Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Research paper

Copper(II) and nickel(II) complexes of an *N*-pendent bis-(cyanoethyl) derivative of an isomeric hexamethyl tetraazamarocyclic ligand: Synthesis, characterization, electrolytic behavior and antimicrobial studies



Inorganica Chimica Acta

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ARTICLE INFO

Keywords: N-pendent derivative of tetraazamacrocycle Copper(II) and nickel(II) complexes Spectroscopic studies Electrolytic behavior Antimicrobial activities

ABSTRACT

Hexamethyl derivative salt of the fourteen membered tetraazamacrocycle, $Me_6[14]$ diene.2HClO₄ (L.2HClO₄) has been synthesized by the condensation of ethylenediamine with acetone in presence of quantitative amount of perchloric acid. This diene ligand salt on reduction with NaBH₄ followed by extraction with CHCl₃ at pH above 12 resulted in a mixture of isomeric ligands, $Me_6[14]$ anes which were separated by fractional crystallization from xylene and designated by 'tet-a' and 'tet-b'. Interaction of 'tet-b' with excess of acrylonitrile yielded an *N*pendent derivative 'tet-bx' in which two cyanoethyl groups were attached on less crowded two *trans*-N atoms. Interactions of nickel(II) acetate tetrahydrate and copper(II) perchlorate hexahydrate with 'tet-bx' followed by subsequent addition of NaClO₄·6H₂O and HClO₄ in case of nickel(II) produced square planar orange [Nii('tetbx')](ClO₄)₂ and six coordinated octahedral reddish purple [Cu('tet-bx')(ClO₄)₂] complex respectively. The axial addition reactions on [Nii('tet-bx')](ClO₄)₂ with NCS, NO₃, NO₂, Cl, Br and I afforded different colored six coordinated octahedral axial addition products: violet [Nii('tet-bx')(NCS)₂]; violet [Ni('tet-bx')(NO₄)] (clO₄)]; green [Ni('tet-bx')(ClO₄)] respectively. All compounds have been characterized by different analytical and spectroscopic parameters. The antimicrobial activities of the concerned ligand and its complexes have been investigated against different bacteria and fungi.

1. Introduction

Evolution of medicinal sector is a prominent way to ensure the health security for the general people and it is also remarkably related to the socio economic development of any country. In this connection, the scientists are working to make different pharmacologically important synthesized compounds those can play an important role in the drug discovery sector of Medicinal Chemistry. In this way, macrocyclic ligands and their different metal complexes have taken a mentionable position due to their good activity as pharmacological agents [1–7]. Thus people are reporting different works on macrocycles including their biological activities. On the other hand, macrocycles with *N*-pendent arms are specially focused by the researchers due to their

multifarious applications [8–17]. Exhaustive reports on macrocyclic compounds [1–7] and their *N*-pendent derivative compounds [8–17] have been reviewed. Thus it appeared reasonable to perform a thorough study on some new N pendent macrocyclic compounds and their different metal complexes. To materialize this objective, at first, the parent diene ligand salt, $Me_6[14]$ diene.2HClO₄ (L.2HClO₄) and an isomeric ligand tet-b of its saturated analouge, $Me_6[14]$ ane have been synthesized by the procedure described in literature [18,19], then *N*-pendent derivative 'tet-bx' of tet-b has been furnished by the interaction with acrylonitrile as alkylating agent. Thereafter four coordinated square planar nickel(II) and six coordinated octahedral copper(II) complexes by the direct reaction of the concerned metal salts with 'tet-bx' and axial addition complexes of four coordinated square planar

https://doi.org/10.1016/j.ica.2020.120172

Received 12 August 2020; Received in revised form 29 November 2020; Accepted 29 November 2020 Available online 3 December 2020 0020-1693/© 2020 Elsevier B.V. All rights reserved.



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nickel(II) complex have been prepared, characterized and their antifungal & antibacterial activities have been evaluated. Thus in this work, studies on nickel(II) and copper(II) complexes of 'tet-bx' have been reported.

2. Results and discussion

2.1. Ligands

2.1.1. Ligand salt $Me_6[14]$ diene.2 $HClO_4$ (L.2 $HClO_4$) and an isomeric ligand 'tet-b'

Ligand salt L.2 $HClO_4$ and an isomeric ligand 'tet-b' (isomer of $Me_6[14]ane$) have been synthesized (Scheme S1) and characterized as described in the literature [18,19].

