Axial Addition in Diastereoisomeric [Ni(Me$_8$[14]ane)](ClO$_4$)$_2$ Complexes and Their Antifungal Activities

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Abstract

A series of diastereoisomeric square planar nickel(II) diperchlorate complexes, [Ni(L)](ClO$_4$)$_2${L= isomeric Me$_8$[14]ane (L$_{A\alpha}$, L$_{B\alpha}$ or L$_{C\alpha}$)}undergo axial ligand addition reactions with NO$_3^-$, Cl$^-$, Br$^-$, SCN$^-$ or ClO$_4^-$ to yield six coordinate octahedral derivatives [NiL(X)$_x$(Y)$_y$].z(H$_2$O)(X=NO$_3$,Cl, Br or SCN; Y= ClO$_4$; x = 1 or 2; y = 1 or 0 and z = 0, 1 or 2). The products have been characterized on the basis of analytical, spectroscopic, magnetic and conductance data. All the derivatives are unstable in open air except one derivative and revert back to original square planar complexes. Antifungal activities of the ligands and their nickel(II) complexes have been investigated against some phytopathogenic fungi.
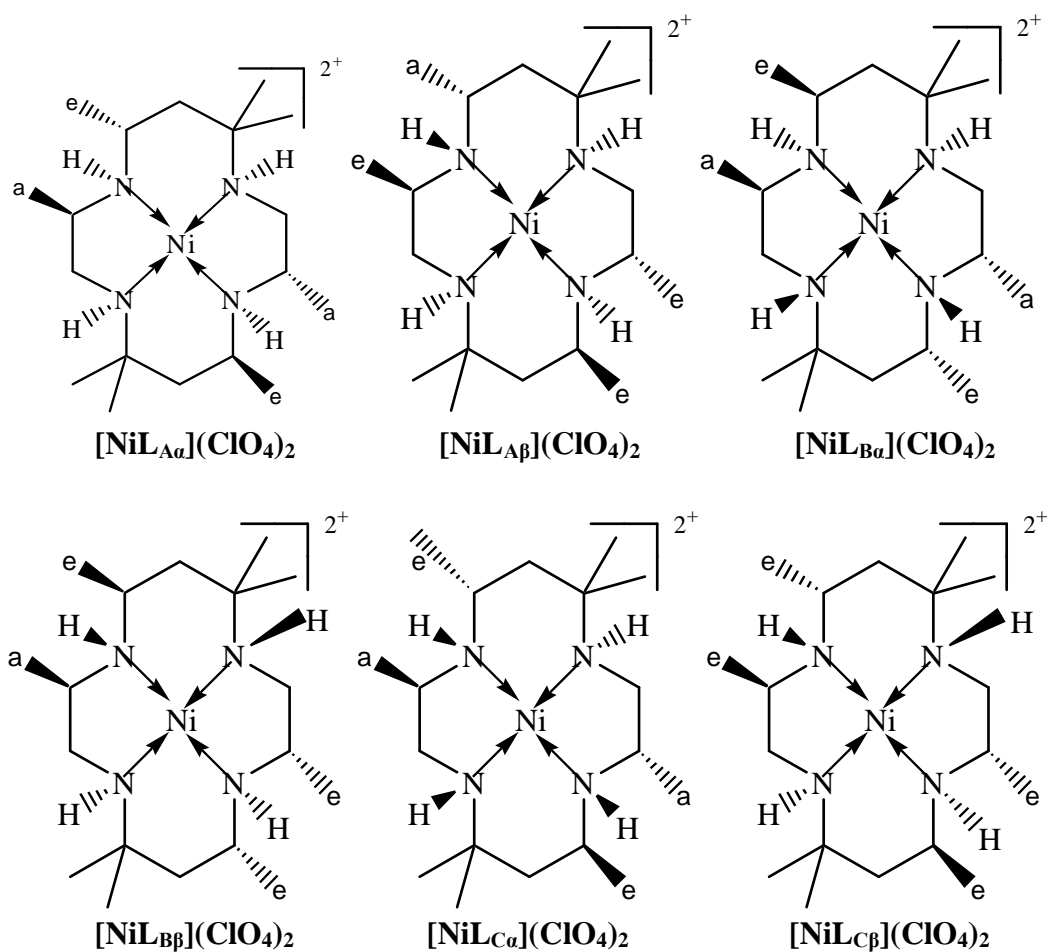
Keywords: Macrocyclic ligands, distereomers, nickel(II), spectroscopic studies, antifungal activities.

GK ¸"Q WvB‡÷wiI AvB‡mvgwiK eM©Rvi mgZjxq wb‡Kj (II) WvBcvi‡K¬‡iU †h̆M, [Ni(L)](ClO$_4$)$_2$ {L=AvB‡mvgwiK Me$_8$[14]ane (L$_{A\alpha}$, L$_{B\alpha}$ A_ev L$_{C\alpha}$)}, NO$_3^-$, Cl$^-$, Br$^-$

A_ev SCN⁻ Øviv Aÿxq wjM¨vÛ msthvRb বিক্রিয়ার gva¨‡g Qqmেলদক msL¨v wewkó GK ¸"Q AóZjKxq th̃M, $[NiL(X)_x(Y)_y].(H_2O)_z$ (X= NO_3, Cl, Br A_ev SCN, Y= ClO_4, x = 1 A_ev 2; y = 1 A_ev 0; z = 0, 1 A_ev 2) Drcv`b K‡i| Drcw`Z th̃Mmgন ‡f̃Z, eYőxexÿY, †PŠ¤KZ¡Ges we`ÿ cwiewnZv we‡kō†Yi gva¨‡g mbv³ Kiv n‡q‡Q| GKwU gvÎ AóZjKxq D™‡Z th̃M e¨ZxZ mKj Drcw`Z AóZjKxq th̃Mmgন gÿ evZvtm A¯ívqx Ges cÿivq gj-eMÆvi mgZjKxq th̃‡M cwiYZ nq| wKQztivM myóKvix Qïv‡Ki wecix‡Z wjM¨vÛ Ges we‡KRj (II) th̃Mmg‡ni AYÿxe we‡ivax সক্রিয়তা wbi ƒcY Kiv n‡q‡Q|

1. Introduction

Axial ligand addition reactions of square planar nickel(II) and copper(II) azamacrocyclic complexes to form six coordinate octahedral complexes have drawn significant interest [1-8]. So, some diastereoisomeric square planar nickel(II) complexes containing isomeric Me_8[14]anes, L_A, L_B and L_C [9] were prepared. Each ligand produced two N-chiral diastereoisomeric nickel(II) complexes [8,10], designated as $[NiL_{A\alpha}](ClO_4)_2$ and $[NiL_{A\beta}](ClO_4)_2$ for L_A; $[NiL_{B\alpha}](ClO_4)_2$ and $[NiL_{B\beta}](ClO_4)_2.H_2O$ for L_B; and $[NiL_{C\alpha}](ClO_4)_2$ and $[NiL_{C\beta}](ClO_4)_2.H_2O$ for L_C (Scheme 1).

