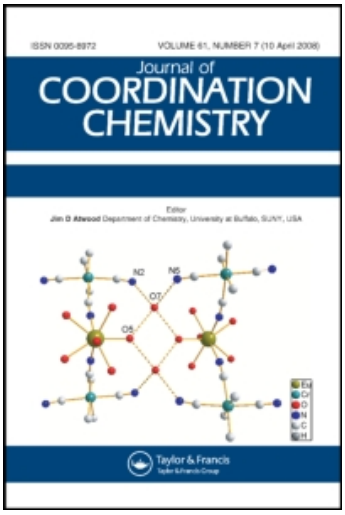

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Axial addition in diastereoisomeric $[Cu(Me_8 14ane)](ClO_4)_2$ complexes: antifungal and antibacterial activities

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Axial addition in diastereoisomeric $[Cu(Me_8[14]ane)](ClO_4)_2$ complexes: antifungal and antibacterial activities

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A series of diastereoisomeric square planar copper(II) perchlorate complexes, $[Cu(Me_8[14]ane)](ClO_4)_2$, undergo axial addition reactions with H_2O, NCS^- NO_2^- and NO_3^- to yield the octahedral species *trans*-$[CuL^1X_2](ClO_4)_n$ (L^1 = isomeric $Me_8[14]ane$; X = H_2O, NCS, NO_2 or NO_3; $n = 2$ when X = H_2O; $n = 0$ when X = NCS, NO_2 or NO_3). The products have been characterized on the basis of analytical, spectroscopic, magnetic and conductance data. Some derivatives are unstable in open air and may react with adventious H_2O to form diaquo complexes. Antifungal and antibacterial activities of the uncomplexed ligands, the square planar copper(II) complexes and their axial addition products have been investigated against a range of phytopathogenic fungi and bacteria.

Keywords: Copper; Azamacrocycles; Axial substitution; Antifungals; Antibacterials

1. Introduction

Axial ligand addition reactions of square planar copper(II) and nickel(II) azamacrocyclic complexes to form six-coordinate complexes have drawn significant interest [1–7]. In this connection, we recently prepared and characterized some diastereoisomeric square planar copper(II) complexes [8] containing isomeric $Me_8[14]anes$, L_A, L_B and L_C [9] (scheme 1). Each ligand yielded two *N*-chiral diastereoisomeric copper(II) complexes [8], designated as $[CuL_{A\alpha}](ClO_4)_2$ and $[CuL_{A\beta}](ClO_2)_2$ for L_A,

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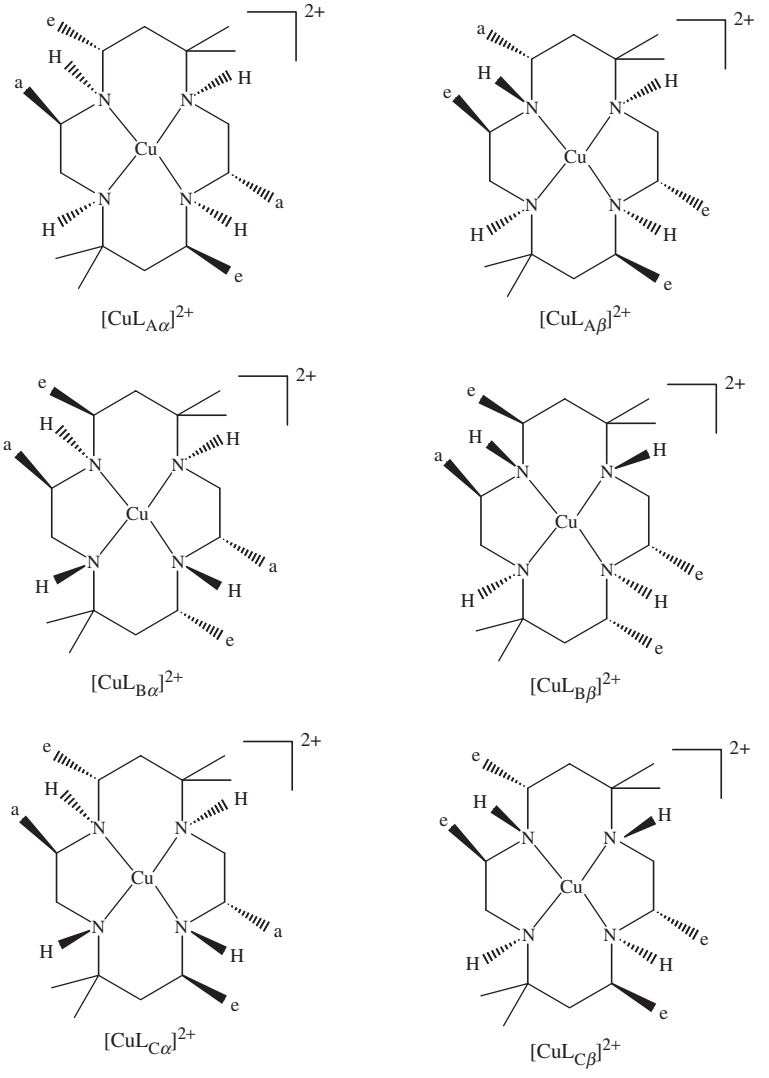

