

Research Article

Synthesis, Crystal Structure, and Antimicrobial Properties of [Diaquabis(hexamethylenetetramine)diisothiocyanato- κ N]nickel(II) Complex

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A nickel(II) complex with hexamethylenetetramine and thiocyanate ion as coligands has been synthesized and characterised by infrared spectroscopy and ultraviolet-visible spectroscopic techniques. The crystal structure of the complex was determined by single crystal X-ray diffraction and the ligands were found to coordinate terminally through N-atoms. The ligand and the complex were screened for their activity against resistant strains of bacteria (*Salmonella enteric*, *Shigella flexneri*, *Escherichia coli*, and *Staphylococcus aureus*) and fungi (*Candida albicans*, *Candida krusei*, *Candida parapsilosis*, and *Candida neoformans*).

Dedicated to Professor Moise Ondoh Agwara on his 60th anniversary

1. Introduction

Recently, the design and synthesis of novel coordination compounds, inorganic-organic hybrid materials, and coordination polymers with desired physicochemical properties are at the frontiers of inorganic chemistry research [1–6]. To achieve this goal, the rational design of particular structures employing different synthetic approaches needs to be developed, followed by a study of the structure-property relationships. The rational choice of building blocks, metal centres and ligands, is of crucial importance in the deliberate construction of coordination networks and the design of metal-based supramolecular architectures [7, 8]. Among the ligands employed in the construction of these networks, hexamethylenetetramine (HMTA), as a potential tetradentate ligand or hydrogen bond acceptor, seems quite suitable in self-assembly systems.

Hexamethylenetetramine is a commercially available organic molecule which possesses three fused rings in the

chair conformation similar to the cage-like structure of adamantane [9]. It is cheap, ecofriendly, and readily available for reactions with many hydrated salts. It forms molecular complexes, with varied coordination patterns ranging from monodentate [10], bridging [11, 12], nonchelating to hydrogen-bonded frameworks [13–15], inducing the formation of one-, two-, and three-dimensional framework structures. Biologically, HMTA has several uses like a cosmetic biocide in eye make-up preparation, preservative in lotions and creams, or antiseptic agent for the treatment of urinary tract infections [16, 17].

Among the inorganic anions serving as coligands, thiocyanate SCN^- (an ambidentate ligand) is very important due to its great tendency to combine with a variety of metal ions, forming either thiocyanato (M-SCN) or isothiocyanato (M-NCS) complexes and also bridges metal ions. In addition, the antagonism between the ligands HMTA and SCN^- (neutral and ionic) as well as the solvent molecules influence in the coordination sphere is fundamental in supramolecular

assembly [18–22]. Hence, the nature of these complexes depends on the interplay between the metal ion, the counter ion, and HMTA [23].

Within the scope of our ongoing research on the structure and applications of coordination compounds, based on N-, and N,O-donor heterocyclic ligands and coligands (thiocyanate, azide, etc.), we have synthesized a number of different materials and together with selected examples from the literature evaluated their antimicrobial properties [16, 23–28].

The emergence of drug-resistant bacterial and fungal strains has become a worldwide cause for concern [29, 30]. This increasing resistance of microbes to antibacterial and antifungal drugs has necessitated the search for new compounds to target pathogenic microbes [29, 30]. Several efforts have been made to develop antimicrobial agents to fight against these resistant pathogens among which are the protection of the efficacy and appropriate use of existing drugs as well as research and development of new antimicrobial agents that are not affected by the currently known, predicted, or unknown mechanisms of resistance [31–33]. The incorporation of metals into antibacterial molecules is expected to enhance the bactericidal or fungicidal properties of these drugs.

In this work, we report the synthesis and crystal structure of a nickel(II) hexamethylenetetramine complex with thiocyanate coligand. The biological activity of the complex towards some resistant pathogens, evaluated using *in vitro* assays, is also presented.

2. Experimental

2.1. Materials. NiSO₄·6H₂O, hexamethylenetetramine, and ammonium thiocyanate were obtained from Sigma Aldrich. Methanol was obtained from Riedel-de Haen (Germany). The chemicals were of analytical grade and were used as such, while the solvent was distilled according to standard methods.