[NiL$_{A\alpha}$](ClO$_4$)$_2$ [NiL$_{A\beta}$](ClO$_4$)$_2$ [NiL$_{B\alpha}$](ClO$_4$)$_2$

[NiL$_{B\beta}$](ClO$_4$)$_2$ [NiL$_{C\alpha}$](ClO$_4$)$_2$ [NiL$_{C\beta}$](ClO$_4$)$_2$

Scheme 1. Structures of diastereoisomeric nickel(II) complexes of Me$_8$[14]anes

Owing to steric effects exerted by the eight peripheral methyl groups in these complexes, it was expected that axial addition might be difficult. However, in one study [11], a number of corresponding diastereoisomeric square planar copper(II) complexes underwent axial addition [11]. Hence it seemed possible that similar types of reactions could also be carried out on nickel(II) complexes. In the present

study, the syntheses and characterization of axial addition products of the square planar diastereoisomeric nickel(II) complexes have been reported. As well, antifungal activities of the parent square planar complexes and their axial addition reaction products have also been reported.

2. Results and Discussion

The structures of the diastereoisomeric square planar nickel(II) perchlorate complexes employed in the present study were assigned previously [9] and are shown in Scheme 1. Diastereoisomeric square planar nickel(II) perchlorate complexes undergo axial ligand addition reactions to form six coordinate *trans*-addition products without change of configuration and conformation of the original square planar nickel(II) perchlorate complexes. These six coordinate complexes were found to be unstable in open air except $[NiL_{C\alpha}(NCS)_2]$ and revert back to original square planar complexes. As some of them are highly unstable on exposure to moisture, so during the course of recording spectra, they are converted into square planar complexes to some extent immediately. Moreover, these complexes have low extinction coefficients that is why some of the expected bands for six coordinate octahedral nickel(II) complexes could not be recorded in their electronic spectra but conductivity values of 0 $ohm^{-1}cm^2mol^{-1}$ of these complexes in chloroform in which the colors of the complexes remained intact strongly supported the formation of six coordinate non-electrolytic complexes. Among the different N-chiral isomers, yields of complexes $[NiL_{A\beta}](ClO_4)_2$, $[NiL_{B\beta}](ClO_4)_2.H_2O$ and $[NiL_{C\beta}](ClO_4)_2.H_2O$ were too small to be used for further addition reactions. Thus only $[NiL_{A\alpha}](ClO_4)_2$, $[NiL_{B\alpha}](ClO_4)_2$ and $[NiL_{C\alpha}](ClO_4)_2$

complexes have been used for axial ligand addition. Since the six coordinated octahedral nickel(II) complexes are paramagnetic due to presence of two unpaired electrons in their d^8 system and ^{1}H-NMR of paramagnetic complexes are less informative, so, ^{1}H-NMR spectra of them could not be measured. However, the configuration and conformation of these complexes, especially the axial and equatorial positions of chiral methyl groups and 'up' and 'down' positions of the N-bound hydrogen atoms have been assigned on the basis that the axial ligands do not alter the configurations and conformations of the ligands found in the original square planar complex [3,11]. Characteristic IR data are collected in Table1and other physical data are listed in Table 2. It is to be mentioned that to avoid conversion of six-coordinate octahedral species to four coordinate square planar species, freshly prepared samples were used for all spectral measurements

Table 1. Selected IR data (cm^{-1}) for the complexes.

Complex	ν_{NH}	ν_{CH}	ν_{CH3}	ν_{CC}	ν_{MN}	ν_{ClO4}	Other bands
[NiL$_{A\alpha}$(ClO$_4$)(NO$_3$)] H$_2$O	3160 vs	2980 vs	1390 vs	1190 m	560 w	1120s, 950s, 1070m, 630vs	3420vs,ν_{OH};1630s, δ_{H2O}; 1440w, 1325w, δ_{NO3}; 465w, ν_{MO}
[NiL$_{B\alpha}$(NO$_3$)$_2$].H$_2$O	3195 b	2970 m	1380 vs	1185 w	540 b	–	3430b, ν_{OH}; 1625s, δ_{H2O};1425w, 1336w, δ_{NO3}; 445m, ν_{MO}
[NiL$_{C\alpha}$(NO$_3$)$_2$].H$_2$O	3200 b	2965 m	1380 vs	1180 m	520 sh	–	3400b, ν_{OH}; 1630s, δ_{H2O}; 1440sh, 1320m, δ_{NO3}; 440w, ν_{MO}
[NiL$_{A\alpha}$ (ClO$_4$)Cl].H$_2$O	3110 s	2970 s	1380 s	1120 s	570 m	1125s, 1030s, 950s, 625s	3400vs, ν_{OH}; 1650m, δ_{H2O};
[NiL$_{B\alpha}$Cl$_2$].2H$_2$O	3160 m	2980 s	1380 s	1140 s	515 vw	–	3395b, ν_{OH}; 1610s, δ_{H2O};
[NiL$_{C\alpha}$Cl$_2$].2H$_2$O	3180 s	2965 s	1365 s	1180 s	540 sh	–	3450b, ν_{OH}; 1625s, δ_{H2O};
[NiL$_{A\alpha}$Br(ClO$_4$)].2H$_2$O	3020 s	2985 s	1380 m	1140 m	540 m	1120s, 1080s, 995s, 620s	3450vs, ν_{OH}; 1620m, δ_{H2O};
[NiL$_{B\alpha}$Br$_2$].2H$_2$O	3020 s	2960 m	1375 s	1120 s	525 vw	–	3420vs, ν_{OH}; 1625s, δ_{H2O};
[NiL$_{C\alpha}$Br$_2$].2H$_2$O	3185 m	2965 s	1380 s	1180 s	530 sh	–	3360b, ν_{OH}; 1625b, δ_{H2O};
[NiL$_{A\alpha}$(NCS)$_2$].H$_2$O,	3220 s	2985 s	1360 s	1185 m	630 s	–	3400s, ν_{OH}; 1640vs, δ_{H2O}; 2025vs, ν_{CN}; 820m, ν_{CS};
[NiL$_{B\alpha}$(NCS)$_2$].H$_2$O	3220 vs	2985 s	1365 s	1150 s	515 s	–	3400b, ν_{OH}; 1640vs, δ_{H2O}; 2050vs, ν_{CN}; 820m, ν_{CS}; 470w, δ_{NCS}
[NiL$_{C\alpha}$(NCS)$_2$]	3220 s	2960 s	1370 s	1160 s	530 w	–	2080vs, ν_{CN}; 820s, ν_{CS}; 472w, δ_{NCS}

Here ν and δ denote stretching and bending modes expressed in cm^{-1}. Relative band intensities are denoted by s, m, w, vs meaning strong, medium, weak, very strong and shoulder respectively.
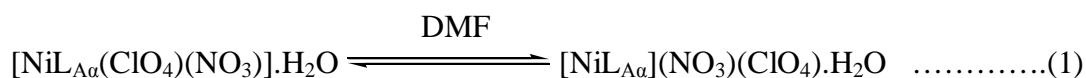
2.1 Nitratonickel(II) complexes