2.1.2. N-pendent ligand, 'tet-bx'

'tet-bx'(trans-N1,N8-bis(2-cyanoethyl)-Infrared spectrum of 2,4,4,9,11,11-hexamethyl-1,5,8,12-tetraazacyclotetradecane) (Scheme S1). exhibits ν_{NH} , $\nu_{\text{C-H}}$, ν_{CH3} and $\nu_{\text{C-C}}$ bands at 3271 cm⁻¹, 2965 cm⁻¹, 1385 cm⁻¹ and 1141 cm⁻¹ respectively (Table 1). However this spectrum further shows a band at 2245 cm⁻¹ (Table 1) for ν_{C-N} which indicates the presence of cvano-ethyl groups as *N*-pendent arms [16–17]. The mass spectrum (Table 2, Scheme S2) of 'tet-bx' reveals fragments at m/z 391, 392 and 338 etc. where 391 corresponds to both $[M + H]^+$ and base peak, 392 corresponds to M + 2 ion and 338 is due to removal of one molecule of vinyl cyanide from $[M + H]^+$. The ¹H NMR spectrum (Table 3) of 'tet-bx' displays two singlets at 1.05 ppm and 1.12 ppm corresponding to 6 protons each, which can be assigned to equatorial and axial components of the gem-dimethyl groups respectively and one doublet at 0.95 ppm corresponding to 6 protons. This requires that methyls on C(2) and C(9) chiral carbons should be in an equivalent configuration which can be assigned to equatorial methyls. A diequatorial arrangement is observed in the structure (Scheme S1) in which the C(2), C(9) methyls occupy a rac-configuration. The methylene and methine protons of the ring appear as multipletes at 1.90 ppm, 2.58 ppm and 2.76 ppm. Other two multiplets at 2.97 ppm and 3.10 ppm can be assigned to methylene protons of NH proton substituted cyano-ethyl groups. The spectrum further displays a signal at 7.26 ppm due to NH protons. The ¹³C NMR spectrum of 'tet-bx' displays only 11 resonances (Table 4). The 11 peaks (half the number of carbon atoms) can be accounted for pair wise equivalency of carbon atoms. This observation is in support of the symmetric arrangement as has already been assigned

Table 1

IR spectral data of the ligand and its metal complexes.

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Table 2

Mass spectral data of the ligand and its metal complexes.

Compounds	Peaks at m/z
'tet-bx'	391 (M + H) ⁺ ; 392 (M + 2); 338 (Fragment)
[Ni('tet-bx')](ClO ₄) ₂	341 (Base peak); 394, 343 (Fragments)
[Cu('tet-bx')(ClO ₄) ₂]	346 (Base peak); 584, 484, 391(Fragments)

Table 3

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¹H NMR spectral data of the ligand and its metal complexes.

Compounds	Types of proton signals			
	CH_3 at δ ppm	Methylene, Methine and NH at δ ppm		
'tet-bx'	1.05 (e, s, 6H), 1.12(a, s, 6H), 0.95 (e, d, 6H)	1.90(m), 2.58(m), 2.76(m), 2.97 (m) 3.10(m), 7.26(s)		
[Ni('tet-bx')] (ClO ₄) ₂	1.09(e, s, 6H), 1.23(a, s, 6H), 0.98(e, d, 6H)	1.79(m), 1.92(m), 2.24(m), 2.67 (m), 3.35(m)		

(a-axial, e-equatorial, s-singlet, d- doublet, m-multiplet).

¹³ C NMR	spectral data of t	he ligand.	
Ligand	Types of carbon	signals at δ ppm	
	Peripheral	Ring carbons	Carbons of cyanoethyl
	carbons		groups
'tet-	14.37, 18.68,	28.79, 40.31,45.62,	51.76, 52.84, 120
bx'	24.52	46.33, 46.92	

on the basis of its ¹H NMR spectrum. The first three peaks in the region of 14–25 ppm can be assigned to six carbon atoms of six peripheral methyl carbons. The fourth peak at 28.79 ppm is appeared for the C_3 and C_{10} carbons which are comparatively more shielded than those of other ring carbons. The next four peaks in the region of 40–50 ppm are accounted for eight ring carbons C_2 , C_4 , C_6 , C_7 , C_9 , C_{11} , C_{13} and C_{14} where these eight carbons are pair wise equivalent [20,21]. Other two peaks at 51.76 ppm & 52.84 ppm are due to four methylene carbons of two cyanoethyl branch. The most down field peak at about 120.00 ppm can be attributed to two cyano carbons which are expected to be highly deshielded. It is expected that less crowded N—H protons at 1 and 8 positions in isomeric ligand tet-b are substituted by pendent 2-cyanoethyl groups to result in a new *N*-pendent bis(cyanoethyl)

Ligand and metal complexes	Assignment (cm ⁻¹)						
	ν _{N-H}	ν_{C-H}	ν_{CH3}	ν C-C	ν_{M-N}	ν_{C-N}	Other bands
'tet-bx'	3271 m	2965 m	1385 m	1141 w	-	2245vs	-
[Ni('tet-bx')](ClO ₄) ₂	3167 vs	2997 s	1383 s	1157 m	532w	2245 s	1087w, 624 vs
[Cu('tet-bx')(ClO ₄) ₂]	3182 vs	2974 s	1380 s	1153 m	538w	2256 s	1087 vs, 1041 w
							624 vs
[Ni('tet-bx')(NCS) ₂]	3217w	2970 m	1381 s	1180 s	540w	2249 m	$\nu_{CN}=2063~vs$
							$\nu_{CS} = 862 \text{ m}$
							$\delta_{NCS} = 478 w$
$[Ni('tet-bx')NO_3(ClO_4)].$	3196 m	2970 m	1384 m	1188 m	542w	2250 m	$(\nu_{\rm NO3}) = 1460$ w, 1344 m
							ν _{ClO4} 623 s 1099 s
$[Ni('tet-bx')NO_2(H_2O)]$ (ClO ₄)	3140w	2970 w	1385w	1145 w	524w	2252 w	$\nu_{\rm asym}(\rm NO_2) = 1458~m$
							$\nu_{\rm sym}(\rm NO_2) = 1377 \ w$
							$\delta_{NO2} = 829$
							$(\nu_{\rm OH}) = 3429 \text{W}$
							$V_{\rm M-O} = 447 \text{ W}$
$[Ni(tet_bv')Cl(ClO_b)]$	3100 m	2968 m	1375 s	1172 m	551 w	2250 s	V _{CIO4} 028 \$ 1085 II
$[Ni((tet-bx')Br(H_0)](C[0_1))$	3070 w	2900 m	1377 s	1172 m 1172 m	528w	2230 3 2240 m	(1/22) = 3429bs
	3070 W	2570 11	13// 3	11/2 W	3201	2249 III	$(v_{OH}) = 342503$
							$V_{\rm M-O} = 120$ W
[Ni('tet-bx')I(ClO ₄)]	3147 m	2960 w	1371 s	1186 m	522w	2245	$\nu_{\rm ClO4}$ 613 m 1093 s