Scheme 1. Structures of diastereoisomeric copper(II) complexes of Me_8[14]anes.

$[CuL_{B\alpha}](ClO_4)_2$ and $[CuL_{B\beta}](ClO_4)_2$ for L_B, and $[CuL_{C\alpha}](ClO_4)_2$ and $[CuL_{C\beta}](ClO_4)_2$ for L_C.

Owing to steric effects exerted by the eight methyl groups in these complexes, it was expected that axial addition might be difficult. However, in recent studies [10, 11], a number of corresponding diastereoisomeric square planar nickel(II) complexes underwent axial addition [11]. Hence it seemed possible that similar types of reactions could also be carried out on copper(II) complexes. In the present study, the synthesis and characterization of axial addition products of the square planar diastereoisomeric copper(II) complexes are reported. As well, antifungal and antibacterial activities of the parent square planar complexes and their axial addition reaction products are reported.

2. Experimental

2.1. *Synthesis*

The axial addition products were prepared from the square planar complexes, $[CuL](ClO_4)_2$ ($L = L_{A\beta}$, $L_{B\alpha}$ & $L_{C\alpha}$) following literature methods [7, 11]. Among the *N*-chiral isomers, $[CuL_{A\alpha}](ClO_4)_2$ did not undergo any addition reaction and yields of $[CuL_{B\beta}](ClO_4)_2$ and $[CuL_{C\beta}](ClO_4)_2$ were too small to prepare addition compounds.

Caution: Perchlorates are potentially explosive materials and should be handled with care, especially in the solid-state.

2.1.1. *Trans*-$[CuL_{C\alpha}(H_2O)_2](ClO_4)_2$. The purple $[CuL_{C\alpha}](ClO_4)_2$ complex (0.02 g) was dissolved in MeCN (20 cm^3), placed in a sample tube and EtOH (2 cm^3) added. The solution was lightly covered for slow evaporation. Over time, the solution changed colour from purple to pink-violet. On concentration by evaporation, a few pink-violet crystals of *trans*-$[CuL_{C\alpha}(H_2O)_2](ClO_4)_2$ were obtained. These were filtered off, washed with EtOH, then diethylether and dried *in vacuo*. Anal. Calcd for $C_{18}H_{44}Cl_2CuN_4O_{10}$ (%): C, 35.39; H, 7.26; N, 9.17; Cu, 10.40. Found: C, 35.37; H, 7.30; N, 9.14; Cu, 10.38.

2.1.2. *Trans*-$[CuL_{A\beta}(NCS)_2]$. $[CuL_{A\beta}](ClO_4)_2$ (0.287 g, 0.5 mmol) and KSCN (0.097 g, 1.0 mmol) separately in hot MeOH (20 cm^3) were mixed hot and a violet colour appeared. The mixture was heated on a steam bath to dryness. The residue was extracted with $CHCl_3$ and the extract evaporated to dryness to give the purple-blue product, which was stored in a desiccator over silica gel, m.p. 220°C. Anal. Calcd for $C_{20}H_{40}CuN_6S_2$ (%): C, 48.80; H, 8.19; N, 17.07; S, 13.03; Cu, 12.91. Found: C, 48.78; H, 8.24; N, 17.05; S, 13.04; Cu, 12.87.

2.1.3. *Trans*-$[CuL_{B\alpha}(NCS)_2]$. $[CuL_{B\alpha}](ClO_4)_2$ (0.287 g, 0.5 mmol) was suspended in hot dry MeOH (30 cm^3) and KSCN (0.097 g, 1.0 mmol) in the same solvent (30 cm^3), was added hot. A blue-violet colour slowly appeared. The mixture was heated on a water bath for 15 min, cooled, and precipitated $KClO_4$ removed by filtration. The filtrate was taken to dryness on a water bath and the residue extracted with $CHCl_3$. The $CHCl_3$ extract was evaporated to dryness to give the blue product, which was dried in a vacuum desiccator over silica gel, m.p. >225°C. Anal. Calcd for $C_{20}H_{40}CuN_6S_2$ (%): C, 48.80; H, 8.19; N, 17.07; S, 13.03; Cu, 12.91. Found: C, 48.75; H, 8.22; N, 17.09; S, 13.00; Cu, 12.86.