Interaction of $[NiL_{A\alpha}](ClO_4)_2$, $[NiL_{B\alpha}](ClO_4)_2$ and $[NiL_{C\alpha}](ClO_4)_2$ with KNO_3 in the ratio of 1:2 produced light red, pink and red products respectively. All analytical and experimental data are consistent with the molecular formula $[NiL_{A\alpha}(ClO_4)(NO_3)].H_2O$ (mononitratoperchloratocomplex), $[NiL_{B\alpha}](NO_3)_2].H_2O$ (dinitrato complex) and $[NiL_{C\alpha}](NO_3)_2].H_2O$ (dinitrato complex) respectively. The infrared spectra (Table 1) of all these complexes exhibit υ_{NH}, ν_{CC}, ν_{CH} and ν_{Ni-N} bands in the expected positions. The spectra further exhibit bands at 1425-1440 cm^{-1} and 1320-1336 cm^{-1} due to coordinated NO_3^- groups. Position of these bands and their separation values (115 cm^{-1}) correspond to unidentate mode of co-ordination [12]. These complexes also show M-O bands at 440-465 cm^{-1} which strongly support the presence of unidentate NO_3^- group. Presence of bands at 3400-3430 cm^{-1} due to υ_{OH} and at 1625-1630 cm^{-1} due to δ_{HOH} is an indication of the presence of lattice water [3]. The spectrum of $[NiL_{A\alpha}(ClO_4)(NO_3)].H_2O$ further displays bands at 1120 cm^{-1}, 1070 cm^{-1}, 950 cm^{-1} and 630 cm^{-1} due to υ_{ClO4}^- band. The splitting of a band at 1070 cm^{-1} into 1120 cm^{-1} and 950 cm^{-1} is an indication of the presence of coordinated perchlorate. The position of these perchlorate bands strongly supports the unidentate mode of coordination [13]. Inability to replace all ClO_4^- ions by NO_3^- and axial addition of ClO_4^- in the case of $[NiL_{A\alpha}](ClO_4)_2$ can be explained from the fact that since this complex (Str. I, Scheme 1) have all the

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hydrogen atoms of NH groups in one side of NiN$_4$ plane, so, the other side is free to accommodate big sized ligand like ClO$_4^-$ which already exists in its original square planar complex. Similar coordination of ClO$_4^-$ ions are also observed in the copper(II) complexes of its parent diene ligand [14]. Absence of any band at around 1100 cm^{-1} and 620 cm^{-1} [Table-1] in the infrared spectra of [NiL$_{B\alpha}$(NO$_3$)$_2$].H$_2$O and [NiL$_{C\alpha}$(NO$_3$)$_2$].H$_2$O demonstrate that all the perchlorates are replaced by NO$_3^-$ groups in these cases.

Table 2. Physical appearance, electronic, magnetic and conductivity data for the complexes.

Complex	Color in the solid state	d-d bands		Molar conductivity (Ω⁻¹ cm² mol⁻¹) and color in solution						μ$_{eff}$ (BM)
		Solvents	λ$_{max}$ in nm (log ε$_{max}$)	Color in CHCl$_3$	Ω⁻¹ cm² mol⁻¹	Color in DMF	Ω⁻¹cm² mol⁻¹	Color in water	Ω⁻¹cm² mol⁻¹	
[NiL$_{A\alpha}$(ClO$_4$)(NO$_3$)].H$_2$O	Red	Nujol	849, 755, 468, 368, 339, 244	Light red	0	Pink yellow	92	Yellow	180	2.90
[NiL$_{B\alpha}$](NO$_3$)$_2$].H$_2$O	Pink	Nujol Chloroform DMF	593, 459, 352, 246 809(12), 793(sh), 476(22) 917(12), 466(22)	Light pink	0	-	-	Yellow	200	2.80
[NiL$_{C\alpha}$(NO$_3$)$_2$].H$_2$O	Red	Nujol DMF	924, 638, 537, 455 809(3), 772(12), 492(39)	Light red	0	-	-	Yellow	190	2.85
[NiL$_{A\alpha}$(ClO$_4$)Cl].H$_2$O	Red	Nujol Chloroform	733, 638, 480, 279 808(4), 794, 483(39)	Light red	0			Yellow	210	2.80
[NiL$_{B\alpha}$Cl$_2$].2H$_2$O	Pink	Nujol Chloroform	924, 638, 537,455 809(3), 772(12), 763(9), 492(39)	Light pink	0			Yellow	220	2.86
[NiL$_{C\alpha}$Cl$_2$].2H$_2$O	Light pink	Nujol Chloroform	864, 705, 468, 249 778, 478(32),385(22)	Light pink	0			Yellow	185	2.90
[NiL$_{A\alpha}$Br(ClO$_4$)].2H$_2$O	Red	Nujol Chloroform	640, 471, 286 994(3), 721, 482(23)	Red	0	Reddish yellow	94	Yellow	200	2.89
[NiL$_{B\alpha}$Br$_2$].2H$_2$O	Brick red	Chloroform DMF	918(5), 792, 485(27) 814(4), 472(57), 271	Light red	0	-	-	Yellow	170	2.76
[NiL$_{C\alpha}$Br$_2$].2H$_2$O	Reddish brown	Chloroform Water	991, 890(4), 708,476 450(83), 235	Light red	0	-	-	Yellow	185	2.91
[NiL$_{A\alpha}$(NCS)$_2$].H$_2$O,	Violet	Nujol Chloroform DMF	599(sh),469, 351,246 967(9), 744, 506,250 468, 381(11), 243	Light violet	0	Yellow	180	Yellow	200	2.93
[NiL$_{B\alpha}$(NCS)$_2$].H$_2$O	Pink	Nujol Chloroform	905, 720, 536, 248 808(33), 791(30),224	Light pink	0	-	-	Light yellow	192	2.88
[NiL$_{C\alpha}$(NCS)$_2$]	Deep violet	Nujol Chloroform DMF	910, 758, 659, 442 914(29), 745(23),250 452(103), 235	Violet	0	-	-	Yellow	198	2.79

The complexes are non-electrolytes (0 ohm^{-1}cm^{2}mol^{-1}) in CHCl$_3$ solution, in which colors of complexes remain intact. The molar conductivity value of 92 ohm^{-1} cm^{2}mol^{-1} of pink yellow DMF solution of [NiL$_{A\alpha}$(ClO$_4$)(NO$_3$)].H$_2$O corresponding to 1:1 electrolyte may be assigned for an equilibrium between square planar and octahedral complexes which can be expressed by equation 1.