2.2. Synthesis of the Complex [Ni(HMTA)₂(NCS)₂(H₂O)₂·H₂O. A 15 mL methanol solution of hexamethylenetetramine (0.280 g; 2.0 mmol) was added dropwise to a 15 mL methanol/H₂O (2:1 v/v) solution of NiSO₄·6H₂O (0.291 g; 1 mmol) while stirring at room temperature. After stirring for 30 minutes, ammonium thiocyanate (0.156 g; 2 mmol) in 10 mL methanol was added into the solution. The mixture was further stirred for two hours and stored for a week during which time bluish-green needle-like crystals suitable for single crystal X-ray diffraction were obtained. They were filtered, washed with diethylether, and dried over silica gel in a desiccator.

2.3. Characterisation. The infrared spectrum of the complex was recorded using a Bruker ALPHA-P spectrophotometer directly on a small sample of the complex in the range 400–4000 cm⁻¹ while the UV-visible spectrum of an ethanolic solution of the complex was recorded using a Bruker HACH DR 3900 UV-visible spectrophotometer at room temperature.

2.4. X-Ray Crystal Structure Determination. Intensity data for the compound was collected using a Bruker AXS Kappa APEX II single crystal CCD Diffractometer, equipped with graphite-monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. The selected crystal for the diffraction experiment had a dimension of $0.25 \times 0.25 \times 0.2 \text{ mm}^3$. Accurate unit cell parameters were determined from the reflections of 36 frames measured in three different crystallographic zones by the method of difference vectors. The data collection, data reduction, and absorption correction were performed by APEX2, SAINT-Plus, and SADABS programs [38]. The structure was solved by direct methods procedure using SHELXS-97 program [39] and the nonhydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F^2 using SHELXL-97 program [39]. The positions of all the nonhydrogen atoms were identified from difference electron density map and were fixed accordingly. Hydrogen atoms were treated by a mixture of independent and constrained refinement.

2.5. Antimicrobial Tests. The *in vitro* antimicrobial activities of the metal salts, metal complex, ligands, and reference drugs were evaluated by disk diffusion and broth microdilution methods. The antimicrobial tests were carried out in the Laboratory of Phytobiochemical and Medicinal Plant Study, University of Yaoundé I, Cameroon. Four strains of bacteria (*Salmonella enteric*, *Shigella flexneri*, *Escherichia coli*, and *Staphylococcus aureus*) and four strains of fungi (*Candida albicans*, *Candida krusei*, *Candida parapsilosis*, and *Candida neoformans*) were used for this study. All the species were derived from stock cultures obtained from the Medical Bacteriology Laboratory of “Centre Pasteur du Cameroun”, Yaoundé, Cameroon. Chloramphenicol and fluconazole were used as reference antibacterial and antifungal drugs, respectively.

2.5.1. Diffusion Tests. *In vitro* antibacterial activities of the ligand, metal salt, and the complex were evaluated using disc diffusion method. Mueller-Hinton Agar was employed as microbial growth medium. The antibacterial diffusion tests were carried out as previously reported [26].

Mueller-Hinton agar was prepared from a commercially available dehydrated base according to the manufacturer's instructions. Several colonies of each microorganism were collected and suspended in saline (0.9% NaCl). Then, the turbidity of the test suspension was standardized to match that of a 0.5 McFarland standard (corresponding to approximately 1.5×10^8 CFU/mL for bacteria or 1×10^6 to 5×10^6 cells/mL for yeast). Each compound or reference was accurately weighed and dissolved in the appropriate diluents (DMSO at 10%, methanol at 10%, or distilled water) to yield the required concentration (2 mg/mL for compound or 1 mg/mL for reference drug), using sterile glass-ware.

Whatman filter paper number 1 was used to prepare discs approximately 6 mm in diameter, which were packed up with aluminum paper and sterilized by autoclaving. Then, 25 μ L of stock solutions of compound or positive control was

delivered to each disc, leading to 50 μg of compound or 25 μg of reference drug.