2.1.4. *Trans*-$[CuL_{C\alpha}(NCS)_2]$. A suspension of $[CuL_{C\alpha}](ClO_4)_2$ (0.287 g, 0.5 mmol) in MeOH (20 cm^3) and a solution of KSCN (0.097 g, 1.0 mmol) in the same solvent (20 cm^3) were mixed together A blue-violet colour appeared immediately. The reaction mixture was heated on a steam bath and evaporated to dryness. The blue-violet product was extracted in hot $CHCl_3$, filtered and the blue-violet filtrate was evaporated to dryness on a water bath. The blue product, *trans*-$[CuL_{C\alpha}(NCS)_2]$, obtained was dried in a vacuum desiccator over silica gel, m.p. >222°C. Anal. Calcd for $C_{20}H_{40}CuN_6S_2$ (%): C, 48.80; H, 8.19; N, 17.07; S, 13.03; Cu, 12.91. Found: C, 48.77; H, 8.20; N, 17.08; S, 13.01; Cu, 12.85.

2.1.5. *Trans*-[$CuL_{A\beta}(NO_2)_2$]. A suspension of $[CuL_{A\beta}](ClO_4)_2$ (0.287 g, 0.5 mmol) in dry MeOH (20 cm^3) was added to a suspension of KNO_2 (0.086 g, 1.0 mmol) in the same solvent (20 cm^3). A pink-violet colour appeared immediately. The reaction mixture was heated on a steam bath to dryness. The residue was dissolved in hot $CHCl_3$, filtered and evaporated to dryness to yield the violet product, which was stored in a vacuum desiccator over silica gel, m.p. >220°C. Anal. Calcd for $C_{18}H_{40}CuN_6O_4$ (%): C, 46.19; H, 8.62; N, 17.95; Cu, 13.58. Found: C, 46.16; H, 4.66; N, 17.93; Cu, 13.52.

2.1.6. *Trans*-[$CuL_{B\alpha}(NO_2)_2$]. $[CuL_{B\alpha}](ClO_4)_2$ (0.287 g, 0.5 mmol) and KNO_2 (0.086 g, 1.0 mmol) were dissolved separately in hot dry MeOH (20 cm^3) and mixed while hot. Work-up was as for *trans*-$[CuL_{A\beta}(NO_2)_2]$, m.p. >220°C. Anal. Calcd for $C_{18}H_{40}CuN_6O_4$ (%): C, 46.19; H, 8.62; N, 17.95; Cu, 13.58. Found: C, 46.14; H, 8.64; N, 17.91; Cu, 13.53.

2.1.7. *Trans*-[$CuL_{C\alpha}(NO_2)_2$]. $[CuL_{C\alpha}](ClO_4)_2$ (0.287 g, 0.5 mmol) and KNO_2 (0.086 g, 1.0 mmol) suspended separately in hot dry MeOH (40 cm^3) were mixed. Work-up was as for *trans*-$[CuL_{A\beta}(NO_2)_2]$, m.p. >235°C. Anal. Calcd for $C_{18}H_{40}CuN_6O_4$ (%): C, 46.19; H, 8.62; N, 17.95; Cu, 13.58. Found: C, 46.15; H, 4.64; N, 17.91; Cu, 13.51.

2.1.8. *Trans*-[$CuL_{A\beta}(NO_3)_2$]. A hot suspension of KNO_3 (0.101 g, 1.0 mmol) in absolute MeOH (20 cm^3) was added to a hot suspension of $[CuL_{A\beta}](ClO_4)_2$ (0.287 g, 0.5 mmol) in the same solvent (20 cm^3). A pink colour appeared immediately. The mixture was evaporated to dryness on a water bath. $CHCl_3$ was added, the mixture filtered to remove $KClO_4$ and the filtrate evaporated to dryness. A violet product was collected and dried under vacuum over silica gel, m.p. >235°C. Anal. Calcd for $C_{18}H_{40}CuN_6O_6$ (%): C, 43.24; H, 8.06; N, 16.80; Cu, 12.71. Found: C, 43.20; H, 8.10; N, 16.78; Cu, 12.66.