$$[NiL_{A\alpha}(ClO_4)(NO_3)].H_2O \underset{}{\overset{DMF}{\rightleftharpoons}} [NiL_{A\alpha}](NO_3)(ClO_4).H_2O \quad ....(1)$$
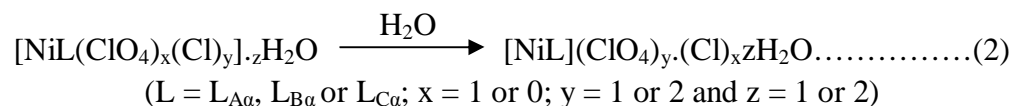
Changes of color in DMF are accounted for formation of different compound in DMF. Such anomaly is also observed for analogous nickel(II) complexes [7]. Similar observation was also noted for corresponding copper(II) complexes of the same ligands [15]. However, the molar conductivity values (180 to 200 ohm^{-1}cm^2 mol^{-1}) of yellow aqueous solutions of all these complexes corresponding to 1:2 electrolyte demonstrates that water forces anions to come out of the coordination sphere to convert six coordinate octahedral complexes to four coordinate square planar complexes. Though 1:2 electrolytes can be assigned either for square planar [NiL]$^{2+}$ or for diaqua complexes [NiL(H$_2$O)$_2$]$^{2+}$ but it is more likely to assign as square planar complexes, since yellow DMF solution and yellow acetonitrile/water (1/20, v/v) solution of [NiL$_{B\alpha}$](ClO$_4$)$_2$ (a square planar complex, structure of which has been confirmed by X-ray analysis) shows the conductance value corresponding to 1:2 electrolyte. This behavior is in contrast to the corresponding copper(II) complexes, which were found to form diaqua complexes in their aqueous solutions [14]. Since the compound [NiL$_{A\alpha}$(ClO$_4$)(NO$_3$)].H$_2$O was found to convert into square planar readily, so all the expected d-d bands corresponding to octahedral

nickel(II) complexes could not be recorded for this complex. However, d-d band at 468 nm is observed for square planar nickel(II) complex. The electronic spectra of other two dinitrato complexes exhibit d-d bands (Table 2) corresponding to octahedral nickel(II) complexes as do other octahedral nickel(II) complexes [3,7]. The bands around 244 to 246 nm are attributed to charge transfer transition. The magnetic moments of 2.80-2.90 BM (Table 2) are in good agreement with paramagnetic octahedral nickel(II) complexes. From the above discussion the octahedral structures I, II and III can be assigned for [NiL$_{A\alpha}$(ClO$_4$)(NO$_3$)].H$_2$O, [NiL$_{B\alpha}$](NO$_3$)$_2$].H$_2$O and [NiL$_{C\alpha}$](NO$_3$)$_2$].H$_2$O respectively.

[NiL$_{A\alpha}$(ClO$_4$)(NO$_3$)].H$_2$O   [NiL$_{B\alpha}$](NO$_3$)$_2$].H$_2$O   [NiL$_{C\alpha}$](NO$_3$)$_2$].H$_2$O

I   II   III

2.2 Chloridonickel(II) complexes

Reactions of $[NiL_{A\alpha}](ClO_4)_2$, $[NiL_{B\alpha}](ClO_4)_2$ and $[NiL_{C\alpha}](ClO_4)_2$ with KCl in the ratio of 1:2 yielded yellowish mass. Extraction of the products by chloroform and evaporation of the solvent gave red, pink and light pink products respectively. Analytical data, conductance data, megnetochemical (Table 2) data and spectroscopic (Table 1 and Table 2) measurements fit well with the molecular formula $[NiL_{A\alpha}(ClO_4)Cl].H_2O$ (choloridoperchlorato complex), $[NiL_{B\alpha}Cl_2].2H_2O$ (dichlorido complex) and $[NiL_{C\alpha}Cl_2].2H_2O$ (dichlorido complex) respectively.

The infrared spectra (Table 1) of these complexes reveal bands to $\nu_{NH,}$ ν_{CC}, ν_{CH} and ν_{Ni-N} bands in the expected region. Appearance of bands at around 3400 cm^{-1} due to ν_{OH} and at around 1610 cm^{-1} due to δ_{HOH} is an indication of the presence of lattice water [3]. The infrared spectrum of $[NiL_{A\alpha}(ClO_4)Cl].H_2O$ further exhibits bands at 1125, 1030, 950 and 625 cm^{-1} due to υ_{ClO4}^- band. The splitting of the band at 1030 cm^{-1} into 1125 cm^{-1} and 950 cm^{-1} is an indication of presence of unidentate coordinated perchlorate [17]. Absence of any band at around 1100 cm^{-1} and 620 cm^{-1} in the IR spectra of $[NiL_{B\alpha}Cl_2].2H_2O$ and $[NiL_{C\alpha}Cl_2].2H_2O$ can be accounted for the replacement of both the ClO_4^- ions. Partial replacement of ClO_4^- ions and axial addition of ClO_4^- ion in case of $[NiL_{A\alpha}(ClO_4)Cl].H_2O$ can be explained as explained earlier (Sec. 2.1). The molar conductivity values of 0 ohm^{-1} cm^{2}mol^{-1} of these complexes in CHCl$_3$ (solvent in which, colors of solid samples remained intact) strongly support the non-electrolytic nature of these complexes i.e. all the anions are in the coordination sphere. However, conductance values of 170-210 ohm^{-1}cm^2 mol^{-1} of yellow aqueous solutions of these complexes corresponding to

1:2 electrolyte indicate the 100% conversion of octahedral species into square planar species as explained earlier [11]. This phenomenon can be expressed by reaction 2.
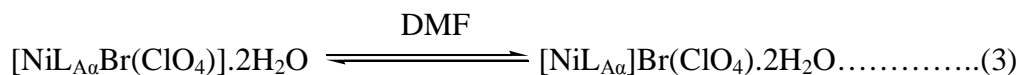
$$[NiL(ClO_4)_x(Cl)_y].zH_2O \xrightarrow{\;\;H_2O\;\;} [NiL](ClO_4)_y.(Cl)_x zH_2O \ldots\ldots\ldots\ldots(2)$$

$$(L = L_{A\alpha}, L_{B\alpha} \text{ or } L_{C\alpha}; x = 1 \text{ or } 0; y = 1 \text{ or } 2 \text{ and } z = 1 \text{ or } 2)$$

From the above evidences the following structures IV, V and VI have been assigned for [NiL$_{A\alpha}$(ClO$_4$)Cl].H$_2$O, [NiL$_{B\alpha}$Cl$_2$].2H$_2$O and [NiL$_{C\alpha}$Cl$_2$].2H$_2$O respectively.
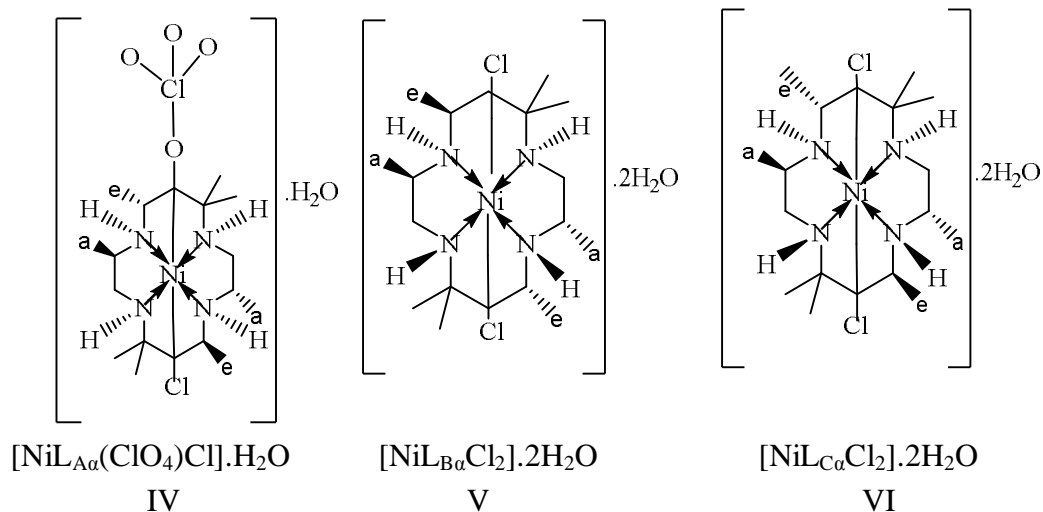
[NiL$_{A\alpha}$(ClO$_4$)Cl].H$_2$O   [NiL$_{B\alpha}$Cl$_2$].2H$_2$O   [NiL$_{C\alpha}$Cl$_2$].2H$_2$O

IV   V   VI

The d-d bands (Table 2) in their electronic spectra with lower molar extinction co-efficients and magnetic moment values (Table 2) are consistent with the above assigned structures.