(ν denotes stretching mode in cm⁻¹ & s, m, w, vs meaning strong, medium, weak, very strong respectively).

derivative 'tet-bx'. Thus all these evidences are in favor of the structure Str.-01 of 'tet-bx' is shown below.



2.2. Metal complexes of 'tet-bx'

2.2.1. Metal complexes prepared by direct reactions of 'tet-bx' with metal salts

2.2.1.1. [Ni('tet-bx')](ClO₄)₂. Infrared spectrum (Table 1) of this complex exhibits v_{NH} , $v_{\text{C-H}}$, v_{CH3} , $v_{\text{C-C}}$ and $v_{\text{Ni-N}}$ bands at 3167 cm⁻¹, 2997 cm⁻¹, 1377 cm⁻¹, 1157 cm⁻¹ and 532 cm⁻¹ respectively and also shows bands at 2245 cm⁻¹ for $v_{\text{C-N}}^{--}$ of cyano-ethyl groups [15–17] and 1087 cm⁻¹ & 624 cm⁻¹ for v_{CIO4}^{--} respectively. The position as well as nonsplitting of band [22] at 1087 cm⁻¹ support the non-coordination of ClO₄ ions in this complex. The mass spectrum of the complex did not reveal the molecular ion peak (M⁺⁻) at m/z 648.21. However other fragments at m/z 394, 341 (base peak), 343 have been identified (Table 2, Scheme S3). The molar conductivity value 258 ohm⁻¹ cm²mol⁻¹ (Table 5) of this complex in acetonitrile demonstrates that the complex is 1:2 electrolyte i.e. two ClO₄ ions are out of coordination sphere as expected [23]. Again value of 73 O⁻¹cm²mol⁻¹ in DMSO solution corresponding to 1:1 electrolyte can be assigned for equilibrium between square planar and octahedral geometry as shown in expression 01.

$$[Ni('tet - bx')](ClO_4)_2 \stackrel{DMSO}{\rightleftharpoons} [Ni('tet - bx')(ClO_4)_2]$$
(1)

The electronic spectrum of this complex displays d-d bands at 477–485 nm in DMSO and acetonitrile (Table S1) which can be assigned to the ${}^{1}A_{1}g \rightarrow {}^{1}B_{1}g$ transition for square planar nickel(II) complexes [24]. The higher value of ε_{max} specially in acetonitrile in the visible region (Table S1) supports the existence of square planar configuration of this nickel(II) complex [24]. The absorption bands at 219–270 nm in the UV region are assigned to charge transfer transitions. These bands do not provide any worthwhile information related to the geometry of this complex. Though the cyano group (-C=N) of 2-cyanoethyl arm has

Table 5	
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Molar	conductance and	magnetochemical	data for metal	complexes.

Complexes	Molar Conductance (ohm ⁻ ¹ cm ² mole ⁻¹)			μ_{eff} (BM)
	DMSO	$CHCl_3$	Acetonitrile	
[Ni('tet-bx')](ClO ₄) ₂	73	-	258	Diamagnetic
[Cu('tet-bx')(ClO ₄) ₂]	68	0	286	1.78
[Ni('tet-bx')(NCS) ₂]	70	0	245	1.63
[Ni('tet-bx')(NO3)(ClO4)].	38	0	219	1.53
[Ni('tet-bx')(NO ₂)(H ₂ O)](ClO ₄)	68	-	175	1.38
[Ni('tet-bx')Cl(ClO ₄)]	32	0	168	1.57
[Ni('tet-bx')Br(H ₂ O)](ClO ₄)	66	-	170	1.63
[Ni('tet-bx')I(ClO ₄)]	37	0	174	1.71

'-' means not soluble.

coordinating property, but the experimental data show that these groups did not coordinate to the nickel(II) ion to form six coordinated complex The magnetic moment value (Table 5) of this complex corresponds to diamagnetic complex as expected for square planar orientation with dsp^2 hybridization. Appearance of two singlets at 1.09 ppm and 1.23 ppm each corresponding to six protons in its ¹H NMR spectrum (Table 3) can be assigned to equatorial and axial components of the *gem*-dimethyl groups and one doublet at 0.98 ppm corresponding to 6H to two equatorially oriented methyl protons on C(2) and C(9) carbons. This requires that the C(2) and C(9) chiral methyls should be in an equivalent configuration which can be assigned to equatorial methyls. The spectrum also shows downfield multiplets at 1.79, 1.92, 2.24, 2.67 and 3.35 ppm due to methylene, methine and NH protons. Thus the structure of this complex can also be assigned by a similar diequatorial structure, Str.- I (Chart 1) as ligand 'tet-bx' (Str-O1).