2.1.9. *Trans*-[$CuL_{B\alpha}(NO_3)_2$]. A hot suspension of KNO_3 (0.101 g, 1.0 mmol) in absolute MeOH (20 cm^3) was added to a hot suspension of $[CuL_{B\alpha}](ClO_4)_2$ (0.287 g, 0.5 mmol) in the same solvent (20 cm^3). Work-up was as for *trans*-$[CuL_{A\beta}(NO_3)_2]$, m.p. >235°C. Anal. Calcd for $C_{18}H_{40}CuN_6O_6$ (%): C, 43.24; H, 8.06; N, 16.80; Cu, 12.71. Found: C, 43.20; H, 8.11; N, 16.78; Cu, 12.67.

2.1.10. *Trans*-[$CuL_{C\alpha}(NO_3)_2$]. A hot suspension of KNO_3 (0.101 g, 1.0 mmol) in absolute MeOH (30 cm^3) was added to a hot suspension of $[CuL_{C\alpha}](ClO_4)_2$ (0.287 g, 0.5 mmol) in the same solvent (20 cm^3). The mixture was stirred with heating for 30 min during which time the colour changed to violet. Subsequent work-up was as for *trans*-$[CuL_{A\beta}(NO_3)_2]$, m.p. >235°C. Anal. Calcd for $C_{18}H_{40}CuN_6O_6$ (%): C, 43.23; H, 8.06; N, 16.80; Cu, 12.71. Found: C, 43.21; H, 8.10; N, 16.79; Cu, 12.68.

2.2. *Physical measurements*

Electronic spectra of the samples were recorded on a Shimadzu spectrophotometer. Conductance measurements were carried out on a Hanna instruments HI-8820 conductivity bridge at $25 \pm 0.1^{\circ}C$. Magnetic measurements were conducted on a Sherwood Scientific balance calibrated with $[HgCo(SCN)_4]$. IR spectra were recorded on a Perkin-Elmer model-883 spectrophotometer (KBr disks). C, H, N, S analyses were carried out in the Department of Chemistry, University of Hamburg, Germany. Standard titrimetric methods were employed for analysis of copper.

2.3. *Antifungal activities*

Antifungal activities of the precursor square planar copper(II) complexes and their axial addition products against selected phytopathogenic fungi was assessed by the poisoned food technique. Potato dextrose agar (PDA) was used as growth medium. DMF was used to prepare solutions of the compounds. The solutions were then mixed with sterilized PDA to maintain the concentration of the complexes at 0.01%; 20 cm^3 of these were each poured into a petri dish. After the medium had solidified, a 5 mm mycelial disc for each fungus was placed in the centre of each assay plate against the control. Linear growth of the fungus was measured in mm after five days incubation at $25 \pm 2^{\circ}C$.

2.4. *Antibacterial activities*

Antibacterial activities of the ligands, square planar copper(II) complexes and addition products against selected bacteria were assessed by the disc diffusion method. Paper discs 6 mm in diameter and petriplates 70 mm in diameter were used. Pour plates were made with sterilized melted Nutrient agar (NA) (45°C) and after solidification of the plates, suspensions of the test organisms were spread uniformly over the plate using sterilized glass rods. After soaking with test chemicals (1% in $CHCl_3$/1% in CH_3CN), the paper discs were placed at the centre of the inoculated plate. A control plate was also maintained in each case with $CHCl_3/CH_3CN$. The plates were kept for 4 h at low temperature (4°C) in order to allow the test chemicals to diffuse from the paper disc into the surrounding medium. The plates were then incubated at $35 \pm 2^{\circ}C$ to allow growth of the test organisms and checked at 24 h intervals. Activity is expressed in terms of the diameter of the zone of inhibition in mm. Each experiment was repeated in triplicate.

3. Results and discussion

The structures of the diastereoisomeric square planar copper(II) perchlorate complexes employed in the present study have been assigned previously [8] and are shown in scheme 1. Among the different *N*-chiral isomers, $[CuL_{A\alpha}](ClO_4)_2$, did not undergo axial addition. This may be explained by the structure shown in scheme 1. All *N*-bound hydrogen atoms lie on the same side of the CuN_4 plane and preclude the entrance of a ligand from that side. Steric interactions involving the methyl groups also play

