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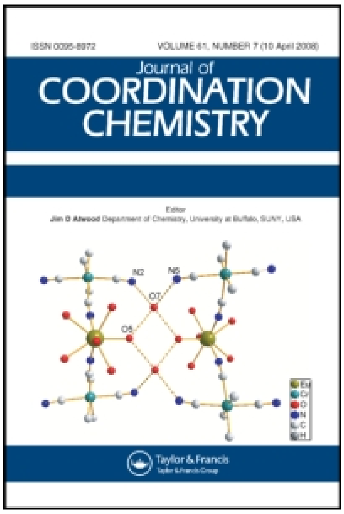

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Axial ligand substitution in diastereoisomeric *trans*-$[Co(Me_8[14]ane)Cl_2]^+$ complexes and their anti-fungal activities

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Three isomeric $Me_8[14]$anes, L_A, L_B and L_C, on aeration with cobalt(II) acetate tetrahydrate and subsequent treatment with concentrated HCl and $HClO_4$, give green *trans*-$[CoLCl_2]ClO_4$ diastereoisomers. Whereas the macrocyclic ligands L_A and L_B yield two *N*-chiral diastereoisomers, L_C gives one isomer. The complexes undergo axial ligand substitution with small ligands such as NO_2^-, SCN^-, OH^- and H_2O to produce corresponding *trans* products. Anti-fungal activities of the complexes against a range of phytopathogenic fungi have been investigated.

Keywords: Cobalt complexes; aza-Macrocyclic ligands; Axial substitution; Anti-fungal activity

1. Introduction

Axial ligand substitution of cobalt(III) complexes of azamacrocyclic ligands has attracted considerable attention for well over twenty years. Accordingly, a variety of substitution products of *trans*-dichlorocobalt(III) complexes with different macrocycles has been reported [1–11]. Our contribution to such chemistry [12–14] has revolved around the preparation and characterization of diastereoisomeric *trans*-dichlorocobalt(III) complexes, *trans*-$[CoLCl_2]ClO_4$, where L = an isomeric $Me_8[14]$ane.

