



Synthesis, X-ray Crystal Structure, Fluorescence Studies and Antimicrobial Screening of Thiocyanato ($\mu_{1,1}$ -NCS) Linked New Zn(II) Mononuclear Complex Derived from Pyridine Co-ligand

Dhrubajyoti Majumdar^{1*}, Anjali Jha^{2*}, Priyanka Bhatt²

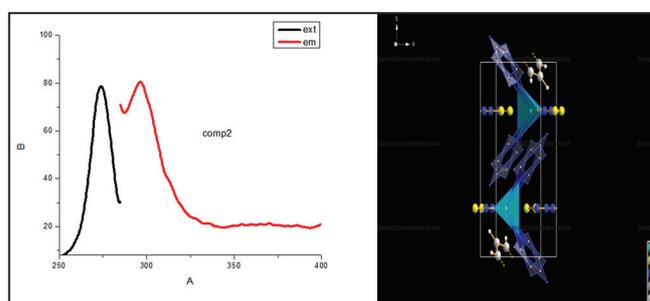
¹Department of Chemistry, Tamralipta Mahavidyalaya Tamluk, West Bengal - 721 636, India. ²Department of Chemistry, GIS, GITAM University, Rushikonda, Visakhapatnam - 530 045, India.

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ABSTRACT

One-pot reaction of Zn(II) acetate dihydrate, pyridine, and potassium thiocyanate in a 1:1:2 M ratio in methanol solution at room temperature result in neutral white mononuclear complex crystal 1 of the type $[Zn(L)_2(\mu_{1,1}\text{-NCS})_2]$. [L=Pyridine]. Single crystal X-ray diffraction was ambiguously used to confirm the complex 1 structure. Complex 1 has been characterized by different well-known physicochemical techniques, Fourier transform infrared spectra, UV-Vis spectroscopic study, and common elemental analyses (carbon, hydrogen and nitrogen). Molar conductivity study directly indicates Complex 1 is nonelectrolyte. Complex 1 crystallizes in monoclinic system, space group $P 2(1)/m$, with the values $a=5.567(5)$, $b=11.085(5)$, and $c=12.132(5)$ Å; $\alpha=90.000^\circ(5)$, $\beta=96.725^\circ(5)$, and $\gamma=90.000^\circ(5)$; $V=743.5\text{Å}^3$ and $Z=4$. X-ray structural study reveals that in complex 1 environment of Zn(II) metal ion has perfect tetrahedral coordination sphere, where Zn(II) metal is tetrahedrally coordinated to the nitrogen donor atoms of two pyridine ligands and the two N-bonded SCN^{-1} ions showing awesome binding fashion ($\mu_{1,1}$ -NCS) of thiocyanato pseudohalide template. The crystal lattice stabilization is not maintained by any kinds of hydrogen bonding and hence π - π interactions never lead to supramolecular architectures in the crystal system. The synthesized Zn(II) complex 1 has been screened for antibacterial activity against some important Gram-negative and Gram-positive bacteria such as *Escherichia coli*, *Bacillus subtilis*, and *Candida albicans*. Complex 1 exhibits enhanced antibacterial activity in comparison to free pyridine ligand. Apart from, complex 1 is fluorescence silent with respect to pyridine coligand.

Graphical abstract



Key words: Zn(II) complex, SCN^{-1} ion, Single X-ray crystal structure, Antimicrobial effect, Fluorescence activity.

HIGHLIGHTS

- A new mononuclear pyridine-thiocyanato linked Zn(II) complex 1 has been synthesized
- Complex 1 has been characterized by common elemental analysis, Fourier transform infrared, UV-Vis spectroscopic study
- Single X-ray crystallography was performed for newly synthesized complex 1
- Complex 1 lead no supramolecular architectures via hydrogen bonding
- The fluorescence behavior of Zn(II) complex 1 and respective pyridine coligand have been

*Corresponding Author:

E-mail: dmajumdar30@gmail.com, anjalijha@gitam.edu

analyzed to find out fluorescence silent or active nature

- Antimicrobial efficacy of complex 1 has been analyzed against some important pathogens.