The dried surface of a Mueller-Hinton agar plate was inoculated by flooding over the entire sterile agar surface with 500 μL of inoculum suspensions. The lid was left ajar for 3 to 5 minutes to allow for any excess surface moisture to be absorbed before applying the drug impregnated discs. Discs containing the compounds or antimicrobial agents were applied within 15 minutes of inoculating the MHA plate. Six discs per Petri dish were plated. The plates were inverted and placed in an incubator set to 35°C. After 18 hours (for bacteria) and 24 hours (for yeasts) of incubation, each plate was examined. The diameters of the zones of complete inhibition (as judged by the unaided eye) were measured, including the diameter of the disc. Zones were measured to the nearest whole millimeter, using sliding calipers, which was held on the back of the inverted Petri plate. Three replicas were performed for each sample and mean values of the growth inhibition zone were calculated. Compounds were considered active when the IZ was greater than 6 mm.

3. Results and Discussion

3.1. Synthesis of the Complex. The reaction of hexamethylenetetramine, ammonium thiocyanate, and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ yielded the complex $[\text{Ni}(\text{HMTA})_2(\text{NCS})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$. The complex was bluish-green in colour and it was obtained in high yield, 74%.

3.2. Description of the Crystal Structure. The crystal structural data of the complex are summarized in Table 1. The ORTEP view of the crystal structure together with the atom numbering scheme is shown in Figure 1. The packing diagram of the complex and the H-bonding scheme seen along the crystallographic *b*-axis are shown in Figures 2 and 3, respectively. Selected bond distances and bond angles for the complex are presented in Table 2.

The complex crystallizes in the monoclinic crystal system with space group *C2/c*. The asymmetric unit consists of one HMTA molecule, one thiocyanate anion, one coordinated water molecule, one lattice water molecule, and one Ni(II) ion. The crystal structure of the complex reveals that the Ni(II) coordination environment is a slightly distorted octahedron (NiN_4O_2 chromophore) in which it is covalently bonded to two terminal HMTA N-atoms (Ni-N4 2.238(2) Å) in transaxial positions, two water O-atoms (Ni-O1 2.058(2) Å) and two terminal NCS^- N-atoms (Ni-N2 2.031(2) Å), in the equatorial plane. The Ni atom is located in an inversion centre. This arrangement is similar to that of related structures reported in the literature [35–37]. The NCS^- groups show almost linearity with N-C-S angle of 179.52° in the complex as previously reported for analogous Co and Mn structures [35–37]. The connection between Ni atoms and NCS^- groups is slightly bent with a Ni-N2-C8 angle of 172.68°. Furthermore, the O atoms of both water molecules and the N atoms of both NCS^- anions are each mutually trans to each other, as evidenced by the bond angles O1-Ni-O1 180° and N2-Ni-N2 180°, respectively. Each lattice water

TABLE 1: Crystal data and structure refinement for the complex.

Empirical formula	$\text{C}_{14}\text{H}_{32}\text{N}_{10}\text{NiO}_4\text{S}_2$
Formula weight	527.33
Temperature	100 K
Wavelength (Å)	$\lambda = 0.71073$
Crystal system	Monoclinic
Space group	<i>C2/c</i>
Unit cell dimensions	
<i>a</i> (Å)	18.085(4)
<i>b</i> (Å)	7.4019(16)
<i>c</i> (Å)	17.422(4)
α (°)	90
β (°)	91.527(2)
γ (°)	90
Unit cell volume	2331.4(9)
<i>Z</i>	4
<i>F</i> (000)	1112.0
Density (calculated)	1.502 Mg/m ³
Absorption coefficient	1.054 mm ⁻¹
Crystal size	0.16 × 0.203 × 0.501 mm ³
Theta range for data collection	2.25 to 28.15
Indexes (<i>h, k, l</i>) _{max}	(24, 9, 23)
Reflections collected	6943
Independent and observed reflections	2681 [<i>R</i> (int) = 0.0240], 2563
Completeness to theta = 26°	99.8%
Refinement method	Full-matrix least squares on <i>F</i> ²
Data/restraints/parameters	2681/0/158
Goodness-of-fit on <i>F</i> ²	1.051
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0269, <i>wR</i> ₂ = 0.0695
Final <i>R</i> indices (all data)	<i>R</i> ₁ = 0.0279, <i>wR</i> ₂ = 0.0689
Largest diff. peak and hole	0.875 and -0.567 e ⁻ Å ⁻³