2.2.1.2. [Cu('tet-bx')(ClO₄)₂]. Infrared spectrum of this complex (Table 1) displays ν_{NH} , ν_{C-H} , ν_{CH3} , ν_{C-C} , ν_{C-N}^{-} , ν_{CU-N} and ν_{ClO4} bands at expected regions. However the splitting of the band at around 1100 cm⁻¹ of ClO₄ demonstrates the coordination mode of ClO₄ ion. In the mass spectrum of this complex, the molecular ion peak (M^{+.}) was not observed as expected at m/z 653.06. However other fragments at m/z 584, 484, 391 & 346 (base peak) have been clarified in Table 2 (Scheme S4). The molar conductivity value (Table 5) 0 ohm⁻¹cm²mol⁻¹ in chloroform (color remains intact) supports the nonelectrolytic nature of this complex, i.e. the two ClO₄ ions are in the coordination sphere. But the value 68 ohm⁻¹cm²mol⁻¹ in DMSO and 286 ohm⁻¹cm² mol⁻¹ in acetonitrile corresponding to 1:1 and 1:2 electrolyte respectively can be assigned for equilibrium between square planar & octahedral geometry (expression 02) and due to the conversion from octahedral to square planar (expression-03) respectively.

$$[Cu('tet - bx')](ClO_4)_2 \stackrel{DMSO}{\rightleftharpoons} [Cu('tet - bx')(ClO_4)_2]$$
⁽²⁾

$$[Cu('tet - bx')](ClO_4)_2 \xrightarrow{CH_3CN} [Cu('tet - bx')(ClO_4)_2]$$
(3)

The magnetic moment value (Table 5) of this complex is in good agreement with paramagnetic copper(II) complexes having one unpaired electron with d⁹ system. The electronic spectrum (Table S1) of this complex displays d-d band at 544 nm in DMSO, 517–546 nm in CHCl₃ and 545 in acetonitrile due to ${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$ transition [25] and charge transfer bands at 335–336 nm in all concerned solvents [26]. Since the ¹H NMR spectra of paramagnetic copper(II) complexes are less informative, so the stereochemistry could not be determined from ¹H NMR spectra, however the stereochemistry of this six coordinated complex [Cu('tet-bx')(ClO₄)₂] has been assigned as corresponding square planar and its axial octahedral nickel(II) products of this study. Thus according to the above analytical evidences the structure Str.-II (Chart-01) can be suggested for the complex [Cu('tet-bx')(ClO₄)₂].

2.2.2. Nickel(II) complexes prepared by axial addition reactions on [Ni ('tet-bx')](ClO_4)₂

2.2.2.1. [Ni('tet-bx')(NCS)₂]. Infrared spectrum of this complex (Table 1) reveals ν_{NH} , ν_{C-H} , ν_{CH3} , ν_{C--N} and ν_{Ni-N} bands at expected regions. However ν_{CN} band at 2063 cm⁻¹, ν_{CS} band at 862 cm⁻¹ and sharp δ_{NCS} peak at 478 cm⁻¹ demonstrate the coordination of *N*-bonded thiocyanate ions [27–29]. The conductance value 0 ohm⁻¹cm²mol⁻¹ (Table 5) in CHCl₃ (color remaining intact) supports the nonelectrolytic nature of the complex as expected. However molar conductivity value 70 ohm⁻¹cm²mol⁻¹ in DMSO corresponding to 1:1 electrolyte may be due to equilibrium between octahedral and square planar (expression 04) but 245 ohm⁻¹cm² mol⁻¹ in acetonitrile (Table 5) corresponding to 1:2 electrolyte can be expressed by the following conversion (expression-05).



Chart 1. Structures of the Copper(II) and Nickel(II) complexes of 'tet-bx'

$$[Ni('tet - bx')](NCS)_2 \stackrel{DMSO}{\rightleftharpoons} [Ni('tet - bx')(NCS)_2]$$
(4)

$$[Ni('tet - bx')](NCS)_2 \xrightarrow{CH_3CN} [Ni('tet - bx')(NCS)_2]$$
(5)

The magnetic moment value of 1.63 BM (Table 5) of this complex indicates that the complex is paramagnetic but less value compared to two unpaired electrons as expected for octahedral nickel(II) complexes with sp^3d^2 hybridization can be accounted for the above two expressions i,e the complex turns its color in moisture indicating the change of geometry from paramagnetic octahedral to diamagnetic square planar to some extent. The electronic spectrum (Table S1) of this complex exhibits bands at 546–872 nm in chloroform which can be due to octahedral nickel(II) complex of the formula assigned [30]. But the bands at 471–478 nm in DMSO and acetonitrile at comparatively shorter wavelengths can be assigned to square planar species. This behavior is due to an octahedral \leftrightarrow square planar equilibrium existing in the complex in these solvents as observed in molar conductivity analysis. The lower

extinction coefficient values also support the formation of octahedral complex [30]. The absorption bands at 234–266 nm are assigned to charge transfer transition. Based on these above evidences as well on the basis that axial addition takes place without change of configuration and conformation of the ligand of the original complex [31–33], the structure, Str.-III (Chart-01) can be assigned to [Ni('tet-bx')(NCS)₂].