1. INTRODUCTION

The well-known Zn group family having d^{10} electronic arrangement always favor unique bivalent state complex formation and it has an important role in several biological active enzymes. Biologically, it is the second most important transition metal. It plays a very important role in cellular phenomena such as enzyme catalysis, apoptosis, and neurotransmission. Hence, complexation behavior of group 12 metal ion of Zn(II) and its congeners Cd(II) or Hg(II) are well flourishing and has emerging research area in the field of coordination chemistry [1-5] specially in the presence of active nitrogen donor ligands which may be monodentate or polydentate. Always suitable design and proper synthetic methods of group 12 metal ions of Zn(II) or Cd(II) have achieved supramolecular chemistry as well as crystal engineering due to their intriguing structural motifs [6-10], functional behaviors such as electronics and optoelectronics [11-13]. Recently, one-pot reaction using proper selection of metal, ligand, and suitable versatile bridging units SCN^{-1} , N_3^{-1} , dicyanamide with proper molar ratio always afford many interesting structural topologies [14,15]. Schiff base containing N-donor donor ligands - such as pyridine, bipyridine, ortho-phenanthroline, pyrazine, methyl or ethyl substituted pyridine - are always useful coordinated ligands because of their easy route of preparation, structural wide varieties, and varied denticities [4,5]. Over the past few decades, research of d^{10} metal ions Zn(II) or Cd(II) with rational design of synthetic methodologies in presence of nitrogen donor ligands have received considerable attention due to their potential applications in the field of luminescence, nonlinear optics, molecules sensing [16-20], biological modeling of metalloenzymes [21,22], and so on. Since d^{10} filled system of Zn(II) metal ion has no optical spectroscopic signature and CFSE value is always zero, a balance between bonding energies and steric repulsions created by the selecting ligands determine the overall coordination number of Zn(II) complexes. The combined effects of softness according to HSAB and lack of CFSE value adopt variable coordination numbers of Zn(II) metal ion in its complexes. Moreover, d^{10} metal ions when associated with ligands that containing aromatic conjugated π ring systems favor the development of fluorescence active properties. Template pseudohalide SCN^{-1} ion coordinates with particular metal ions through different binding fashion like terminal or bridging, hence to build up different coordination networks. Again SCN^{-1} can adopt additional binding mode like $\mu_{1,1}$, $\mu_{1,3}$ via nitrogen or sulfur centers to generate molecular architecture (Scheme 1 and

Figure S1) [23-31]. The present research work stems our interest rigorously to investigate the coordination behaviors of versatile (SCN^{-1}) linker whether as terminal or bridging binding fashion in the presence of pyridine as coligand. Hence in this paper, we have reported Zn(II) mononuclear complex 1 synthetic details, details X-ray crystal structure by single X-ray crystallography, characterization using different microanalytical, and spectroscopic methods. Apart from, antimicrobial activity of the synthesized Zn(II) complex 1 has been studied against some pathogenic bacteria. Antimicrobial assay confirmed that complex 1 exhibit enhanced antibacterial activity of some important Gram-positive and Gram-negative bacteria as compared to free pyridine ligand. Moreover, fluorescence study of complex 1 confirmed that it is fluorescence silent in the presence of pyridine ligand.

2. EXPERIMENTAL

2.1. General Remarks and Physical Measurements

2.1.1. Materials

Commercially available chemicals such as $Zn(OAc)_2 \cdot 2H_2O$, KSCN were purchased from (E. Merck, India). Pyridine purchased from Sigma-Aldrich Chemical Company (USA). Solvent methanol can be used after purified by standard procedures. All chemicals and solvents used in the present research work were AR grade. The synthetic reactions and work-up were done in open air.

2.1.2. Physical measurement

Elemental analyses (carbon, hydrogen and nitrogen) of complex 1 have been determined with a Perkin-Elmer CHN analyzer 2400. Mass spectra of title complex 1 were done with a JEOLJMS-AX 500 mass spectrometer. IR spectra (KBr pellet, $400-4000\text{ cm}^{-1}$) were recorded on a Perkin-Elmer model 883 infrared spectrophotometer. Absorption spectra in methanol solvent of complex 1 were measured using a UV-2450 spectrophotometer (Shimadzu) with a 1 cm path length quartz cell. Melting point of Zn(II) complex 1 has been determined on a Melting Point B-545 apparatus and is uncorrected. All spectra were corrected for the instrumental functions. Perkin-Elmer LS50B spectrofluorimeter model was used for the fluorescence measurements of Zn(II) complex 1 and pyridine at room temperature (298K). The solutions of pyridine and Zn(II) complex 1 were prepared in CH_3OH medium.