molecule forms three H-bonds with O-atom of a coordinated water molecule (O-H...O 2.669 Å), noncoordinated N-atom of HMTA (O-H...N 2.797 Å), and S-atom of SCN^- (O-H...S 3.310 Å). There is another H-bond between the oxygen atom of the coordinated water molecule and a noncoordinated nitrogen of a HMTA molecule (O-H...N distance = 2.806 Å). Adjacent Ni coordination centres are linked by free H_2O molecules via hydrogen bonds also involving two coordinated O-atoms of water molecules and two uncoordinated N-atoms of HMTA molecule in the hydrogen bond net, forming 1D chains. These adjacent chains are further connected to form 2D supramolecular layers parallel to the *ac* plane by S...N and C...C interactions. The two-dimensional layers are further connected by O-H...S and O-H...N hydrogen bonds, along the *b* crystallographic axis, to form a three-dimensional supramolecular structure. This is in agreement with literature reports [35–37]. The H-bonding motifs can be described in Etter's graph set notation as *R*₂²(12) and

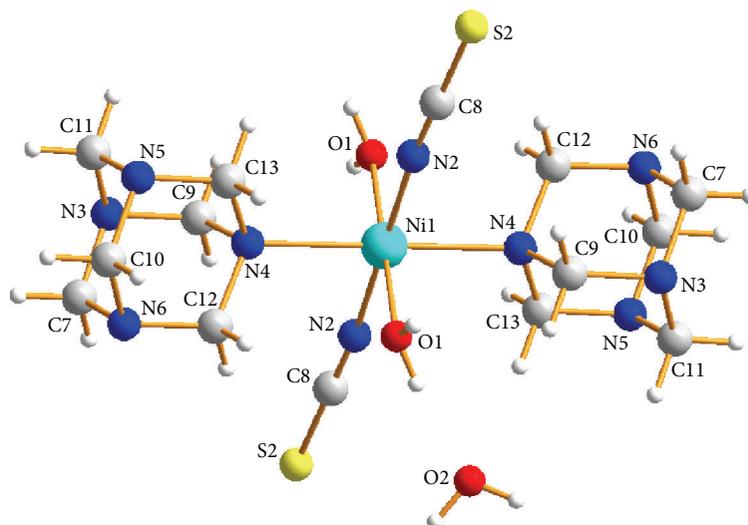


FIGURE 1: ORTEP view of the complex with atom numbering scheme.

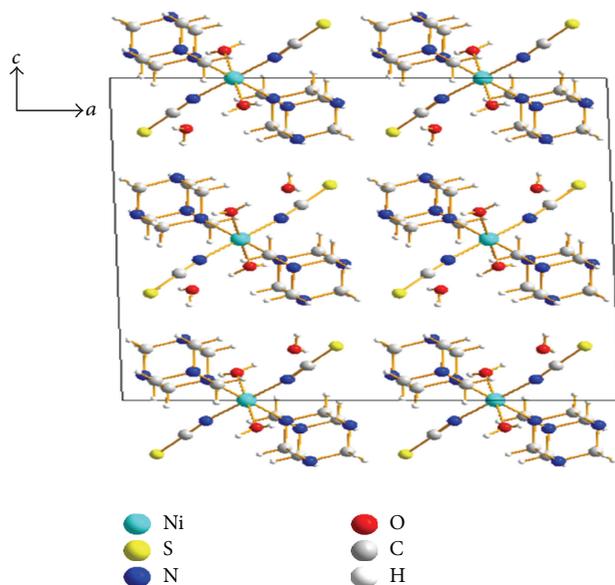
FIGURE 2: Packing diagram of the complex seen along the crystallographic *b*-axis.