2.3 Bromidonickel(II) complexes

$[NiL_{A\alpha}](ClO_4)_2$, $[NiL_{B\alpha}](ClO_4)_2$ and $[NiL_{C\alpha}](ClO_4)_2$ reacted with KBr in the ratio of 1:2 to produce yellowish mass in each case. On extraction with chloroform and evaporation of solvent yielded red, brick red and reddish brown products respectively. These red, brick red and reddish brown products have been formulated as $[NiL_{A\alpha}Br(ClO_4)].2H_2O$, $[NiL_{B\alpha}Br_2].2H_2O$ and $[NiL_{C\alpha}Br_2].2H_2O$ respectively on the basis of their analytical data, conductometric, spectroscopic and megnetochemical analysis. The IR spectra (Table 1) of these complexes exhibit all characteristic bands due to ν_{NH}, ν_{CC}, ν_{CH}, ν_{Ni-N} stretching frequencies in the proper positions. Appearance of ν_{OH} bands at about 3420 cm^{-1} and δ_{HOH} band at about 1620 cm^{-1} indicated the presence of lattice water. The IR spectrum of $[NiL_{A\alpha}Br(ClO_4)].2H_2O$ exhibits the bands at 1120, 1080, 995 and 620 cm^{-1} which can be attributed for the coordinated unidented ClO_4^- group. Axial addition of ClO_4^- ion only in case of $[NiL_{A\alpha}](ClO_4)_2$ is obvious as explained earlier. The molar conductivity value of 0 ohm^{-1}cm^{2}mol^{-1} (Table 2) of these complexes in CHCl$_3$ solution indicated that these complexes are essentially non-electrolytes i.e. two anions are in the coordination sphere which is expected for six coordinated octahedral nickel(II) complexes. However, the conductance value of 94 ohm^{-1}cm^2 mol^{-1} of reddish yellow DMF solution of $[NiL_{A\alpha}Br(ClO_4)].2H_2O$ demonstrates that this complex exists in an equilibrium with its corresponding square planar species in DMF as explained earlier. The phenomenon can be expressed by the reaction 3.
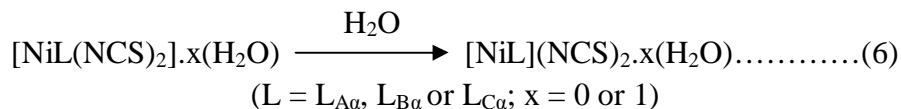
$$[NiL_{A\alpha}Br(ClO_4)].2H_2O \underset{}{\overset{DMF}{\rightleftharpoons}} [NiL_{A\alpha}]Br(ClO_4).2H_2O\ldots\ldots\ldots(3)$$

But the conductance values of 185-200 ohm^{-1}cm^{2}mol^{-1} of their yellow aqueous solutions can be accounted for the 100% conversion of octahedral species into square planar in water as explained earlier. This conversion can be expressed by the reaction 4.

$$[NiL (Br)_x(ClO_4)_y].2H_2O \xrightarrow[H_2O]{} [NiL](Br)_x(ClO_4)_y.2H_2O\ldots\ldots\ldots\ldots(4)$$

$$(L = L_{A\alpha},\ L_{B\alpha}\ or\ L_{C\alpha};\ x = 1\ or\ 2;\ y = 0\ or\ 1)$$

The d-d bands (Table 2) in their electronic spectra with lower molar extinction co-efficient and magnetic moment values (Table 2) are in good agreement with six coordinate octahedral nickel(II) complexes. Based on the above and earlier discussion the structures VII, VIII and IX can be assigned for [NiL$_{A\alpha}$Br(ClO$_4$)].2H$_2$O, [NiL$_{B\alpha}$Br$_2$].2H$_2$O and [NiL$_{C\alpha}$Br$_2$].2H$_2$O respectively.

[NiL$_{A\alpha}$Br(ClO$_4$)].2H$_2$O   [NiL$_{B\alpha}$Br$_2$].2H$_2$O   [NiL$_{C\alpha}$Br$_2$].2H$_2$O