2.1.3. Experimental: Antimicrobial assay

Complex 1 was screened for antimicrobial assay against Gram-positive *Bacillus subtilis* (BS) and Gram-negative *Escherichia coli* (EC), bacterial stains along with and one fungus *Candida albicans* using the well diffusion method [32]. 200 ml of nutrient agar growth medium was dispensed into sterile conical flasks; these were then inoculated with 20 μ l of cultures mixed gently and poured into sterile Petri-dish. After setting

a borer with 6 mm diameter was properly sterilized by flaming and used to make three uniform wells in each Petri-dish. The wells were loaded with 50 μ l of synthesized compound. The solvent DMSO, used for reconstituting the solvent for diluting the compound, was similarly analyzed for control. The plates were incubated at 37°C for 24 h. The above procedure is adopted also for fungal assay, and the medium is potato dextrose agar (instead of nutrient agar) and incubated at 27°C for 48 h. The zone of inhibition was measured with a Hi antibiotic zone scale in mm, and the experiment was carried out in triplicate.

3. SYNTHESIS OF COMPLEX 1

Pyridine (0.0791 g, 1 mmol) in methanol (10 mL) was added dropwise to a solution of Zn(OAc)₂·2H₂O (0.21949 g, 1 mmol) in the same solvent (15 mL). To the resulting colorless solution, after 15 min, a methanolic solution (10 mL) of KSCN (0.1944 g, 2 mmol) was added slowly with constant stirring for 4 h. The final solution was filtered and left for slow evaporation in open air. After a week colorless crystal 1 separated out. Crystal was collected and air dried. The specific details of Zn(II) complex 1, and characterization data are given below. For complex 1 (Yield: 85%), M.Wt. (339.75), Exact Mass: 337.96, m/e: 337.95, Anal. Calc. for C₁₂H₁₀N₄S₂Zn: C, 42.42; H, 2.97; N, 16.49; Found: C, 42.41; H, 2.95; N, 16.50; IR (KBr, ν_{\max} /cm⁻¹): ν (C-C) 1145-1220, ν (C-H) 3020-3080, ν (Zn-N) 540-560, ν (C=N) 1600; ν (NCS) =2058; UV-Vis spectrum, λ_{\max} (CH₃OH): 273.00 nm.

4. X-RAY CRYSTALLOGRAPHIC STRUCTURE DETERMINATION OF COMPLEX 1

Complex 1 the data collections were made using a CCD area detector equipped with a graphite monochromated MO-K α ($K=0.71073\text{\AA}$) source in the ω scan mode at 293 K. The molecular structure of complex 1 has been solved by direct methods and refinement by full-matrix least squares on F² using the SHELXS-97 package [33]. Non-hydrogen atoms were refined with anisotropic thermal parameters. H atoms were placed in their geometrically idealized positions and constrained to ride on their parent atom multi-scan empirical absorption corrected were applied to the data using the program SADABS [34]. During crystal data refinement common programs used are SHELXS-97 and ORTEP. Different crystallographic pictures are generated using software Mercury 3.8v, Diamond 4.2.2v, Crystal and Olex-2. A summary of the crystallographic data and structure refinement parameters of complex 1 is given in Table 1. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1495142. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K.: <http://www.ccdc.cam.ac.uk/cgi-bin/>

Table 1: Summary of crystallographic data and refinement parameters for complex 1.