2.2.2.2. [Ni('tet-bx')(NO₃)(ClO₄)] & [Ni('tet-bx')(NO₂)(H₂O)](ClO₄). Infrared spectra of these complexes (Table 1) exhibit $\nu_{\rm NH}$, $\nu_{\rm C-H}$, $\nu_{\rm CH3}$, $\nu_{\rm C-C}$, $\nu_{\rm C-N}$ and $\nu_{\rm Ni-N}$ bands in the expected regions. The spectrum of [Ni ('tet-bx')(NO₃)(ClO₄)] further displays bands at 1460 cm⁻¹ and 1344 cm⁻¹ attributed to coordinated NO₃ group (Table 3.8). The separation of these bands by 116 cm⁻¹ is accounted for unidentate mode of coordination [29]. Moreover [Ni('tet-bx')(NO₂)(H₂O)](ClO₄) exhibits the $\nu_{\rm asym}$ (NO₂) and $\nu_{\rm sym}$ (NO₂) bands at 1458 cm⁻¹ and 1377 cm⁻¹ respectively. Appearance of bands at 829 cm⁻¹ and a broad $\nu_{\rm OH}$ band at 3429 cm⁻¹ in this complex can be attributed to $\delta_{\rm NO2}$ frequency and coordinated water molecule respectively. The spectrum of aquanitro complex also reveals weak band at 447 cm⁻¹ due to M–O stretching band. Presence of bands at 1083–1099 cm⁻¹, 623–628 cm⁻¹ and appearance of splitting of perchlorate bands at 1099 cm⁻¹ can be safely assigned for coordination of unidentate ClO₄ group in [Ni('tet-bx')(NO₃)(ClO₄)] but non-splitting of band at 1083 cm⁻¹ accounts for non-coordination of ClO₄ in [Ni('tet-bx')(NO₂)(H₂O)](ClO₄) (Table 1). The conductance value 0 ohm⁻¹cm² mol⁻¹ in CHCl₃ & 38 ohm⁻¹cm² mol⁻¹ in DMSO (Table 5) for [Ni('tet-bx')(NO₃)(ClO₄)] is an indication of non-electrolytic nature and 68 ohm⁻¹cm²mol⁻¹ (Table 5) in DMSO for [Ni('tet-bx')(NO₂)(H₂O)](ClO₄) demonstrates that the complex is 1:1 electrolyte as expected. But 175–219 ohm⁻¹cm² mol⁻¹ in acetonitrile indicates 1:2 electrolyte due to conversion of nonelectrolyte & 1:1 electrolyte to 1:2 electrolyte (expression 06 & 07).

$$[Ni('tet - bx')(NO_3)(ClO_4)] \xrightarrow{CH_3CN} [Ni('tet - bx')(NO_3)(ClO_4)]$$
(6)

$$[Ni('tet - bx')(NO_2)(H_2O)(ClO_4)] \xrightarrow{CH_3CN} [Ni('tet - bx')(NO_2)(ClO_4)(H_2O)]$$
(7)

The magnetic moment values of these complexes explore the paramagnetism. Electronic spectra (Table S1) of these complexes in concerned solvents display the expected d-d bands corresponding to octahedral nickel(II) complex [30] but the band at 469 nm for [Ni('tetbx')(NO₂)(H₂O)](ClO₄) in acetonitrile in which color changes from its solid state corresponds to the square planar nickel(II) complex [24], indicating conversion of octahedral to square planar complex. The stereochemistry of these complexes has also been assigned on the same basis as described in earlier section [31–33]. Thus by considering the above facts, the structure Str.-IV & Str.-V (Chart-01) can be suggested for [Ni('tet-bx')(NO₃)(ClO₄)] & [Ni('tet-bx')(NO₂)(H₂O)](ClO₄) respectively .

2.2.2.3. [Ni('tet-bx')XY](ClO₄)_x (Where X = Cl, Br, or I; $Y = ClO_4$ or H_2O and x = 0 or 1). Infrared spectra of these complexes explore $v_{\rm NH}$, $v_{\rm C-H}$, $\nu_{CH3},\,\nu_{C-C},\,\nu_{ClO4}$ and ν_{M-N} bands in the expected regions (Table 1). The splitting of band at around 1100 cm⁻¹ in [Ni('tet-bx')(ClO₄)Cl] and [Ni ('tet-bx')I(ClO₄)] is an indication of coordination of ClO₄ but nonsplitting of that band for [Ni('tet-bx')Br(H₂O)](ClO₄) attribute for the non-coordination. Presence of a band at 3429 cm⁻¹ and M–O stretching band at 428 cm⁻¹ in the complex [Ni('tet-bx')Br(H₂O)](ClO₄) demonstrates the presence of coordinated H₂O molecule (Table 1). Appearance of bands at 2245–2250 cm⁻¹ are attributed to ν_{C-N} of cyano-ethyl groups in these complexes. The conductance value (Table 5) 0 ohm ¹ cm² mol⁻¹ in chloroform and 32–37 ohm⁻¹ cm²mol⁻¹ in DMSO for [Ni ('tet-bx')(ClO₄)Cl] and [Ni('tet-bx')I(ClO₄)] (Table 5) are indication of non-electrolytic nature but 66 ohm⁻¹ cm²mol⁻¹ in DMSO for [Ni('tet-bx') (Br)(H₂O)](ClO₄) can be accounted for the 1:1 electrolyte as expected. Conductance values 168–174 ohm⁻¹cm² mol⁻¹ in acetonitrile support the 1:2 electrolytic criteria and the cause of this phenomenon has already been discussed in earlier sections. These complexes are also paramagnetic (Table 5) as expected. The electronic spectra of these complexes display d-d bands at 543-864 nm with lower extinction coefficient values in DMSO and chloroform supporting the six coordinated octahedral structure of them [30] and also show bands at 443-479 nm in acetonitrile corresponding to square planar complexes [24]. From the above discussion the structure Str.-VI (Chart-01) can be assigned for these halonickel(II) complexes.