TABLE 2: Selected bond lengths (Å) and angles (°) for the complex.

Ni1-O1	2.058(2)	N6-C7	1.476(2)
Ni1-N2	2.031(2)	N6-C10	1.485(2)
Ni1-N4	2.238(2)	N6-C12	1.475(2)
Ni1-O1	2.058	S2-C8	1.642(1)
Ni1-N2	2.031	N2-C8	1.161(2)
Ni1-N4	2.238	N3-C7	1.481(2)
S2-C8	1.642(1)	N3-C9	1.469(2)
N2-C8	1.161(2)	N3-C11	1.484(2)
O1-Ni1-N2	90.08	Ni1-N2-C8	172.68
O1-Ni1-N4	93.73	Ni1-N4-C9	108.74
O1-Ni1-O1	180	Ni1-N4-C12	113.34
O1-Ni1-N2	89.92	Ni1-N4-C13	112.96
O1-Ni1-N4	86.27	S2-C8-N2	179.52
N2-Ni1-N4	92.64	N4-Ni1-N4	180
N2-Ni1-O1	89.92	O1-Ni1-N2	90.08
N2-Ni1-N2	180	O1-Ni1-N4	93.73
N2-Ni1-N4	87.36	N2-Ni1-N4	92.64
N4-Ni1-O1	86.27	Ni1-N2-C8	172.68
N4-Ni1-N2	87.36	Ni1-N4-C9	108.74
Ni1-N4-C13	112.96	Ni1-N4-C12	113.34

$R_4^4(16)$ [40, 41]. The nickel atoms form linear chains running along the *b*-direction with an interlayer Ni-Ni distance of 7.402 Å, while the Ni...Ni distances within hydrogen-bonded chains and between adjacent chains in the same layer are 9.465 Å and 9.771 Å, respectively.

A comparison of the M-N (HMTA), M-N (NCS⁻), and M-O (H₂O) bond distances for similar structures found in the literature [34–37] is shown in Table 3. The axial Ni-N (HMTA) bond length is slightly shorter than those of Co-N and Mn-N but longer than that of Cu-N. The Ni-N (NCS⁻) bond length is similar to those of Co and Cu but is shorter than that of Mn. The Ni-O bond is slightly shorter than the other M-O bonds. While the Ni complex

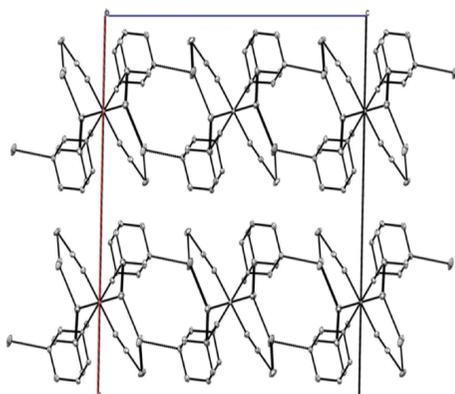
obtained has a unique coordination centre, the complexes, [Mn(hmt)₂(H₂O)₂(NCS)₂].[Mn(H₂O)₄(NCS)₂].2H₂O and [Co(NCS)₂(hmt)₂(H₂O)₂].[Co(NCS)₂(H₂O)₄].H₂O, contain two distinct six coordinate M(II) centres alongside two lattice water molecules and one lattice water molecule, respectively. The independent uncharged components [M(NCS)₂(hmt)₂(H₂O)₂], [M(NCS)₂(H₂O)₄], and H₂O are linked together by three kinds of hydrogen bonds (O-H...N, O-H...O and O-H...S) to form a three-dimensional supramolecular structure [35–37]. On the other hand, the coordination environment of the Cu atom in the complex K[Cu(C₆H₁₂N₄)₂(NCS)₃].2H₂O is trigonal bipyramidal with

TABLE 3: Comparison of bond parameters for similar structures $[M(\text{hmt})_2(\text{H}_2\text{O})_2(\text{NCS})_2]$ ($M = \text{Cu}, \text{Co}, \text{Mn}, \text{and Ni}$).