Empirical formula	C ₁₂ H ₁₀ N ₄ S ₂ Zn
Formula weight	339.733
Temperature (K)	293 (2) K
Wavelength (Å)	0.71069
Crystal system	Monoclinic
Space group	P21/m
Unit cell dimensions	
a (Å)	5.5671 (4)
b (Å)	11.085 (8)
c (Å)	12.1321 (8)
α (°)	90.000 (5)
β (°)	96.726 (5)
γ (°)	90.000 (5)
Volume (Å ³)	743.562
Z	2
Density _{cal} (Mg m ⁻³)	1.517
Absorption coefficient (mm ⁻¹)	1.922
F (000)	344
Θ Range (°) for data collection	26.00
Index ranges	-7 ≤ h ≤ 7 -15 ≤ k ≤ 15 -17 ≤ l ≤ 17
Goodness-of-fit on F ²	1.009
Completeness to theta	0.999
Independent reflections [R _{int}]	1614
Refinement method	Full-matrix least squares on F ²
Reflections collected	2370
Final R indices [I > 2 σ (I)]	R ₁ =0.0332, ω R ₂ =0.0816
Largest difference peak and hole (eÅ ⁻³)	0.337 and -0.256

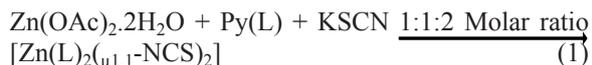
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5. RESULTS AND DISCUSSION

5.1. Synthesis

Mononuclear 4-coordinated complex 1 of the type [Zn(L)₂(μ -1,1-NCS)₂] was isolated as colorless crystal through one-pot synthetic methodology. A methanolic solution of Zn(OAc)₂·2H₂O was slowly added to the methanolic solution of pyridine and potassium thiocyanate solution at (1:1:2) M ratio with constant stirring 4 h to prepare white crystal of complex 1. Mononuclear Zn(II) complex has been characterized by different physicochemical techniques and IR, UV-

Vis and mass spectroscopic studies. The synthetic reaction is summarized in Equation 1.



5.2. Characterization of Mononuclear Zn(II) Complex 1

The infrared spectra of complex 1 are consistent with the structural data given in this paper. The lowering frequency of C=N group indicates the coordination of C=N nitrogen to the Zn metal center. According to literature of Zn-Py(N) complexes, IR spectrum is found to be 650-570 cm^{-1} and our synthesized complex 1 a nice IR band observed within the range 557-542 cm^{-1} . This is directly confirmed the Zn-Py(N) bond formation for the synthesized complex. The literature $\nu(\text{C}=\text{N})$ frequencies of SCN^{-1} could be used for differentiation purpose between S-bonded (2110-2140 cm^{-1}) and N-bonded (<2110 cm^{-1}) complexes [35]. Complex 1 strong IR band near at 2058 cm^{-1} clearly indicates the formation of Zn-N thiocyanate ($\mu\text{-}1,1\text{-SCN}^{-}$) linkage which is consistent with the crystal structure. Hence here SCN^{-1} can be coordinated with Zn(II) metal as terminal fashion through N atom. Complex 1 IR absorption bands near at 3020-3080 and 1145-1220 cm^{-1} are due to vibration of C-H and C-C stretching. Colorless CH_3OH solution of complex 1 show ligand based transition at 273 nm, and this is assignable to $\pi \rightarrow \pi^*$ transition (Figure S2).

6. X-RAY CRYSTAL STRUCTURE OF COMPLEX 1

The molecular structure ORTEP was depicted in Figure 1. Some selected important crystal metrical parameters are presented in Table S1. A perspective view of single crystal X-ray reveals that complex 1 crystallizes in monoclinic system having space group P 2(1)/m. The crystal system consists of no cationic part provided it is mononuclear neutral in nature. The Zn(II) atom is bonded to two Py(N) donor atoms together with two SCN^{-1} bonded through nitrogen atoms leading to form $\text{ZnL}_2(\text{SCN}^{-})_2$ tetrahedral

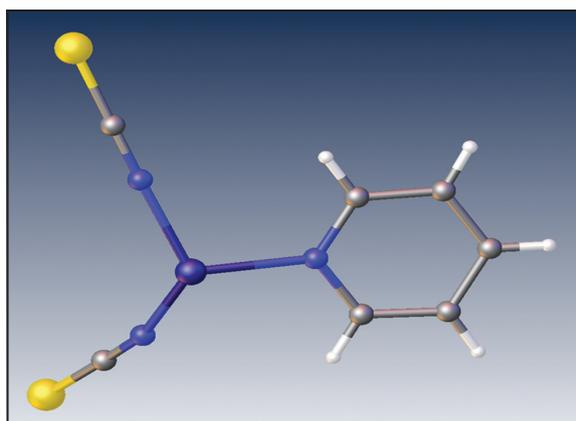


Figure 1: An ORTEP view of complex 1.