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

Complex	ν_{NH}	ν_{CH}	ν_{CH_3}	ν_{CC}	ν_{MN}	Other bands
$[CuL_{C\alpha}(H_2O)_2](ClO_4)_2$	3195w	2970w	1380vs	1186w	535br	3400ms, ν_{OH}; 1100vs, 620vs, ν_{ClO_4}; 450m, ν_{MO}
$[CuL_{A\beta}(NCS)_2]$	3130w	2965s	1365m	1180w	525w	2025vs, ν_{CN}; 820w, ν_{CS}; 480w, δ_{NCS}
$[CuL_{B\alpha}(NCS)_2]$	3140s	2985s	1375m	1180w	525w	2050vs, ν_{CN}, 815w, ν_{CS}, 480w, δ_{NCS}
$[CuL_{C\alpha}(NCS)_2]$	3130w	2990s	1375m	1180w	550w	2050vs, ν_{CN}; 820sh, ν_{CS}; 480w, δ_{NCS}
$[CuL_{A\beta}(NO_2)_2]$	3192vs	2992s	1375vs	1195m	550w 445w	1445s, ν_{aNO_2}; 1360vs, ν_{sNO2}; 820w, δ_{NO_2}
$[CuL_{B\alpha}(NO_2)_2]$	3180vs	2970s	1370vs	1193m	555vw 430sh	1445m, ν_{aNO_2}; 1365m, ν_{sNO_2}; 820sh, δ_{NO_2}
$[CuL_{C\alpha}(NO_2)_2]$	3182vs	2968s	1380vs	1195s	570vw 440w	1465s, ν_{aNO_2}; 1375s, ν_{sNO_2}; 825m, δ_{NO_2}
$[CuL_{A\beta}(NO_3)_2]$	3180vs	2985vs	1378s	1194s	545w	1450w, 1335sh, ν_{NO_3}; 450w, ν_{MO}
$[CuL_{B\alpha}(NO_3)_2]$	3188s	2990vs	1370s	1195s	550w	1450w, 1336w, ν_{NO_3}; 440w, ν_{MO}
$[CuL_{C\alpha}(NO_3)_2]$	3100s	2980vs	1376s	1195s	540w	1425w, 1310w, ν_{NO_3}; 450w, ν_{MO}

an important role in axial addition, in that axial methyl groups congest the axial sites whereas equatorial groups favour addition [12]. Yields of complexes $[CuL_{B\beta}](ClO_4)_2$ and $[CuL_{C\alpha}](ClO_4)_2$, were too small to be used for further study. Thus only $[CuL_{A\beta}](ClO_4)_2$, $[CuL_{B\alpha}](ClO_4)_2$, and $[CuL_{C\alpha}](ClO_4)_2$ have been used for axial ligand addition.

Since the copper(II) complexes are paramagnetic, ^1H NMR spectra 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 conformations of the ligands found in the original square planar complex [12]. Characteristic IR data are collected in table 1 and other physical data are listed in table 2.

3.1. *Copper(II) diaquo complex*

The molar conductivity value of $163\,\Omega^{-1}\,cm^2\,mol^{-1}$ corresponds to 1:2 electrolyte behaviour in acetonitrile solution and IR data are in agreement with the formulation as *trans*-$[CuL_{C\alpha}(H_2O)_2](ClO_4)_2$. The IR spectrum exhibits characteristic ν_{NH}, ν_{CN}, ν_{C-C}, ν_{CH} and ν_{CH_3} bands at expected positions. Other than these, the complex further shows $\nu_{ClO_4}^{-}$ bands at 1100 and 620 cm^{-1}. A distinct ν_{OH} band at 3400 cm^{-1} can be assigned to coordinated water and the band at 1615 cm^{-1} is attributed to the δ_{HOH} bending mode [13]. The spectrum also displays medium intensity bands around 450 cm^{-1}, which can be assigned to M–O stretching. The conversion of violet $[CuL_{C\alpha}](ClO_4)_2$ complex to pink-violet $[CuL_{C\alpha}(H_2O)_2](ClO_4)_2$ is effected by slow evaporation of solvent in the open air. Such conversions have also been reported for analogous complexes [14]. It has been shown that copper(II) centres in macrocycles generally have square planar or tetragonally distorted geometries and that these give rise to broad bands in the visible region due to overlap of $A_{1g} \rightarrow B_{1g}$, $B_{2g} \rightarrow B_{1g}$ and $E_g \rightarrow B_{1g}$ transitions [7]. The present complex shows a broad d–d band at 536 nm in the solid state, at 538 nm in CH_3CN and at 518 nm in DMF solutions, consistent with the above. The tetragonally distorted octahedral geometry with two H_2O molecules at axial sites has been confirmed by an X-ray structure determination [15]. Importantly, and in keeping with the above, the X-ray analysis showed that axial substitution

