | 1460(ms) | 2092(vs) | 804(w) | 666(s) | 516(m) | 486(m) | 571, 290 | [Fe(CN) ₆] ₂ | 3300(s) | 1096(s) | 1360(w) | 2138(m) | 12 | [Cd(en) ₃] ₃ | 3275(m) | 1023(s) | 1448(m) | 2100(sh) | 761(s) | 690(s) | 524(m) | 466(m) | 435, 430, 297, 264 | [Fe(CN) ₆] ₂ | 3325(s) | 1124(s) | 1348(w) | 2050(w) | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 9 | [Ni(en) ₃] ₃ | 3360(m) | 1091(vs) | 1460(m) | 2106(s) | 870(w) | 669(s) | 522(m) | 407(m) | 530, 450, 425, 287 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | [Fe(SCN) ₆] ₂ | 3390(m) | 1274(m) | 1410(m) | 2160(m) | | | | | | 10 | [Cu(en) ₂] ₃ | 3280(s) | 1040(m) | 1380(w) | 2100(s) | 802(s) | 615(m) | 520(m) | 493(m) | 530, 350 | [Fe(CN) ₂] ₃ | 3350(m) | 1106(m) | 1468(m) | 2115(m) | 11 | [Zn(en) ₃] ₃ | 3161(m) | 1033(m) | 1460(ms) | 2092(vs) | 804(w) | 666(s) | 516(m) | 486(m) | 571, 290 | [Fe(CN) ₆] ₂ | 3300(s) | 1096(s) | 1360(w) | 2138(m) | 12 | [Cd(en) ₃] ₃ | 3275(m) | 1023(s) | 1448(m) | 2100(sh) | 761(s) | 690(s) | 524(m) | 466(m) | 435, 430, 297, 264 | [Fe(CN) ₆] ₂ | 3325(s) | 1124(s) | 1348(w) | 2050(w) | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 10 | [Cu(en) ₂] ₃ | 3280(s) | 1040(m) | 1380(w) | 2100(s) | 802(s) | 615(m) | 520(m) | 493(m) | 530, 350 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | [Fe(CN) ₂] ₃ | 3350(m) | 1106(m) | 1468(m) | 2115(m) | | | | | | 11 | [Zn(en) ₃] ₃ | 3161(m) | 1033(m) | 1460(ms) | 2092(vs) | 804(w) | 666(s) | 516(m) | 486(m) | 571, 290 | [Fe(CN) ₆] ₂ | 3300(s) | 1096(s) | 1360(w) | 2138(m) | 12 | [Cd(en) ₃] ₃ | 3275(m) | 1023(s) | 1448(m) | 2100(sh) | 761(s) | 690(s) | 524(m) | 466(m) | 435, 430, 297, 264 | [Fe(CN) ₆] ₂ | 3325(s) | 1124(s) | 1348(w) | 2050(w) | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 11 | [Zn(en) ₃] ₃ | 3161(m) | 1033(m) | 1460(ms) | 2092(vs) | 804(w) | 666(s) | 516(m) | 486(m) | 571, 290 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | [Fe(CN) ₆] ₂ | 3300(s) | 1096(s) | 1360(w) | 2138(m) | | | | | | 12 | [Cd(en) ₃] ₃ | 3275(m) | 1023(s) | 1448(m) | 2100(sh) | 761(s) | 690(s) | 524(m) | 466(m) | 435, 430, 297, 264 | [Fe(CN) ₆] ₂ | 3325(s) | 1124(s) | 1348(w) | 2050(w) | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 12 | [Cd(en) ₃] ₃ | 3275(m) | 1023(s) | 1448(m) | 2100(sh) | 761(s) | 690(s) | 524(m) | 466(m) | 435, 430, 297, 264 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | [Fe(CN) ₆] ₂ | 3325(s) | 1124(s) | 1348(w) | 2050(w) | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |

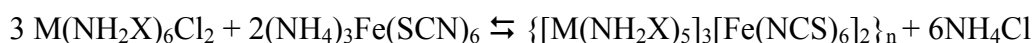
*vs = very strong; s = strong; ms = medium strong; m = medium; w = weak; vw = very weak; sh = shoulder.