structural framework. In this tetrahedral framework, SCN^{-1} can function as promising $\mu\text{-}1,1\text{-NCS}$ bonding fashion. The two Py(N) donor atoms attached Zn1-N1 bond lengths are 2.031Å, beside two Zn-N(SCN) bond lengths are 1.959Å, 1.936Å. The coordination geometry is completely tetrahedral where two Py(N) are mutually transposition and two N-bonded NCS is nearly linear and is connected to Zn(II) in a complete linear fashion. The N1-Zn1-N2 and N1-Zn1-N3 bond angles values are 109.07°, 105.55° that nearly equal to standard tetrahedral bond angle values further supporting tetrahedral geometry. Thiocyanate ion (N-bonded) linear bonding fashion in complex 1 was further supported by bond angle values Zn1-N1-C1 and Zn1-N1-C5 119.5°, 122.7°. Trapping of water molecule is totally absent in the crystal system; hence, there will be no extended hydrogen bonding that leads $\pi \rightarrow \pi^*$ molecular stacking or supramolecular interactions. Complex 1 exhibit several types of molecular packing along the proper crystallographic axis (Figure 2a and b).

7. ANTIMICROBIAL ASSAY: RESULTS AND DISCUSSION

After the analysis of antimicrobial activity, it was observed that complex 1 was found to be more active against Gram-negative bacteria EC followed by against Gram-positive BS. Such increased activity of the complex 1 can be explained on the basis of chelation theory (Odds, 1989) [36]. According to that the lipid membrane surrounding the cell favors the passage of only lipid-soluble materials, due to that better antimicrobial activity was exhibited. Further on chelation, the polarity of the metal ion will be reduced to a greater extent, and by this hydrogen bond may be possible, due to the overlapping of the ligand orbital and partial sharing of positive charge of the metal ion with donor groups. Furthermore, the complex 1 may also involve the formation of a hydrogen bond through the pyridine ring. However, the poor antifungal activity shown by the complex 1 could be attributed to its resistant nature to fungus. Further studies are under process. The zone of inhibition of the synthesized complex 1 for antibacterial and antifungal activity at 10 $\mu\text{g/mL}$ concentration shown in Table 2.

8. FLUORESCENCE SPECTRAL STUDIES

Schiff base complexes with Zn(II) or Cd(II) d^{10} metal ions fluorescence spectral studies is one of the most promising properties as it opens up the new opportunity for photochemical applications [37]. Although our synthesized complex 1 does not belong to Schiff base

Table 2: EC, BS, CA.

Complex	EC	BS	CA
1	22	15	5

EC: *Escherichia coli*, BS: *Bacillus subtilis*, CA: *Candida albicans*

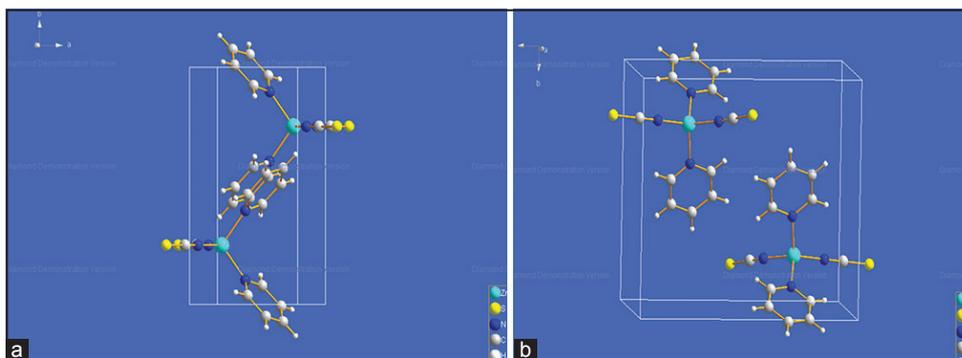


Figure 2: (a and b) Molecular packing of complex 1.