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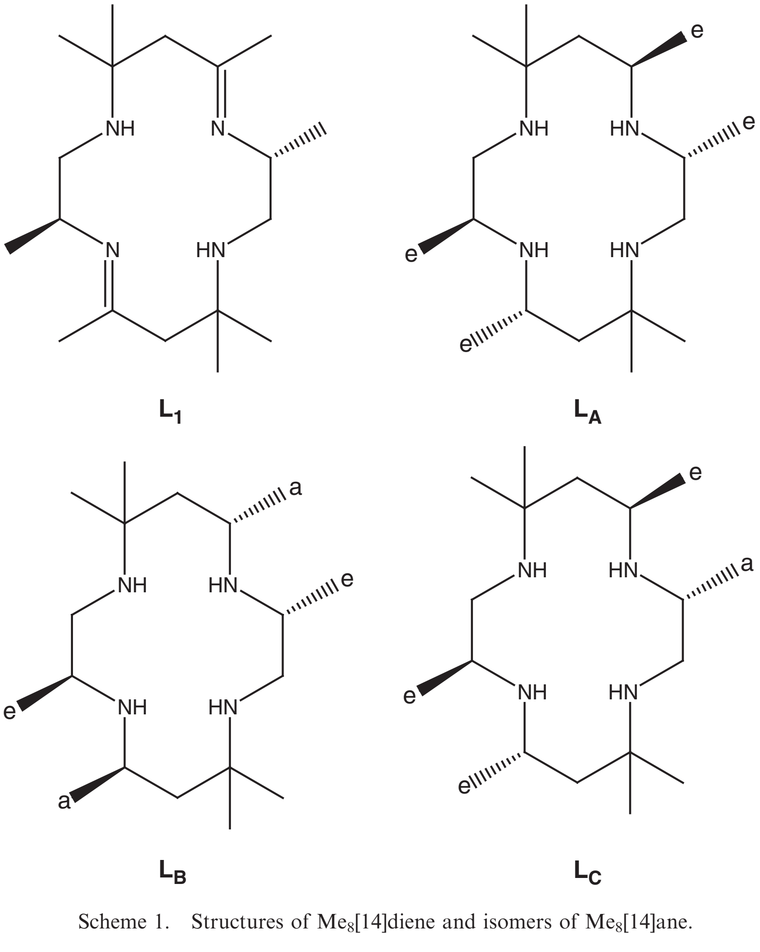
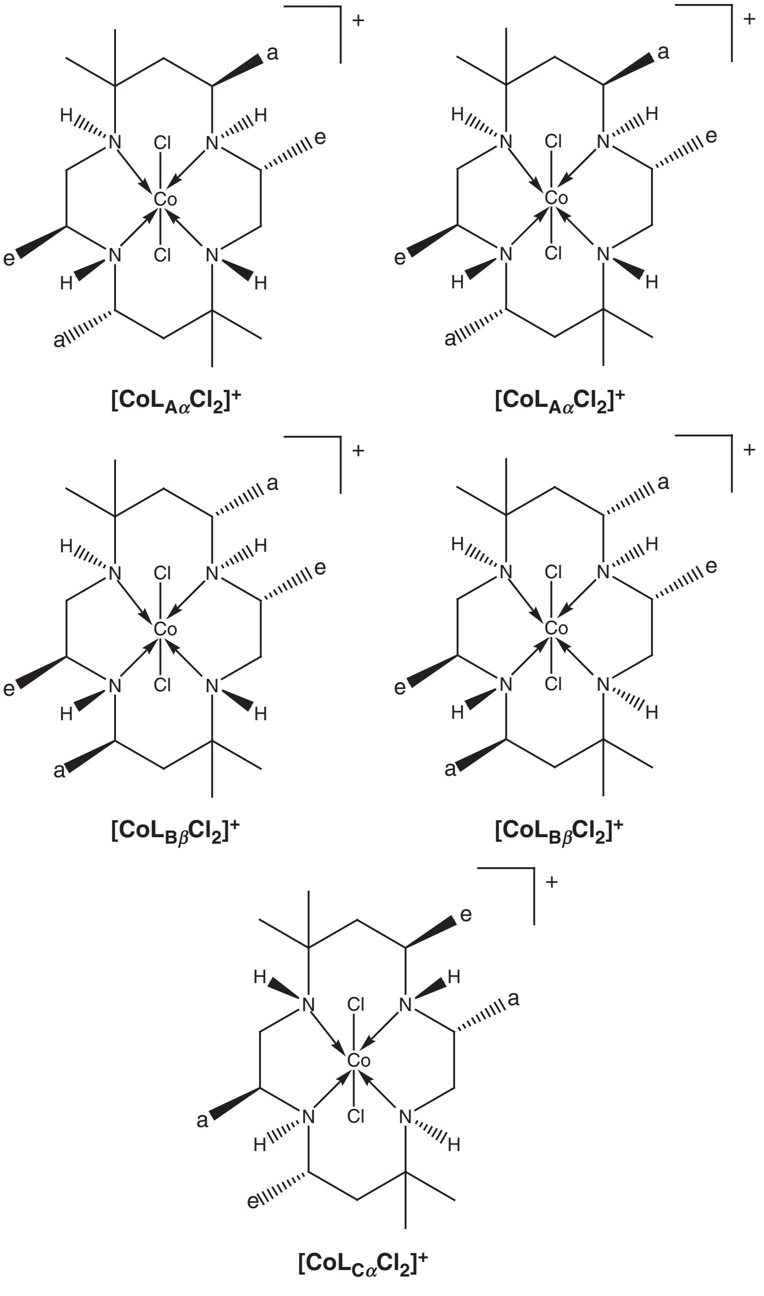
It has been established that stereospecific condensation of 1,2-propanediamine with acetone yields only the 3,10-C-*meso* isomer of the macrocycle 3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, Me_8[14]diene, L_1, as determined by ^{1}H NMR [15, 16] and X-ray crystallography [17]; scheme 1. Reduction of L_1 with $NaBH_4$ yields three isomeric Me_8[14]anes, L_A, L_B and L_C; scheme 1. In terms of the aforementioned cobalt(III) chemistry, L_A and L_B were found to yield two *N*-chiral diastereoisomers (see scheme 2), designated as $[CoL_{A\alpha}Cl_2]ClO_4$ and $[CoL_{A\beta}Cl_2]ClO_4$ for L_A, and $[CoL_{B\alpha}Cl_2]ClO_4$ and $[CoL_{B\beta}Cl_2]ClO_4$ for L_B. L_C yielded one *N*-chiral diastereoisomer designated as $[CoL_{C\alpha}Cl_2]ClO_4$ [12–14].