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

Complex	Colour in the solid-state	d–d bands		Molar conductivity ($\Omega^{-1}\,cm^2\,mol^{-1}$) and colour in solution								μ_{eff} (BM)
		Solvent	λ_{max}/nm ($\log \varepsilon_{max}$)	Colour in CH_3CN		Colour in $CHCl_3$		Colour in DMF		Colour in water		
$[CuL_{C\alpha}(H_2O)_2](ClO_4)_2$	Pink-violet	Nujol	536	Pink-violet	163							1.76
		Acetonitrile	538(240)									
		DMF	518(2.05)									
$[CuL_{A\beta}(NCS)_2]$	Purple-blue	Chloroform	559(2.19)			Purple-blue	0	Violet	25	Pink	159	1.76
$[CuL_{B\alpha}(NCS)_2]$	Blue	Chloroform	741(2.09)			Blue	0	Light blue	85	Pink	162	1.78
$[CuL_{C\alpha}(NCS)_2]$	Blue	Chloroform	572(2.17)			Blue	0	Light blue	87	Pink-violet	155	1.80
$[CuL_{A\beta}(NO_2)_2]$	Violet	Chloroform	534(2.07)			Violet	0	Blue-violet	60	Pink	179	1.69
		Water	496(1.94)									
$[CuL_{\beta\alpha}(NO_2)_2]$	Violet	Chloroform	534(1.61)			Violet	0	Light blue	49	Pink	180	1.68
		Water	555(2.35)									
$[CuL_{C\alpha}(NO_{2)2})$	Blue	Chloroform	555(2.25)			Blue	0	Light blue	55	Pink-violet	185	1.71
$[CuL_{A\beta}(NO_3)_2)$	Violet	Chloroform	536(1.67)			Violet	0	Blue-violet	69	Pink	170	1.75
		DMF	534(2.11)									
$[CuL_{\beta\alpha}(NO_3)_2]$	Pink-violet	Chloroform	513(1.45)			Pink-violet	0	Blue	59	Pink	151	1.77
		Water	502(1.98)									
$[CuL_{C\alpha}(NO_3)_2]$	Deep violet	Chloroform	526(2.17)			Violet	0	Blue	42	Pink-violet	160	1.73
		DMF	535(2.07)									

occurred with retention of original stereochemistry of the square planar precursor complex [8]. The magnetic moment value (1.76 BM) is normal.

3.2. *Copper(II) diisothiocyanato complexes*

Since thiocyanate is considered to be a stronger ligand than the others employed in this study, it was anticipated that this would add easily to the axial sites of the square planar copper(II) complexes. Thus, reactions of $[CuL_{A\beta}](ClO_4)_2$, $[CuL_{B\alpha}](ClO_4)_2$ and $[CuL_{C\alpha}](ClO_4)_2$ with KSCN each afforded the purple-blue products, *trans*-$[CuL(NCS)_2]$. Electronic absorption and magnetic data (table 2) are consistent with a tetragonally distorted octahedral structure. IR spectra show characteristic ν_{N-H}, ν_{C-C}, and ν_{C-H} bands in expected regions. The appearance of ν_{CN} bands in the region 2025–2040 cm^{-1}, ν_{CS} bands around 815–820 cm^{-1} and δ_{NCS} bands in the region 470–480 cm^{-1} confirms the presence of *N*-bonded thiocyanate [13]. The complexes in $CHCl_3$ are non-electrolytes and the lack of colour change in $CHCl_3$ solution indicates that it retains its geometry and conformation in this solvent. The thiocyanato complexes containing the $L_{B\alpha}$ and $L_{C\alpha}$ ligands have conductance values of 85 and 87 $\Omega^{-1}\,cm^2\,mol^{-1}$, respectively, in DMF solution. This probably arises due to equilibrium between octahedral and square planar geometries in the presence of DMF, as observed for similar complexes [7]. Aqueous solutions of the complexes exhibit very different colours than in the solid-state, pink for *trans*-$[CuL_{A\beta}(SCN)_2]$ and *trans*-$[CuL_{B\alpha}(SCN)_2]$, and pink-violet for *trans*-$[CuL_{C\alpha}(SCN)_2]$. Conductance values lie in the range 155–162 $\Omega^{-1}\,cm^2\,mol^{-1}$, and clearly correspond to 1 : 2 electrolytes. The complete replacement of thiocyanate groups by H_2O in aqueous solution has been noted in related systems [14, 16].