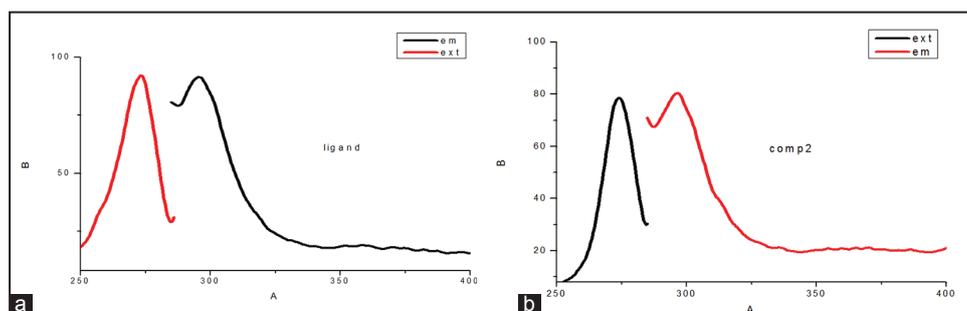


Figure 3: (a and b) Silent fluorescence spectra of pyridine ligand and complex 1 in methanol solvent.

complex category, yet we study fluorescence properties in a comparative approach for pyridine ligand and complex 1 in methanol solvent at room temperature (298 K). Quenching of fluorescence of a ligand by particular transition metal ions during stable complex formation is a rather common fact which is always explained by some well-known important processes such as magnetic perturbation, redox activity, and electronic energy transfer. Such a quenching is observed by the occurrence of photoinduced electron transfer process of nonbonding electrons of the ligand. But when such PET is prevented by a stable complex formation after metal and Schiff base ligand interaction fluorescence intensity greatly enhanced due to metal ligand chelation effect and the overall process is referred as “CHEF.” Complex 1 displays emission spectra at 297.5 nm while pyridine ligand has an identical band 295 nm when both are excited at 273 and 272.5 nm. The above result confirmed that complex 1 is fluorescence silent. Complex 1 fluorescence inactivity is due to the fact that pyridine has small size aromatic ring with respect to polydentate Schiff base ligand containing large aromatic ring π cloud conjugation effect. Apart from, since Zn(II) is d^{10} metal ion system it is difficult to oxidize or reduce. Hence in complex 1 no emission originating from MLCT/LMCT. Thus, the emission observed in complex 1 is tentatively assigned to the $\pi \rightarrow \pi^*$ intra ligand fluorescence (Figure 3a and b).

9. CONCLUDING REMARKS

We have successfully synthesized complex 1 as a white crystal in methanol solvent medium, and

the reference complex 1 has been characterized by different microanalytical instruments IR, UV-Vis, mass spectroscopic studies. The versatile thiocyanate ligand (SCN^{-1}) due to its bemusing coordinating ability act as a linker during complex 1 formation and reflecting SCN^{-1} ion awesome ($\mu_{1,1}$ -NCS) binding fashion. In addition with pyridine as coligand leading to form colorless mononuclear perfect Zn(II) tetrahedral environmental complex 1. Antimicrobial efficacy of complex 1 has been studied against some important Gram-positive and Gram-negative bacteria. Result successfully confirmed that complex 1 exhibits strong antimicrobial effect toward some Gram-positive and Gram-negative bacteria. Complex 1 in the presence of pyridine ligand is fluorescence silent.

10. ACKNOWLEDGMENT

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***Bibliographical Sketch**



Prof. Dhrubajyoti Majumdar presently Asst. Professor (Stage 3) and head of UG section, Department of chemistry, Tamralipta Mahavidyalaya (Govt. aided college), Tamruk-721636, PurbaMedinipur, West Bengal, India. He obtained his M.sc degree (Inorganic chemistry special Paper) from Raja Bazar Science college, Calcutta University in 1992. Presently he has been teaching at the UG section in Tamralipta Mahavidyalaya. Prof. Majumdar published over 15 papers in international journals with high index and actively engaged research in the field of Zn(II), Cd(II), Hg(II) Schiff base N,O-donor ligand complexes with incorporation of versatile pseudohalides bridging (N₃-/SCN-/Cl-/SeCN-/OCN-).