Interactions of L_A, L_B and L_C with other metal centres have been investigated. In one study [18], a number of square planar nickel(II) complexes were prepared by reaction of the ligands with nickel(II) acetate and subsequent treatment with lithium perchlorate. In another study, Hazari *et al.* [19] were successful in preparing some copper(II) complexes. As indicated above, synthesis of *trans*-$[CoLCl_2]ClO_4$ has been achieved. Owing to the putative steric hindrance exerted by the eight methyl groups in these macrocyclic ligands, it was originally thought that axial substitution reactions would be difficult. However, subsequent studies proved that axial substitutions in



Scheme 1. Structures of Me_8[14]diene and isomers of Me_8[14]ane.



Scheme 2. Structures of diastereoisomeric cobalt(III) complexes of Me_8[14]anes.

trans-$[ZnL(OH_2)_2](ClO_4)_2$ [20], as well as in *trans*-$[CuL_1(ClO_4)_2] \cdot 2H_2O$ [21], are feasible. Hence it seemed likely that similar axial substitutions could also be carried out on *trans*-$[CoLCl_2]ClO_4$. In this context, a number of axial substitution products of *trans*-$[CoLCl_2]ClO_4$ diastereoisomers with unidentate ligands such as

NO_2^-, SCN^-, OH^- and H_2O, have been isolated, characterized and their anti-fungal activities investigated. The results of this study are reported herein.

2. Experimental

2.1. *Synthesis*

The parent ligand 3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, Me_8[14]diene, L_1, was synthesized as described in the literature [15] and reduced with $NaBH_4$ in a 1 : 1 water–methanol mixture to yield L_A, L_B and L_C that were subsequently isolated by fractional crystallization from xylene [14]. The *trans*-dichlorocobalt(III) complexes shown in scheme 2 were then prepared, again following a literature procedure [12]. Axial ligand substitution products were prepared by following methods adopted earlier [7, 22] for related complexes and as detailed below.

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

2.1.1. *Trans*-[$CoL_{A\alpha}(ONO)_2$]ClO_4. *trans*-[$CoL_{A\alpha}Cl_2$]ClO_4 (0.2707 g, 0.5 mmol) and $NaNO_2$ (0.069 g, 1.0 mmol) were suspended in dry MeOH (20 cm^3). After heating the mixture on water bath for 15 min, the brown-yellow solution was filtered hot. The filtrate was concentrated on a water bath until crystallization commenced. After cooling, the brown-yellow product *trans*-[$CoL_{A\alpha}(ONO)_2$]ClO_4 was filtered off, washed with dry EtOH and by Et_2O, and dried *in vacuo*. Anal. Calcd for $C_{18}H_{40}ClCoN_6O_8$ (%): C, 38.41; H, 7.16; N, 14.93. Found: C, 38.37; H, 7.22; N, 14.91.