VII   VIII   IX

2.4 Diisothiocyanatonickel(II) complexes

Since both ClO_4^- ions of $[NiL_{A\alpha}](ClO_4)_2$ could not be replaced by NO_3^-, Cl^- and Br^- ions so, it was expected that SCN^- being the strong and linear ligand may be able to replace both ClO_4^- ions easily. Thus extraction by $CHCl_3$ of products produced by the reactions of $[NiL_{A\alpha}](ClO_4)_2$, $[NiL_{B\alpha}](ClO_4)_2$ and $[NiL_{C\alpha}](ClO_4)_2$ with KSCN and evaporation of $CHCl_3$ extract yielded violet, pink and deep violet products respectively. All the analytical and experimental data support the coordination of two thiocyanate ions to metal ions, presence of one molecule of lattice water in the first two cases and absence of lattice water in the third case. Thus these products correspond to molecular formula $[NiL_{A\alpha}(NCS)_2].H_2O$, $[NiL_{B\alpha}(NCS)_2].H_2O$ and $[NiL_{C\alpha}(NCS_2)_2]$ respectively. The infrared spectra of these complexes show all characteristic ν_{NH}, ν_{CC} and ν_{CH} bands in expected regions (Table 1). Absence of sharp υ_{ClO4^-} bands at around 1100 cm^{-1} and 620 cm^{-1} in these complexes reveal that though these complexes have been prepared from their perchlorate complexes, the ClO_4^- ions are fully replaced by NCS ions. The present complexes exhibit υ_{CN} band at 2025-2080 cm^{-1}, ν_{CS} band at 820 cm^{-1} and ν_{NCS} band at 470 cm^{-1} which do not correspond to any ligand absorption band in this region and is therefore assigned for fully N-bonded thiocyanate group and thus these complexes are isothiocyanato complexes. The IR spectra of $[NiL_{A\alpha}(NCS)_2].H_2O$ and $[NiL_{B\alpha}(NCS)_2].H_2O$ further reveal the bands at 3,400 cm^{-1} due to ν_{OH} and 1640 cm^{-1} due to δ_{HOH} which is an indication of the presence of lattice water [3]. The molar conductivity value 0 ohm^{-1} cm^2mol^{-1} for these complexes in $CHCl_3$ strongly support the non-electrolytic nature of these complexes i.e. two thiocyanate ions are coordinated to nickel atom. No
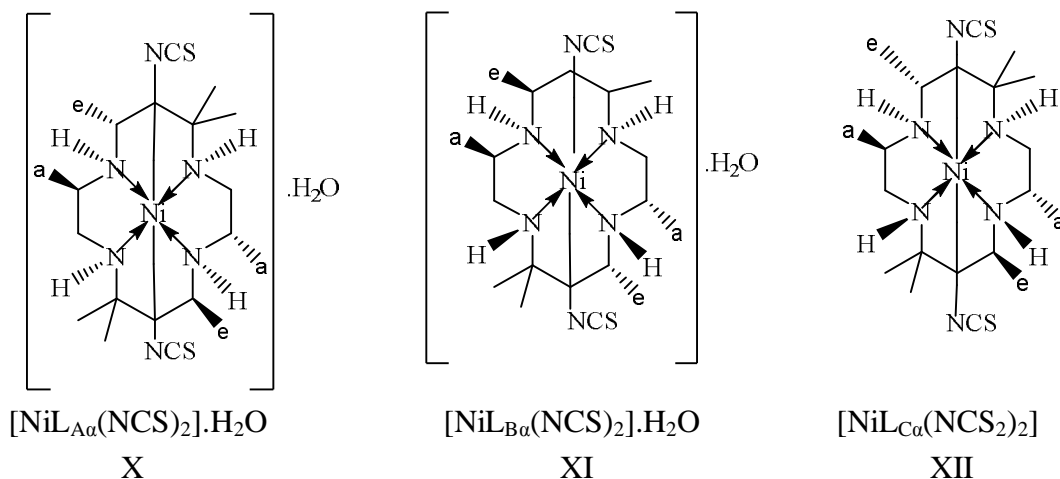
change of color of these complexes in this solvent indicates that the complexes do not change its geometry and conformation in this solvent. The complex [NiL$_{A\alpha}$(NCS)$_2$].H$_2$O shows conductance value of 188 ohm^{-1}cm^{2}mol^{-1} in its yellow DMF solution which corresponds to 1:2 electrolyte. This phenomenon can be accounted for the conversion of octahedral geometry to square planar geometry in presence of DMF.

$$[NiL_{A\alpha}(NCS)_2].H_2O \underset{}{\overset{DMF}{\rightleftharpoons}} [NiL_{A\alpha}](NCS)_2.H_2O \dots\dots\dots\dots..(5)$$
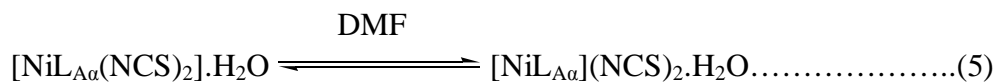
Conductance values (198-200 ohm^{-1}cm^{2}mol^{-1}) of their yellow aqueous solutions corresponding to 1:2 electrolytes provide evidence that water forces the anions out of the coordination sphere to form square planar complexes. Though 1:2 electrolytes can be assigned either for square planar complexes or for diaqua complexes, but it is more likely to assign square planar complexes as explained earlier. Formation of square planar complexes can be expressed by the equation 6.

$$[NiL(NCS)_2].x(H_2O) \xrightarrow{H_2O} [NiL](NCS)_2.x(H_2O) \dots\dots\dots(6)$$
$$(L = L_{A\alpha}, L_{B\alpha} \text{ or } L_{C\alpha}; x = 0 \text{ or } 1)$$

The d-d bands at 452-468 nm of their DMF and aqueous solutions can also be accounted for square planar species. The d-d bands (Table 2) at 805-910 nm and 536-758 nm of their solid spectra and magnetic moment values (Table 2) of 2.79-2.93 BM also support the six coordinated octahedral structures. Thus octahedral structures X, XI and XII can be assigned for [NiL$_{A\alpha}$(NCS)$_2$].H$_2$O, [NiL$_{B\alpha}$(NCS)$_2$].H$_2$O and [NiL$_{C\alpha}$(NCS$_2$)$_2$] respectively.

[NiL$_{A\alpha}$(NCS)$_2$].H$_2$O
X

[NiL$_{B\alpha}$(NCS)$_2$].H$_2$O
XI

[NiL$_{C\alpha}$(NCS$_2$)$_2$]
XII

2.5 Antifungal activities

Recently studies on antifungal activities of macrocycles and their complexes have attracted tremendous attention [14, 16-19]. The antifungal activities on these isomeric ligands and some of their copper(II) complexes have already been studied in detail [15]. So it appeared interesting to examine the activities of other metal like nickel(II) complexes of these ligands. For the purpose, investigation on the antifungal activities of the ligands, distereoisomers of square planar nickel(II) complexes of these ligands and axial addition products of them have been carried out against the selective phytopathogenic fungi (i) *Alternaria alternata* and (ii) *Macrophomina phaseolina*. The results (Table 3) show that these complexes exhibit high activities in comparison with corresponding copper(II) complexes [15]. But low activities have been observed with the six coordinated Co(III) complexes of these ligands and corresponding diene ligand [16,17]. So, it can be concluded that nature of metals also plays a significant role on inhibition of

Table 3. *In-vitro* antifungal activities of ligands and their nickel complexes

Compounds	% inhibition of mycelial growth	
	Alternaria alternata	*Macrophomina phaseolina*
L$_A$	27.78	14.60
[NiL$_{A\alpha}$](ClO$_4$)$_2$	20.61	11.32
[NiL$_{A\beta}$](ClO$_4$)$_2$	18.95	10.58
[NiL$_{A\alpha}$(ClO$_4$)(NO$_3$)].H$_2$O	7.76	10.76
[NiL$_{A\alpha}$(ClO$_4$)Cl].H$_2$O	17.58	12.33
[NiL$_{A\alpha}$Br(ClO$_4$)].2H$_2$O	17.52	10.0
[NiL$_{A\alpha}$(NCS)$_2$]H$_2$O	13.76	5.55
L$_B$	25.92	13.53
[NiL$_{B\alpha}$](ClO$_4$)$_2$	17.95	10.20
[NiL$_{B\beta}$](ClO$_4$)$_2$.H$_2$O	15.92	9.76
[NiL$_{B\alpha}$(NO$_3$)$_2$].H$_2$O	3.59	11.10
[NiL$_{B\alpha}$Cl$_2$].2H$_2$O	6.50	10.0
[NiL$_{B\alpha}$Br$_2$].2H$_2$O	7.64	8.32
[NiL$_{B\alpha}$(NCS)$_2$].H$_2$O	5.55	7.02
L$_C$	25.0	16.65
[NiL$_{C\alpha}$](ClO$_4$)$_2$	19.04	4.43
[NiL$_{C\beta}$](ClO$_4$)$_2$.H$_2$O	17.54	3.52
[NiL$_{C\alpha}$(NO$_3$)$_2$].H$_2$O	5.57	14.52
[NiL$_{C\alpha}$Cl$_2$].2H$_2$O	11.12	12.32
[NiL$_{C\alpha}$Br$_2$].2H$_2$O	10.19	12.23
[NiL$_{C\alpha}$(NCS)$_2$]	8.64	10.43

mycelial growth. Some of the complexes of L$_B$ and L$_C$ are found to show higher values against *Macrophomina phaseolina* in compared to other fungi and some show lower compared to others, whereas those of L$_A$ show higher values against *Alternaria alternata*. This observation is in good agreement with the corresponding copper(II) complexes. But it is in contrast to the result with diene ligand and its

complexes [16], where the complexes were found to have higher activity values against *Alternaria alternata* than the other fungi. For a given organism, all complexes have a comparable effect on the mycelial growth. However, in order to understand the functions responsible for antifungal activities of macrocycles and their complexes, more studies are needed to be carried out with a series of analogous ligands and their complexes against a series of phytopathogenic fungi.