APPENDIX A: SUPPLEMENTARY MATERIALS

Complex 1 crystal metrical parameters are shown in Table S1. Figures S1-2 show complex 1 SCN^{-1} bridging scheme 1 and UV spectral curve as supplementary information. CCDC 1495142 contains the supplementary crystallographic data (excluding structure factors) in CIF format for the structure reported of complex 1. The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

SUPPLEMENTARY MATERIALS

Supplementary Figures

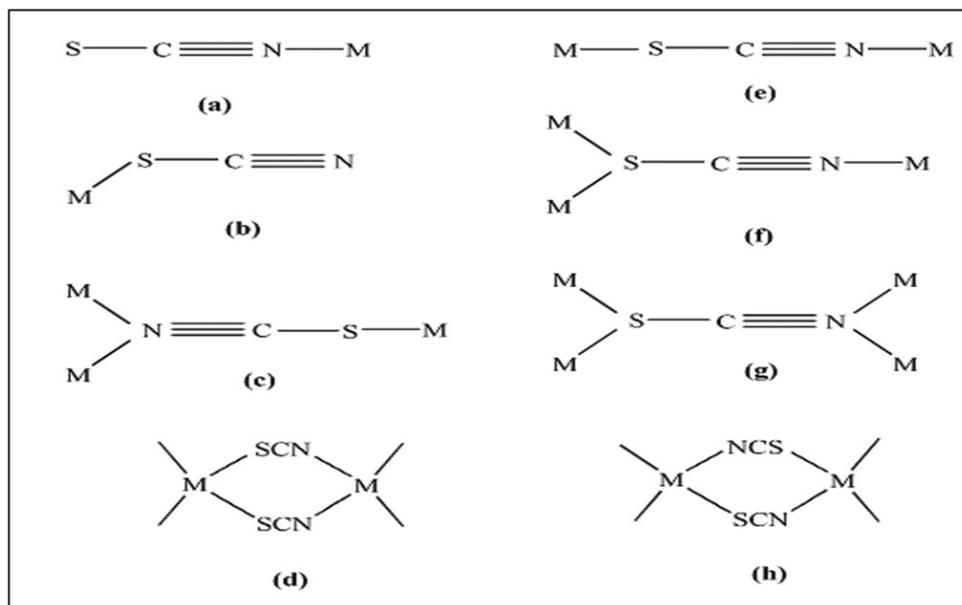


Figure S1: Scheme 1: Versatile bridging modes of SCN - Pseudohalide

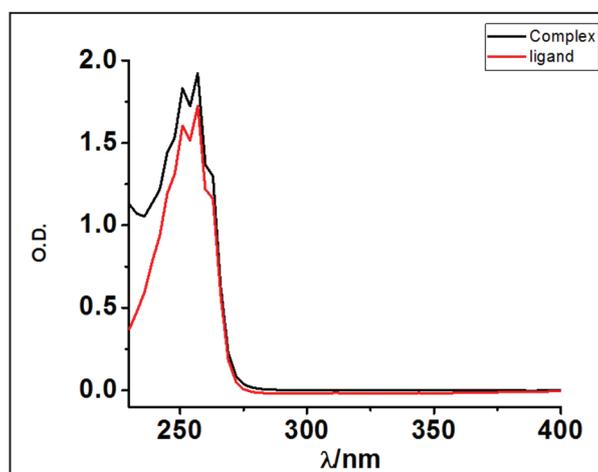


Figure S2: UV-Vis spectra of complex 1.

*Supplementary Table***Table S1:** Selected some bond distances (Å) and angles (°) for complex 1.

Selected some bond distances	Bond distances value (Å)
Zn1-N1	2.031
Zn1-N3	1.959
Zn1-N2	1.9136
S2-C7	1.611
N1-C1	1.335 (3)
N1-C5	1.331 (3)
N3-C7	1.115
N2-C6	1.132
N1-C1	1.335 (3)
N1-C5	1.331 (3)
Selected angles	Bond angles value (°)
N1-Zn1-N3	105.55
N1-Zn1-N2	109.07
N1-Zn1-N1	105.94
N3-Zn1-N2	120.7
N3-Zn1-N1	105.55
N2-Zn1-N1	109.07
Zn1-N1-C1	119.5
Zn1-N1-C5	122.7
Zn1-N3-C7	165.7
Zn1-N2-C6	177.4