2.3. Antibacterial activities

Antibacterial activities of the concerned *N*-pendent macrocyclic ligand, its copper(II) and nickel(II) complexes, concerned non-coordinated metal salts and standard antibacterial agent have been evaluated against two important selected gram-positive and two gram-negative bacteria and results of this study have been summarized in

the Table 6. In our earlier studies [32–36], ligands did not show any antibacterial activity but in this study some activities are explored by the concerned ligand against the experimental bacteria. Here all compounds exhibit notable activities against all concerned bacteria. However copper(II) complex [Cu('tet-bx')(ClO₄)₂] against *S. typhe* and nickel(II) complex [Ni('tet-bx')Cl(ClO₄)] against *P. aeruginosa* reveal potent activity. Though the ligand and metal salts themselves are poisonous, but the stability of the complexes (very much stable even in solutions) prevents the liberation of ligand/metal ions of the complexes in the test media.

2.4. Antifungal activities

The results in vitro antifungal evaluation of the ligand, its metal complexes, non-coordinated metal salts and standard fungicide, Griseofulvin are shown in Table 7. Investigation was performed against three fungi. From the results, it is evident that almost all complexes are sensitive towards all the used three fungal phytopathogens (Table 7). However it is to be noted that though some compounds show promising activity, but some exhibit lower activity against some of the pathogens. However some of them explore more activity than the standard Griseofulvin. Such as [Ni('tet-bx')Cl(ClO₄)] against *M. phaseolina*; 'tet-bx' & [Ni('tet-bx')(NO₂)(H₂O)](ClO₄) against A. niger; [Ni('tet-bx')(NO₃) (ClO₄)] against A. niger & F. equisiti and [Ni('tet-bx')I(ClO₄)] & [Ni('tetbx')(NO₃)(ClO₄)] against F. equisiti exhibit promising activity whereas [Ni('tet-bx')Cl(ClO₄)] against Macrophomina phaseolina and [Ni('tet-bx') (NO₃)(ClO₄)] &[Ni('tet-bx')I(ClO₄)] against F. equisiti are more potent than the standard Griseofulvin. Further two compounds [Ni('tet-bx')] (ClO₄)₂ & [Ni('tet-bx')(NO₂)(H₂O)](ClO₄) reveal stimulation against Fusarium equiseti. It is encouraging to note that most of the test compounds are more or less sensitive towards the tested fungal phytopathogens

 Table 6

 Antibacterial activities of ligand and its metal complexes.

Compounds	ands Zone of inhibition in diameter				
	Gram-positive bacteria		Gram-negativ	e bacteria	
	Bacillus cereus	Staphylococcus aureus	Salmonella typhi	Pseudomonus aeruginosa	
'tet-bx'	8	7	10	7	
[Cu('tet-bx') (ClO ₄) ₂]	11	11	15	11	
[Ni('tet-bx')] (ClO ₄) ₂	11	9	9	9	
[Ni('tet-bx') (NCS) ₂]	8	9	10	9	
[Ni('tet-bx') (NO ₃)(ClO ₄)]	10	11	8	9	
[Ni('tet-bx') (NO ₂)(H ₂ O)] ClO ₄	10	10	9	7	
[Ni('tet-bx')Cl (ClO ₄)]	11	12	10	13	
[Ni('tet-bx')Br (H ₂ O)]ClO ₄	10	8	10	6	
[Ni('tet-bx')I (ClO ₄)]	9	9	8	9	
CuClO ₄	20	16	14	14	
Ni(OOCCH ₃) ₂	9	12	11	10	
Ampicillin (Standard)	24	22	34	25	
Control (DMSO)	0	0	0	0	

Table 7

Antifungal activities of li	igand and its	metal	compl	exes
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Compounds	% inhibition of mycelial growth				
	Macrophomina phaseolina	Aspergillus niger	Fusarium equiseti		
'tet-bx'	25	43	15		
[Cu('tet-bx')(ClO ₄) ₂]	36	25	7		
[Ni('tet-bx')](ClO ₄) ₂	15	10	+		
[Ni('tet-bx')(NCS)2]	12	4	18		
[Ni('tet-bx')(NO ₃) (ClO ₄)]	37	39	23		
[Ni('tet-bx')(NO ₂) (H ₂ O)]ClO ₄	36	45	+		
[Ni('tet-bx')Cl(ClO ₄)]	60	28	20		
[Ni('tet-bx')Br(H ₂ O)] ClO ₄	38	13	9		
[Ni('tet-bx')I(ClO ₄)]	29	23	27		
CuClO ₄	100	37	100		
Ni(OOCCH ₃) ₂	67	38	100		
Griseofulvin (Standard)	45	46	22		

3. Experimental

3.1. Ligands

3.1.1. Ligand salt L.2HClO₄ and isomeric ligand, 'tet-b'

The parent ligand salt $Me_6[14]$ diene.2HClO₄ (L.2HClO₄) was prepared by the method described in literature [18]. The separation and isolation of the isomers 'tet-a' and 'tet-b' have been carried out as procedure adopted in the literature [19].