3. Experimental
3.1 Syntheses

The square plannar nickel(II) diperchlorate complexes, $[NiL_{A\alpha}](ClO_4)_2$ and $[NiL_{A\beta}](ClO_4)_2$ for L_A; $[NiL_{B\alpha}](ClO_4)_2$ and $[NiL_{B\beta}](ClO_4)_2.H_2O$ for L_B and $[NiL_{C\alpha}](ClO_4)_2$ and $[NiL_{C\beta}](ClO_4)_2.H_2O$ for L_C have been prepared as per literature [8,10]. The axial addition products were prepared from the square planar complexes, $[NiL](ClO_4)_2$ (L = $L_{A\alpha}$, $L_{B\alpha}$ or $L_{C\alpha}$) following literature methods [7, 11,14]. Among the N-chiral isomers, the yields of $[NiL_{A\beta}](ClO_4)_2$, $[NiL_{B\beta}](ClO_4)_2.H_2O$ and $[NiL_{C\beta}](ClO_4)_2.H_2O$ were too small to prepare addition products.

3.1.1 $[NiL_{A\alpha}(ClO_4)(NO_3)].H_2O$

A hot suspension of $[NiL_{A\alpha}](ClO_4)_2$ (0.570 g, 1.0 mmol in methanol (30 mL) was added to a hot suspension of KNO_3 (0.202 g, 2.0 mmol) in the same solvent (30 mL). The mixture was stirred with heating on a magnetic stirrer for 3 hours. The resultant deep yellow solution was evaporated to dryness by heating on a water bath. To this 40 mL chloroform was added, stirred well and filtered to remove insoluble potassium perchlorate. Then the filtrate was evaporated to dryness. The

crude product was again dissolved in a minimum quantity of chloroform and filtered to remove white residue from the solution if any. The filtrate was then completely dried on a water bath which resulted a reddish product, [NiL$_{A\alpha}$(ClO$_4$)(NO$_3$)].H$_2$O. This product was found to be very much unstable and turned light yellow within few seconds on exposure to moisture at room temperature. The product was stored in a vacuum desiccator over silica gel. m.p.: 260°C. Anal. Calcd. for C$_{18}$H$_{42}$ClN$_5$O$_8$Ni(%): C, 39.26; H, 7.63; N, 10.18; Ni, 10.67. Found: C, 39.13; H, 7.65; N, 9.95; Ni, 10.25.

3.1.2 [NiL$_{B\alpha}$(NO$_3$)$_2$].H$_2$O

A light pink product, [NiL$_{B\alpha}$(NO$_3$)$_2$].H$_2$O was synthesized from the reaction of [NiL$_{B\alpha}$](ClO$_4$)$_2$ with KNO$_3$, as per procedure described above. m.p.: 280°C (decomposed). Anal. Calcd. for C$_{18}$H$_{42}$N$_6$O$_7$Ni(%): C, 42.13; H, 8.19; N, 10.92; Ni, 11.45. Found: C, 42.03; H, 8.25; N, 10.55; Ni, 11.25.

3.1.3 [NiL$_{C\alpha}$(NO$_3$)$_2$].H$_2$O

A red product, [NiL$_{C\alpha}$(NO$_3$)$_2$].H$_2$O was obtained by the reaction of [NiL$_{C\alpha}$](ClO$_4$)$_2$ with KNO$_3$, by following the same procedure described above. m.p.: 280°C. Anal. Calcd. for C$_{18}$H$_{42}$N$_6$O$_7$Ni(%):C, 42.13; H, 8.19; N, 10.92; Ni, 11.45. Found: C, 42.18; H, 8.23; N, 10.45; Ni, 11.20.

3.1.4 [NiL$_{A\alpha}$Cl(ClO$_4$)].H$_2$O

0.57 g (1 mmol) of the complex [NiL$_{A\alpha}$](ClO$_4$)$_2$ and 0.149 g (2 mmol) of KCl were taken separately in 20 mL of absolute methanol and mixed while hot. The resulting yellow-orange mixture was stirred on a magnetic stirrer for 2 hours and then heated on a water bath till dryness. The expected product was extracted with chloroform leaving behind insoluble white solid. Then the light red chloroform solution was evaporated to dryness to give red residue. Finally the red product was recrystallized from chloroform. The crystals were stored in a vacuum desiccator over silica gel. m.p.: 275°C. Anal. Calcd. for C$_{18}$H$_{42}$Cl$_2$N$_4$O$_5$Ni(%): C, 41.25; H, 8.02; N, 10.69; Ni, 11.21. Found: C, 41.15; H, 8.08; N, 10.30; Ni, 11.00.

3.1.5 [NiL$_{B\alpha}$Cl$_2$].2H$_2$O

A pink product, [NiL$_{B\alpha}$Cl$_2$].2H$_2$O was synthesized from the reaction of [NiL$_{B\alpha}$](ClO$_4$)$_2$ with KCl, by adopting the procedure similar to that for [NiL$_{A\alpha}$Cl(ClO$_4$)]. m.p.: 280°C. Anal. Calcd. for C$_{18}$H$_{44}$Cl$_2$N$_4$ONi (%): C, 45.22; H, 9.21; N, 11.72; Ni, 12.29. Found: C, 45.27; H, 9.15; N, 11.45; Ni, 11.97.

3.1.6 [NiL$_{C\alpha}$(Cl)$_2$].2H$_2$O

A pink product, [NiL$_{C\alpha}$(Cl)$_2$].2H$_2$O was synthesized from the reaction of [NiL$_{C\alpha}$](ClO$_4$)$_2$.2H$_2$O (0.57 g, 1 mmol) and KCl (0.149 g, 2 mmol). Work-up was as for [NiL$_{A\alpha}$Cl(ClO$_4$)].H$_2$O. m.p.: 272°C. Anal. Calcd. for C$_{18}$H$_{44}$N$_4$NiCl$_2$O (%): C, 45.22; H, 9.21; N, 11.72; Ni, 12.29. Found: C, 45.12; H, 9.30; N, 11.35; Ni, 12.05.