3.3. *Copper(II) dinitro complexes*

$[CuL_{A\beta}](ClO_4)_2$, $[CuL_{B\alpha}](ClO_4)_2$ and $[CuL_{C\alpha}](ClO_4)_2$ produce pink-violet derivatives on reaction with $NaNO_2$ in methanol. Subsequent work-up yielded blue-violet products, *trans*-$[CuL(NO_2)_2]$. IR spectra (table 1) display ν_{NH}, ν_{CC}, and ν_{MN} bands in expected positions. Bands at 1445–1465 cm^{-1} and at 1370–1375 cm^{-1} are assigned to $\nu_{asym}(NO_2)$ and $\nu_{sym}(NO_2)$, respectively. Further, the appearance of bands at 820–845 cm^{-1} can be assigned to δ_{NO2} stretching. Finally, the presence of bands in the region 420–445 cm^{-1} strongly supports the assignment of *N*-bound nitro ligands [17]. Additional evidence in support of the assigned molecular formulae come from elemental analysis and conductance values of 0 $\Omega^{-1}\,cm^2\,mol^{-1}$ (table 2) in $CHCl_3$ (in which solvent the colours of the complexes remain intact) corresponding to non-electrolyes. Molar conductivity values of 49–60 $cm^{-1}\,cm^2\,mol^{-1}$ for DMF solutions correspond to 1 : 1 electrolytes, and those of aqueous solutions corresponding to 1 : 2 electrolytes can be accounted for in the same way as for the thiocynanate species. Magnetic moments of 1.68–1.71 BM and d–d bands in electronic spectra at 534–550 nm are in accord with an octahedral structures.

3.4. *Copper(II) dinitrato complexes*

The reaction of $[CuL_{A\alpha}](ClO_4)_2$, $[CuL_{B\alpha}](ClO_4)_2$, and $[CuL_{C\alpha}](ClO_4)_2$ with KNO_3 produced violet, pink-violet and deep-violet products, respectively. Analytical and

physical data are consistent with the formula *trans*-$[CuL(NO_3)_2]$. IR spectra (table 1) exhibit characteristic ν_{CC}, ν_{CH} and ν_{MN} bands in expected regions. Spectra further display bands at 1425–1450 cm^{-1} and 1310–1335 cm^{-1} attributable to the coordinated NO_3 group. The separation of these bands is consistent with a unidentate mode of coordination [13]. The complexes are non-electrolytes in $CHCl_3$ solution, in which colours of complexes remain intact. Molar conductivity values of 42–69 $\Omega^{-1} cm^2 mol^{-1}$ of blue to blue-violet DMF solutions of these complexes correspond to 1 : 1 electrolytes and that their aqueous solutions correspond to 1 : 2 electrolytes, in line with observations above [14, 16]. The d–d band positions and magnetic moments are normal (table 2).

3.5. *Fungitoxicity study*

Antifungal activities of the ligands and some of their complexes are summarised in table 3. Screens have been conducted against four selective phytopathogenic fungi, *Macrophomina phaseolina*, *Alternaria alternata*, *Fusarium equiseti* and *Colletotrichum corcolei*. These fungi are phytopathogens of important crop plants such as jute, chilli, brinjal, etc., and can cause significant loss of yield. Control of such pathogens by non-hazardous fungicides a major concern, especially as fungi gradually develop resistance to known fungicides. It is evident from the results presented in table 3 that the macrocycles and their complexes show some antifungal activity. This was found to decrease upon coordination of the ligands to copper(II), as is usually observed [14, 16]. However, the fungiotoxicity exhibited by the copper(II) complexes is greater than that exhibited by analogous cobalt(III) complexes [18]. The most active complex against *M. phaseolina*, *A. alternate*, *F. equiseti*, and *C. corcolei* was $[CuL_{C\alpha}](ClO_4)_2$, $[CuL_{A\beta}(NCS)_2]$, $[CuL_{C\alpha}(NCS)_2]$ and $[CuL_{\beta\alpha}(NO_2)_2]$, respectively. This observation

Table 3. *In vitro* antifungal activities of the ligands and their copper(II) complexes.