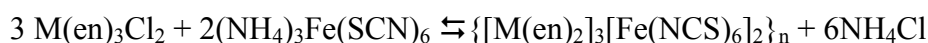
Molar conductance

The molar conductance values of the presently prepared complexes (ca. 10⁻³ M) are shown in Table 6.3. The low conductance values 03-106 ohm⁻¹cm²mol⁻¹ of the prepared complexes in DMF solutions corresponding to 3:2 electrolytes strongly support proposed formulation of the prepared complexes of nonelectrolytic nature. This suggests oxidation states of the metal ions present in such complexes. The high conductance values of the [Cu(NH₃)₆]₃[Fe(SCN)₆]₂ and [Cd(NH₃)₆]₃[Fe(SCN)₆]₂ complexes in DMF solutions indicates their electrolytic nature that strongly supports their ionic formulation due to the electrostatic attraction of both cation and anion.

Geometry

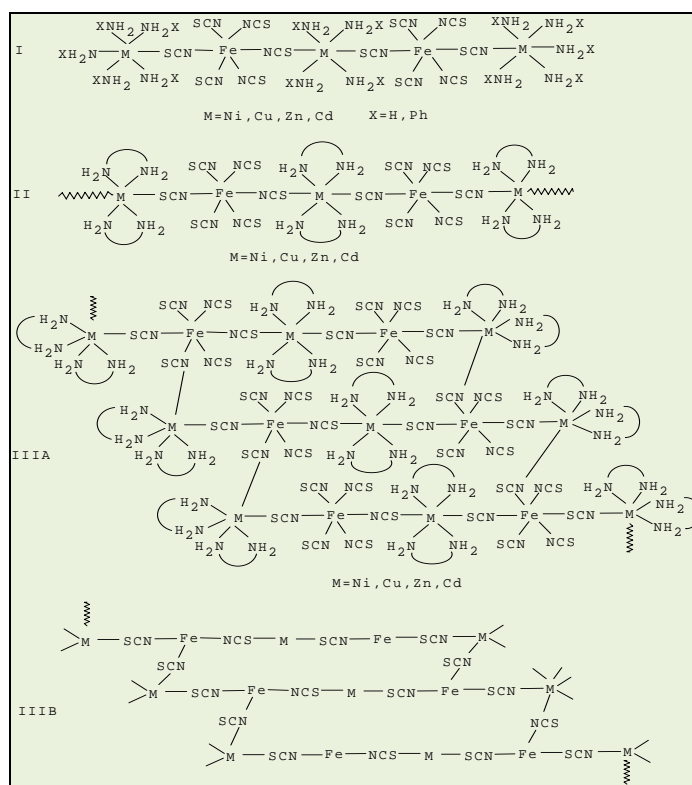
Compound [Ni(en)₂]₄[Fe(CN)₅NO]₂[Fe(CN)₆].5H₂O is obtained by reaction of [Fe(CN)₅NO]²⁻ with [Ni(en)₃]Cl₂ in aqueous solution. The slow dissociation of [Ni(en)₃]²⁺ into [Ni(en)₂]²⁺ leads to the growth of crystals suitable for X-ray diffraction [3,15]. It is supposed that heterobinuclear thiocyanato-bridged complexes have been synthesized by the reaction of cations, [M(NH₂X)₆]²⁺ and [M(en)₃]²⁺ with anion [Fe(NCS)₆]³⁻. Complexes having the compositions, [M(NH₂X)₅]₃[Fe(NCS)₆]₂, and {[M(en)₂]₃[Fe(NCS)₆]₂]_n (where M=Cu, Ni, Zn, Cd; X=H, Ph) are prepared.





Bridge geometry was also confirmed by the ^{13}C nmr of the complex, $[\text{Zn}(\text{aniline})_5]_3[\text{Fe}(\text{NCS})_6]_2$ when splitting of peak at (δ) 123.5 indicates the bridging thiocyanate and that multiplet at (δ) 135 comply with phenyl group of aniline.

Figure 3.
Proposed schematic
view of complex
 $[\{\text{M}(\text{en})_2\}\{\text{Ni}(\text{NCS})_4\}]_n$