M-N (HMTA)	Bond length (Å)	M-N (NCS ⁻)	Bond length (Å)	M-O (H ₂ O)	Bond length (Å)	Ref.
Cu-N	2.09(5) 2.10(5)	Cu-N	1.98(6) 2.08(6) 1.98(7)	None	—	[34]
Mn-N	2.4213(13)	Mn-N	2.1342(15)	Mn-O	2.1865(12)	[35]
Co-N	2.341(5)	Co-N	2.058(5)	Co-O	2.104(5)	[36]
Co-N	2.3274(16)	Co-N	2.0411(19)	Co-O	2.1025(16)	[37]
Ni-N	2.238(2)	Ni-N	2.031(2)	Ni-O	2.058(2)	This work

TABLE 4: Relevant IR bands of the ligands and the complex.

	$\nu_{\text{O-H}}$	$\nu_{\text{H}_2\text{O}}$	$\nu_{\text{C-N}}$	$\nu_{\text{C-N}} (\text{SCN}^-)$	ρ_{CH_2}	$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$
HMTA	—	—	1238	—	810		
Complex	3370	3250	1232	2084	821	778	683 669

FIGURE 3: ORTEP representation of the H-bonding scheme of the complex seen along the crystallographic b -axis.

three equatorial positions occupied by NCS groups and the axial positions by the HMTA molecules [34].

As shown by Lu et al. [37], the close distance of NCS⁻ groups, the large volume of HMTA ligand, and the ratio between the divalent metal and NCS⁻ of 2:1 can probably explain the absence of S...S Van der Waals' interactions in the Mn [35], Co [36], and Ni (this work) complexes.

3.3. Infrared Spectroscopy. The characteristic IR band frequencies of the ligand and complexes are presented in Table 4.

The broad band at 3250 cm⁻¹ and the sharp peak at 1661 cm⁻¹ are assigned to $\nu_{\text{O-H}}$ and $\delta_{\text{H-O-H}}$ of lattice water, respectively, while the peak at 3370 cm⁻¹ is due to $\nu_{\text{O-H}}$ of coordinated water [42]. The CH₂ stretching vibrational band of HMTA appears at 2957 cm⁻¹. The band at 1238 cm⁻¹ assigned to the C-N stretch of HMTA is shifted to 1232 cm⁻¹ in the complex while the band at 810 cm⁻¹ in the free ligand assigned to the CH₂ rocking vibration of HMTA is shifted to 821 cm⁻¹ in the complex, indicating coordination of the ligand [27]. The sharp peak at 2084 cm⁻¹ is assigned to the

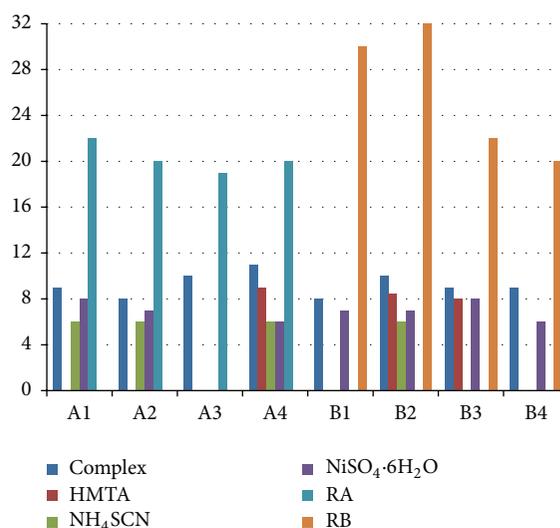


FIGURE 4: Histogram of inhibition zone of ligands, metal salt, and complex against bacteria.

C-N stretching vibration of SCN⁻ [43]. The appearance of new peaks at 778 cm⁻¹, 683 cm⁻¹, and 669 cm⁻¹, respectively, indicates M-O and M-N bonding between the metal and the ligands.