3.1.7 [NiL$_{A\alpha}$Br(ClO$_4$)].2H$_2$O

The hot methanolic suspension of [NiL$_{A\alpha}$](ClO$_4$)$_2$ (0.57 g, 1.0 mmol) was added to the hot methanolic suspension of KBr (0.238 g, 2.0 mmol) in a 100 mL beaker. The mixture was stirred on a magnetic stirrer for 2 hours. Then resulting orange mixture was evaporated to dryness by heating it on a water bath. The orange product was extracted with 30 mL hot chloroform and undissolved product was rejected. The light red extract was taken to dryness by heating on a water bath. Finally, a red product of [NiL$_{A\alpha}$Br(ClO$_4$)].2H$_2$O was collected and dried under vacuum desiccator. m.p.: 280°C. Anal. Calcd. for C$_{18}$H$_{44}$BrClN$_4$O$_6$Ni(%): C, 36.85; H, 7.50; N, 9.95; Ni, 10.01. Found: C, 36.79; H, 7.43; N, 9.25; Ni, 9.87.

3.1.8 [NiL$_{B\alpha}$Br$_2$].2H$_2$O

Brick red crystals of [NiL$_{B\alpha}$(Br)$_2$].2H$_2$O were obtained using [NiL$_{B\alpha}$](ClO$_4$)$_2$ instead of [NiL$_{A\alpha}$](ClO$_4$)$_2$ as per procedure described above. m.p.: 230°C. Anal. Calcd. for C$_{18}$H$_{44}$Br$_2$N$_4$O$_2$Ni(%): C, 38.12; H, 7.76; N, 9.88; Ni, 10.36. Found: C, 38.21; H, 7.69; N, 9.40; Ni, 10.20.

3.1.9 [NiL$_{C\alpha}$Br$_2$].2H$_2$O

A brown product of [NiL$_{C\alpha}$Br$_2$].2H$_2$O was obtained using [NiL$_{C\alpha}$](ClO$_4$)$_2$ instead of [NiL$_{A\alpha}$](ClO$_4$)$_2$, by adopting the procedure similar to that for [NiL$_{A\alpha}$Br(ClO$_4$)].2H$_2$O. m.p.: 230°C (decomposed). Anal. Calcd. For C$_{18}$H$_{44}$Br$_2$N$_4$O$_2$Ni(%): C, 38.12; H, 7.76; N, 9.88; Ni, 10.36. Found: C, 38.09; H, 7.70; N, 9.50; Ni, 10.05.

3.1.10 [NiL$_{A\alpha}$(NCS)$_2$].H$_2$O

A suspension of [NiL$_{A\alpha}$](ClO$_4$)$_2$ (0.570 g, 1.0 mmol) in hot methanol 30 mL and a solution of KSCN (0.194 g, 2.0 mmol) in the same solvent (30 mL) were mixed while hot. The initial yellow color rapidly changed to an orange color. Then the reaction mixture was stirred with heating on a magnetic stirrer for 2 hours. The mixture was then evaporated to dryness by heating on a water bath. The resulting product was extracted with chloroform leaving behind undissolved potassium perchlorate and filtered. The violet chloroform extract was concentrated to a volume of 5 mL till the precipitation started. After cooling the violet product was filtered, washed with dry ethanol followed by ether and finally dried under vacuum over silica gel. m.p.: 260°C. Anal. Calcd. for C$_{20}$H$_{42}$N$_6$S$_2$ONi (%): C, 47.53; H, 8.31; N, 11.09; Ni, 11.63, S, 12.70. Found: C, 47.47; H, 8.33; N, 10.85; Ni, 11.20; S, 11.95.

3.1.11 [NiL$_{B\alpha}$(NCS)$_2$].H$_2$O

A pink product, [NiL$_{B\alpha}$(NCS)$_2$].H$_2$O was synthesized from the reaction of [NiL$_{B\alpha}$](ClO$_4$)$_2$ with KSCN, by adopting the similar procedure discussed above. m.p.: 280°C (decomposed). Anal. Calcd. for C$_{20}$H$_{42}$N$_6$S$_2$ONi (%) C, 47.53; H, 8.31; N, 11.09; Ni, 11.63, S, 12.70. Found: C, 47.45; H, 8.23; N, 10.95; Ni, 11.35; S, 12.05.

3.1.12 [NiL$_{C\alpha}$(NCS)$_2$]

A violet product, [NiL$_{C\alpha}$(NCS)$_2$] was synthesized from the reaction of [NiL$_{C\alpha}$](ClO$_4$)$_2$.2H$_2$O with KSCN, by adopting the similar procedure described for [NiL$_{A\alpha}$(NCS)$_2$].H$_2$O in section above. m.p.: 225°C (decomposed). Anal. Calcd. for C$_{20}$H$_{40}$N$_6$S$_2$Ni(%): C, 49.29; H, 8.21; N, 11.50; Ni, 12.05; S, 13.17. Found: C, 49.16; H, 8.13; N, 10.92; Ni, 11.90; S, 12.85.

3.1.13 Physical measurement

Infrared spectra were taken as KBr discs in the range 4000-400 cm^{-1} on a Perkin-Elmer-883 infrared spectrophotometer or on a Schimadzu Metared spectrophotometer. Electronic spectra of the samples were recorded on a Schimadzu UV-visible spectrophotometer. Conductance measurements of the metal complexes were done in water, DMF and chloroform solutions at 10^{-3} M using a HANNA instrument with HI 8820N conductivity cell. The magnetic measurements have been carried out by Sherwood scientific magnetic susceptibility balance. Microanalysis of C, H, N of the complexes have been carried out on a C, H, N and S analyzer at the Institut der Anorganische and Angewandte Chemie, Hamburg Universitaet, Germany. For the determination of nickel in complexes accurately weighed amounts of complexes were heated with a mixture of conc. H$_2$SO$_4$, HNO$_3$ and HClO$_4$ to convert nickel complexes into nickel(II) and extraction into water. The solution was then titrated with a standard solution of Na$_2$EDTA using Xylenol orange as indicator.

3.2.4 Antifungal activities

The antifungal activities of the complexes (*in-vitro*) against some selected phytopathogenic fungi were assessed by the poisoned food technique. Potato Dextrose Agar (PDA) was used as a growth medium. Chloroform was initially used to prepare solutions of the ligands and their complexes as solvent, similarly DMSO was used for preparing the solutions of nickel salts. The solutions were then mixed with the sterilized PDA to maintain the concentration of the compounds at 0.01%; 20 mL portion of these mixtures were poured into a petri dish. After the medium had solidified, a 5 mm mycelial disc for each fungus was placed in the center of each essay plate against the control. Linear growth of the fungus was measured in mm after five days incubation at $(25 \pm 2)°C$.

4. Conclusions

This study reveals that, the concerned diastereomeric four coordinated square planar nickel(II) complexes $[Ni(L)](ClO_4)_2$ {L= isomeric $Me_8[14]$ane ($L_{A\alpha}$, $L_{B\alpha}$ or $L_{C\alpha}$)} undergo axial addition reactions with NO_3^-, Cl^-, Br^-, SCN^- or ClO_4^- to afford the corresponding six coordinated octahedral derivative complexes $[NiL(X)_x(Y)_y].z(H_2O)$ (X=NO_3,Cl, Br or SCN; Y= ClO_4; x = 1 or 2; y = 1 or 0 and z = 0, 1 or 2). These derivative complexes were found to show different electrolytic behavior in different solvents; such as some of them were found to exist in equilibrium with the corresponding square planar complexes in DMF and some get converted into square planar geometry in water.

Acknowledgements

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