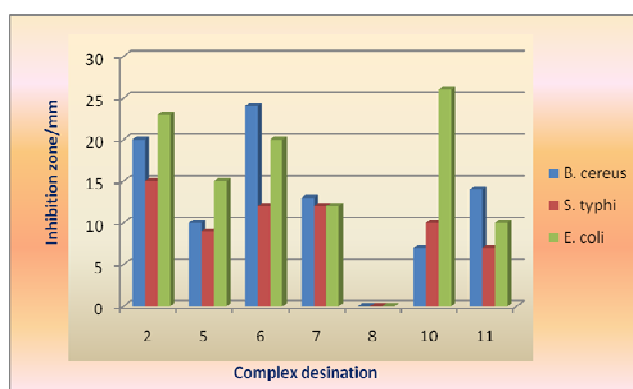
The crystal structure of $[\text{NiL}]_3[\text{Fe}(\text{NCS})_6]_2$ (where L = 5,6,12,13-Me4-[14]-4,11-dieneN4) suggested the exchange interaction between Cu(II) and Fe(III) ions that is transmitted by the thiocyanate groups [16]. Each Fe(III) ion is bound to two Ni^{2+} ions when thiocyanate groups coordinate to the Ni^{2+} ions by their sulphur atom [8]. The unique structure of $[\text{Zn}(\text{cyclam})]_3[\text{Fe}(\text{CN})_6]_2$ consists of alternating $[\text{Zn}(\text{cyclam})]^{2+}$ and $[\text{Fe}(\text{CN})_6]^{3-}$ units and cationic trinuclear entities, $[\text{Zn}(\text{cyclam})-\text{Fe}(\text{CN})_6-\text{Zn}(\text{cyclam})]$ [17]. It is proposed that $[\text{M}(\text{NH}_2\text{X})_5]_3[\text{Fe}(\text{NCS})_6]_2$ is formed by the same alternating cation and anion. The Fe^{3+} centre possesses four non-bridging and two bridging thiocyanate ligands, while the thiocyanate groups are nearly linear. The environment of the Fe^{3+} ion and M^{2+} are octahedral. Two coordination sites of central M^{2+} ions are occupied by two bridging thiocyanate ligands whereas sixth coordination site of terminal $[\text{M}(\text{NH}_3)_5]^{2+}$ or $[\text{M}(\text{aniline})_5]^{2+}$ is occupied by one bridging thiocyanate ligands from anion having entities M-Fe-M-Fe-M in a linear chain. Proposed formulation is given in Figure 3(I). Present prepared bimetallic complexes, $\{[\text{M}(\text{en})_2]_3[\text{Fe}(\text{NCS})_6]_2\}$ are supposed to possess the polymeric chain formed by an alternate array of the *trans*- $[\text{M}(\text{en})_2]^{2+}$ cations and $[\text{Fe}(\text{CN})_6]^{3-}$ anion having neutral M_3Fe_2 units as shown in Figure 3(II). Alternately it is explained that bimetallic assemblies of $[\text{M}(\text{en})_2]_3[\text{Fe}(\text{NCS})_6]_2$ the asymmetric unit consists of two $[\text{Fe}(\text{CN})_6]^{3-}$ anions, two terminal *cis*- $[\text{M}(\text{en})_2]^{2+}$, one central *trans*- $[\text{M}(\text{en})_2]^{2+}$ cations to give M-SCN-Fe-NCS-M-SCN-Fe-

CNS-M unit. Which are cross linked to give polymeric ribbons $\{[M(en)_2]_3[Fe(NCS)_6]_2\}_n$ as shown in Figure 3 (III). This proposed polymeric formulation is confirmed by the structure of Bimetallic assemblies, $[Ni(en)_2]_3[M(CN)_6]_2 \cdot 3H_2O$. When authors proposed that both *cis* and *trans* $[Ni(en)_2]$ and $[M(CN)_6]$ moieties are linked to give S-shaped Ni-NC-M-CN-Ni-NC-M-CN-Ni units which are cross linked to give ribbons [18]. But actual geometry is difficult to elucidate without crystallographic studies. Figure shows the proposed schematic view of complex, $[\{M(en)_2\} \{Ni(NCS)_4\}]_n$.

Effect on the bacterial growth

In the present work, some of the prepared complexes were selected for antibacterial activity against three human pathogenic bacteria. The results of antibacterial activity of the test organisms for different complexes are graphically presented in Figure 4.

Figure 4. Graphical presentation of antibacterial activity of the prepared complexes.



It is found that, except $[Cd(An)_6]_3[Fe(SCN)_6]_2$ all compounds are comparatively more effective against *Escherichia coli*. The remaining complexes are generally quite effective against *Bacillus cereus* except $[Cd(An)_6]_3[Fe(SCN)_6]_2$, $[Cu(en)_2]_3[Fe(CN)_2]$ and all are moderately effective against *Salmonella typhi*. The enhanced activity of the complexes can be explained in terms some important factors such as nature of the metal ion, metal ion coordinating site, hydrophilicity, hypophilicity and presence of coligands 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 metal complexes cannot be ascribed to chelation alone but it's an intricate blend of all of the above contributions.

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 have been clearly characterized by FT-IR spectroscopy, UV-Vis spectra, magnetic and conductivity measurements. The data indicate the formation of such complexes. Conductivity measurements indicate their electrolytic nature consistence to oxidation state of the metal ions present in such complexes. The magnetic measurements indicate some of the complexes to show 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.

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