3.1.2. N-pendent Ligand 'tet-bx'

0.320 g (1.0 mmol) isomeric ligand 'tet-b' with 15 mL acrylonitrile was refluxed for 12 h on a magnetic stirrer. The reaction mixture was cooled to room temperature, filtered and evaporated to dryness. The residue was recrystallized from dichloromethane and ethanol mixture to give a white crystalline solid, 'tet-bx'. Melting point of 'tet-bx' was 146–147 0 C. For 'tet-bx' (390.62): Calcd.: C, 67.65; H, 10.84; N, 21.52. Found: C, 67.72; H, 10.95; N, 21.49.

3.2. Metal complexes of 'tet-bx'

3.2.1. Metal complexes prepared by direct reactions of 'tet-bx' with metal salts

3.2.1.1. [Ni('tet-bx')](ClO₄)₂. 0.25 g (1.0 mmol) of nickel(II) acetate tetrahydrate and 0.390 g (1.0 mmol) of 'tet-bx' were dissolved separately in 30 mL hot methanol and mixed. The solution turned green immediately. The green solution was heated continuously on a water bath to reduce the volume about 20 mL Then 0.368 g (3.0 mmol) of sodium perchlorate hexahydrate was added. While the solution turned blue, then it was acidified by adding 2–3 drops 70% HClO₄. The orange precipitate was started to form immediately. For the completion of the reaction, the mixture was allowed to stand overnight. Then the orange product of [Ni('tet-bx')](ClO₄)₂ was separated by filtration and washed with methanol followed by diethylether, finally stored in a vacuum desiccator over silica gel. For [Ni('tet-bx')](ClO₄)₂ (648.21): Calcd.: C, 40.77; H, 6.53; N, 12.97. Found: C, 40.68; H, 6.54; N, 12.93.

3.2.1.2. $[Cu('tet-bx')(ClO_4)_2]$. 0.48 g (1.0 mmol) of copper(II) perchlorate hexahydrate and 0.390 g (1.0 mmol) of 'tet-bx' were dissolved separately in 25 mL hot methanol and then mixed. The resulting blue solution was heated on a water bath, while reddish-purple product was formed immediately. For the completion of the reaction, the mixture was heated for more five minutes with continuous stirring. After cooling at room temperature, the product was separated by filtration and washed with methanol followed by diethylether and finally stored

in a vacuum desiccator. For [Cu('tet-bx')(ClO₄)₂] (653.06): Calcd.: C, 40.46; H, 6.48; N, 12.87. Found: C, 40.36; H, 6.41; N, 12.86.

3.2.2. Nickel(II) complexes prepared by axial addition reactions on [Ni ('tet-bx')](ClO₄)₂

3.2.2.1. $[Ni('tet-bx')(NCS)_2]$. 0.648 g (1.0 mmol) of [Ni('tet-bx')] (ClO₄)₂ and 0.194 g (2.0 mmol) of KCNS were taken separately in 25 mL acetonitrile and methanol respectively and mixed while hot. The resulting mixture was heated for 30 min on a water-bath to result in a light pink solution leaving behind a white precipitate which was removed by filtration. The resulting filtrate was evaporated to dryness. After cooling, 50 mL chloroform were added to it and stirred well. The white precipitate was separated by filtration. The chloroform extract was evaporated to give a stable light violet product $[Ni('tet-bx')(NCS)_2]$ which was stored in a desiccator over silica gel. For $[Ni('tet-bx')(NCS)_2]$ (565.46): Calcd.: C, 50.97; H, 7.48; N, 19.81. Found: C, 50.99; H, 7.53; N, 19.82.

3.2.2.2. [Ni('tet-bx')(NO₂)(H₂O)](ClO₄). 0.648 g (1.0 mmol) of [Ni ('tet-bx')](ClO₄)₂ and 0.138 g (2.0 mmol) of NaNO₂ were taken separately in 30 mL acetonitrile and methanol respectively and mixed in a beaker while hot. Then the resulting brown solution was heated on a steam-bath to reduce the volume, while a white solid was appeared which was removed by filtration. The resulting filtrate was heated further 30 min for the completion of the reaction and then allowed to cool. On cooling, the green product of [Ni('tet-bx')(NO₂)(H₂O)](ClO₄) was separated by filtration and washed with methanol followed by diethyl ether and finally stored in a desiccator over silica gel. For [Ni ('tet-bx')(NO₂)(H₂O)](ClO₄) (612.78): Calcd.: C, 43.21; H, 7.24; N, 16.00. Found: C, 43.26; H, 7.29; N, 15.98.