3.4. UV-Visible Spectroscopy. The electronic spectrum of the nickel(II) complex exhibits two absorption bands: one band around 25,000 cm⁻¹ and a second broad and split band at 15625–14514 cm⁻¹. These bands have been assigned to $^3A_{2g} \rightarrow ^3T_{1g}(\text{P})$ and $^3A_{2g} \rightarrow ^3T_{1g}(\text{F})$ transitions, respectively [44]. The ratio of 1.72 of the height of the first to that of the second band indicates an octahedral environment around the nickel(II) ion [45].

3.5. Antimicrobial Tests. The metal salt, ligands, metal complex, and reference drugs were tested for antimicrobial activity *in vitro* against four bacteria and four fungi strains. The susceptibility of the bacteria and fungi strains towards the compounds was judged by measuring the diameter of the growth inhibition zone. The results are summarized in Table 5 and displayed in a histogram (Figure 4).

HMTA was found to be active against three of the eight pathogens while the metal complexes showed increased

TABLE 5: Diameter of inhibition zone (mm) of the compounds against bacteria and fungi.

	A ₁	A ₂	A ₃	A ₄	B ₁	B ₂	B ₃	B ₄
Complex	9 ± 0.0	8 ± 0.0	10 ± 0.0	11 ± 0.0	8 ± 0.0	10 ± 0.0	9 ± 0.0	9 ± 0.0
HMTA	0	0	0	9 ± 1.4	0	8.5 ± 0.7	8 ± 0.0	0
NH ₄ SCN	6 ± 0.0	6 ± 0.0	0	6 ± 0.0	0	6 ± 0.0	0	0
NiSO ₄ ·6H ₂ O	8 ± 0.0	7 ± 0.0	0	6 ± 0.0	7 ± 0.0	7 ± 0.0	8 ± 0.7	6 ± 0.0
RA	22 ± 0.0	20 ± 0.0	19 ± 1.4	20 ± 0.0	—	—	—	—
RB	—	—	—	—	30 ± 0.0	32 ± 0.0	22 ± 0.0	20 ± 0.0

A₁: *Staphylococcus aureus*; A₂: *Salmonella enterica*; A₃: *Shigella flexneri*; A₄: *Escherichia coli*; B₁: *Candida albicans*; B₂: *Candida parapsilosis*; B₃: *Candida krusei*; B₄: *Candida neoformans*; RA: reference antimicrobial (chloramphenicol); RB: reference antifungal (fluconazole); —: not tested.

activity against all the pathogens. This indicates that the metal ion probably plays an important role in enhancing the antimicrobial activity of the ligand on interaction with it. The highest activity of the complex is shown against *E. coli* and *S. flexneri*. This increase in activity could be due to the reduction of the polarity of the metal ion by partial sharing of the positive charge with the ligand's donor atoms so that there is electron delocalisation within the metal complex. This may increase the lipophilic character of the metal complex, enabling it to permeate the lipid layer of the organism killing them more effectively [46].

4. Conclusion

The synthesis of a nickel-HMTA complex [Ni(HMTA)₂(NCS)₂(H₂O)₂].H₂O has been reported. The equatorial H₂O and NCS ligands coordinate in a nonlinear manner to the central metal ion while the axial HMTA ligands are terminally coordinated to the Ni(II) ion through one N-atom each. The Ni(II) coordination environment is a slightly distorted octahedron (NiN₄O₂ chromophore). An extended three-dimensional network is assembled via H-bonding interactions involving the lattice water molecule, O-atom of a coordinated water molecule, noncoordinated N-atom of HMTA, and S-atom of SCN⁻. Results of the preliminary antimicrobial screening against four pathogenic bacteria and four fungi species indicate that the complex is moderately active, with highest activity shown against *E. coli* and *S. flexneri*. The complex could be further screened *in vitro* against a wide range of pathogens.

Additional Points

CCDC 1452400 contains the supplementary crystallographic data for the complex. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <https://summary.ccdc.cam.ac.uk/structure-summary?access=refere&ccdc=1452400&authors=che>.

Competing Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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