	% Inhibition of mycelial growth			
Compound	*Macrophomina phaseolina*	*Alternata alternaria*	*Fusarium equiseti*	*Colletotrichums corcolei*
L_A	29.5	22.3	23.7	19.8
$[CuL_{A\alpha}](ClO_4)_2$	15.3	17.0	11.8	13.3
$[CuL_{A\beta}](ClO_4)_2$	18.2	14.7	3.7	11.3
$[CuL_{A\beta}(NCS)_2]$	7.3	20.2	10.3	8.6
$[CuL_{A\beta}(NO_2)_2]$	17.8	14.3	9.8	11.1
$[CuL_{A\beta}(NO_3)_2]$	13.5	15.8	10.3	9.9
L_B	27.6	23.2	19.0	7.6
$[CuL_{B\alpha}](ClO_4)_2$	13.3	14.7	8.3	9.1
$[CuL_{B\beta}](ClO_4)_2$	11.2	16.4	12.8	13.2
$[CuL_{B\alpha}(NCS)_2]$	23.8	11.2	21.7	15.5
$[CuL_{B\alpha}(NO_2)_2]$	15.3	6.7	18.5	21.7
$[CuL_{B\alpha}(NO_3)_2]$	7.9	9.2	12.9	14.5
L_C	31.3	25.6	21.5	18.5
$[CuL_{C\alpha}](ClO_4)_2$	24.4	12.7	13.4	6.4
$[CuL_{C\beta}](ClO_4)_2$	9.3	8.6	18.1	11.5
$[CuL_{C\alpha}(NCS)_2]$	23.9	19.2	22.7	14.2
$[CuL_{C\alpha}(NO_2)_2]$	8.8	17.6	13.5	12.4
$[CuL_{C\alpha}(NO_3)_2]$	14.7	10.6	6.5	4.8

underscores the lack of a structure activity relationship for these complexes in this context. A comparison of activities of the complexes reported here with those of some sulfur-containing Schiff bases and their complexes, [Cu(NNS)X], where HNNS represents the 2-benzoylpyridine Schiff bases of *S*-methyl and *S*-benzyldithiocarbazate, and X = C1, NO_3, allows some interesting conclusions to be drawn [19]. First, the latter are more fungiotoxic. Secondly, the enhancement of activity upon coordination of the NNS ligands was significantly greater, indicating a more prominent role for the metal ion in these systems.

3.6. *Antibacterial study*

Investigations of antibacterial activities of macrocyclic complexes are rare [20]. Therefore, studies of the antibacterial activities of the parent and axially substituted copper(II) complexes have been carried out against the bacteria *Salmonella typhi*, *Shigella dysenteriae*, *Escherichia coli* and *Bacillus cereus*. These are known to cause various diseases (*S. typhi* causes typhoid, *S. dysenteriae* causes dysentery, and both *E. coli* and *B. cereus* cause gastroenteritis). Antibacterial results summarised in table 4 show that the ligands and some of their copper(II) complexes show measurable activities but some complexes do not. Unlike their behaviour towards fungi, some of the complexes are found to exhibit higher anti-bacterial activities than the corresponding ligands. For the L_A ligands, only one complex, $[CuL_{A\beta}](ClO_4)_2$, had activity comparable to that exhibited by the free ligand. By contrast, the other two ligands provided examples where the presence of copper(II) did increase activity. Thus, for L_B, complexes showed seven higher activity values, including five for perchlorate complexes, similarly, and for L_C complexes showed nine comparable or greater activity values than the free ligand; five of these were perchlorate salts. It is noteworthy that for

Table 4. Anti-bacterial activities of the ligands and their copper(II) complexes.

	Diameter of zone of inhibition (mm) after 24 h			
Compound	*Salmonella typhi*	*Shigella dysenteriae*	*Escherichia coli*	*Bacillus cereus*
L_A	12	12	6	13
$[CuL_{A\alpha}](ClO_4)_2$	0	10	0	0
$[CuL_{A\beta}](ClO_4)_2$	7	12	0	8
$[CuL_{A\beta}(NCS)_2]$	0	7	0	9
$[CuL_{A\beta}(NO_2)_2]$	0	0	7	0
$[CuL_{A\beta}(NO_3)_2]$	0	9	0	6
L_B	8	10	9	15
$[CuL_{B\alpha}](ClO_4)_2$	10	11	13	0
$[CuL_{B\beta}](ClO_4)_2$	11	22	0	8
$[CuL_{B\alpha}(NCS)_2]$	10	8	0	0
$[CuL_{B\alpha}(NO_2)_2]$	7	9	14	0
$[CuL_{B\alpha}(NO_3)_2]$	0	7	0	0
L_C	10	8	7	19
$[CuL_{C\alpha}](ClO_4)_2$	0	15	8	0
$[CuL_{C\beta}](ClO_4)_2$	24	16	12	9
$[CuL_{C\alpha}(NCS)_2]$	0	14	7	11
$[CuL_{C\alpha}(NO_2)_2]$	0	7	0	0
$[CuL_{C\alpha}(NO_3)_2]$	0	10	8	7

the bacterium *B. cereus*, no complex had greater activity than that of the corresponding free ligand.

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