Violet [Ni('tet-bx')(NO₃)(ClO₄)], brown [Ni('tet-bx')Cl(ClO₄)] and pink [Ni('tet-bx')I(ClO₄)] were furnished by following the procedure adopted for preparation of [Ni('tet-bx')(NCS)₂] (section: 3.2.2.1) by using KNO₃, KCl and KI respectively instead of KSCN. Again the brown complex [Ni('tet-bx')Br(H₂O)](ClO₄) has been afforded by the method described for the preparation of [Ni('tet-bx')(NO₂)(H₂O)](ClO₄) by using KBr instead of NaNO₂ (section 3.2.2.2).

For [Ni('tet-bx')(NO₃)(ClO₄)] (610.76): Calcd.: C, 43.26; H, 6.99; N, 16.05. Found: C, 43.30; H, 6.90; N, 16.01. For [Ni('tet-bx')(Cl)(ClO₄)] (584.21): Calcd.: C, 45.23; H, 7.25; N, 14.39. Found: C, 45.19; H, 7.28; N, 14.32. For [Ni('tet-bx')I(ClO₄)] (675.66): Calcd.: C, 39.11; H, 6.27; N, 12.44. Found: C, 39.12; H, 6.21; N, 12.48. For [Ni('tet-bx')Br(H₂O)] (ClO₄) (646.67): Calcd.: C, 40.86; H, 6.86; N, 12.99. Found: C, 39.12; H, 6.80; N, 12.96.

3.3. Physical measurements

Microanalyses (C, H, N analyses) and mass and NMR spectra of the compounds have been carried out on a C, H, N analyzer and concerned spectroscopic machine at Department of Chemistry, Friedrich Schiller University, Jena, Germany. IR spectra were recorded on a Shimadzu IR 20 spectrophotometer as KBr disks. Mass spectra were measured on a MAT 95XL Finnigan instrument (Thermo Quest Finnigan, Bremen, Germany) for electrospray ionization (ESI). ¹H NMR spectra were recorded in DMSO with a 400 MHz Bruker DPX-400 spectrometer using TMS as internal standard. UV–visible spectra were recorded on a Shimadzu UV–visible spectrophotometer in DMSO. Conductance measurements were carried out on a conductivity bridge Hanna instrument HI-8820. Magnetic measurements were performed on Gouy Balance which was calibrated using Hg[Co(NCS)₄].

3.4. Antibacterial activities

Antibacterial activities of the concerned compounds were

investigated by the disc diffusion method. Paper discs (6 mm in diameter) and Petri plates (70 mm in diameter) were used throughout the experiment. Pour plates were made with sterilized melted nutrient agar NA (45 °C) and after solidification of the pour plates, the test organisms (suspension in sterilized water) were spread uniformly over the pour plates with a sterilized glass rod separately. The paper discs after soaking with test compounds (1 mg/1mL in DMSO) were placed at the center of the inoculated pour plates. A control plate was also maintained in each case with DMSO. At first the plates were left for four hours at low temperature (4 $^{\circ}$ C) and the test chemicals diffused from the disc to the surrounding medium by this time. The plates were then incubated at (35 \pm 2)°C for growth of the test organisms, and were observed at 24-hours interval. The activity was expressed in terms of the zone of inhibition in mm. The results for all concerned complexes have been reported after subtracting the values for the solvent DMSO itself. Tests were repeated thrice for statistical analysis.

3.5. Antifungal activities

The in vitro antifungal activities of the complexes against selected phytopathogenic fungi were assessed by the poisoned food technique. Potato Dextros Agar (PDA) was used as a growth medium. Dimethylsulphoxide was used as the solvent to prepare solutions of the tested compounds. The solutions were then mixed with the sterilized PDA so as to maintain concentrations of the compounds of 0.01% (ca. 3 μ L). 20 mL of these solutions were each poured into a petri dish. After the medium had solidified, a 5 mm micelial disc of each fungus was placed in the center of each assay plate, along with a control. Linear growth of the fungus was measured in mm after five days of incubation at 25 \pm 2 ^oC.

4. Conclusion

The isomeric ligand 'tet-b' of hexamethyl substituted tetraaza macrocyclic ligand, Me₆[14] ane on interaction with vinyl cyanide (CH₂ = CH-CN) yielded N-pendant bis(2-cyanoethyl) derivative 'tet-bx' where two cyano-ethyl groups are attached on the less crowded trans- N atoms. Interactions of 'tet-bx' with copper(II) and nickel(II) salts produced six coordinated octahedral [Cu('tet-bx')(ClO₄)₂] and four coordinated square planar [Ni('tet-bx')](ClO₄)₂ complex respectively. The complex, [Ni('tet-bx')](ClO₄)₂ underwent axial addition reactions with SCN⁻, NO3, NO2, Cl⁻, Br⁻ and I⁻ to produce six coordinated octahedral diisothiocyanato; mononitratoperchlorato, monoaquanitro, monochloridoperchlorato, monoaquabromido and monoiodidoperchlorato derivative respectively. However, conductance values in DMSO and CH₃CN corresponding to 1:1 or 1:2 electrolytes of some non-electrolytic addition products indicate the ionization i.e. conversion of octahedral to square planar species in these solvents. These newly prepared compounds exhibit mentionable activities as antimicrobial agents.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

The authors would like to extend their sincere appreciation to the

Ministry of Education, People's Republic of Bangladesh to award a research grant (Grant No.- PS2017552) to Professor Dr. Tapashi Ghosh Roy, Department of Chemistry, University of Chittagong, Chittagong-4331, Bangladesh.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ica.2020.120172.

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