2.1.2. *Trans*-[$CoL_{A\beta}(ONO)_2$]ClO_4. $NaNO_2$ (0.069 g, 1.0 mmol) was added to a suspension of *trans*-[$CoL_{A\beta}Cl_2$]ClO_4 (0.2707 g, 0.5 mmol) in hot, dry MeOH (25 cm^3) and reacted as above. Anal. Calcd for $C_{18}H_{40}ClCoN_6O_8$ (%): C, 38.41; H, 7.16; N, 14.93. Found: C, 38.35; H, 7.19; N, 14.92.

2.1.3. *Trans*-[$CoL_{B\alpha}(ONO)_2$]ClO_4. *trans*-[$CoL_{B\alpha}Cl_2$](ClO_4) (0.2707 g, 0.5 mmol) and $NaNO_2$ (0.069 g, 1.0 mmol) were separately suspended in hot MeOH (10 cm^3) and mixed while hot. The hot mixture was heated on water bath for 20 min until the solution turned clear brown-yellow. The solution was further concentrated on a water bath until the product started to crystallize. After cooling to room temperature, brown-yellow crystals of [$CoL_{B\alpha}(ONO)_2$]ClO_4 were filtered off, washed with EtOH and Et_2O and dried *in vacuo*. Anal. Calcd for $C_{18}H_{40}ClCoN_6O_8$ (%): C, 38.41; H, 7.16; N, 14.93. Found: C, 38.37; H, 7.21; N, 14.89.

2.1.4. *Trans*-[$CoL_{B\beta}(ONO)_2$]ClO_4. *trans*-[$CoL_{B\beta}Cl_2$]ClO_4 (0.2707 g, 0.5 mmol) was suspended in dry and hot MeOH (25 cm^3). $NaNO_2$ (0.069 g, 1.0 mmol) was added and the reaction mixture was heated on water bath for 20 min and filtered hot when the solution turned brown-yellow. The brown-yellow filtrate on further evaporation yielded brown-yellow crystals of *trans*-[$CoL_{B\beta}(ONO)_2$]ClO_4 which were recrystallized from MeOH–EtOH. Anal. Calcd for $C_{18}H_{40}ClCoN_6O_8$ (%): C, 38.41; H, 7.16; N, 14.93. Found: C, 38.37; H, 7.18; N, 14.89.

2.1.5. *Trans*-[CoL$_{C\alpha}$(ONO)$_2$]ClO$_4$. *trans*-[CoL$_{C\alpha}$Cl$_2$]ClO$_4$ (0.2707 g, 0.5 mmol) and NaNO$_2$ (0.069 g, 1.0 mmol) were suspended in MeOH (30 cm^3). After heating the mixture on a water bath for 15 min, the solution was filtered hot when the solution turned orange. The filtrate was concentrated on a water bath until crystallization set in. Upon cooling, the bright-yellow product was filtered off, washed with EtOH and Et$_2$O and finally dried in a vacuum desiccator over silica gel. Anal. Calcd for $C_{18}H_{40}ClCoN_6O_8$ (%): C, 38.41; H, 7.16; N, 14.93. Found: C, 38.40; H, 7.20; N, 14.91.

2.1.6. *Trans*-[CoL$_{B\alpha}$Cl(ONO)]ClO$_4$. *trans*-[CoL$_{B\alpha}$Cl$_2$]ClO$_4$ (0.2707 g, 0.5 mmol) was suspended in dry and hot MeOH (20 cm^3). NaNO$_2$ (0.0345 g, 0.5 mmol) was added and the mixture heated on a water bath for 10 min where the solution turned brown. The solution was filtered hot to remove any undissolved solid. The brown filtrate was then concentrated on a water bath until crystallization commenced. After cooling, the brown product was filtered off, washed with EtOH and Et$_2$O and dried *in vacuo*. Anal. Calcd for $C_{18}H_{40}Cl_2CoN_5O_6$ (%): C, 39.14; H, 7.30; N, 12.68. Found: C, 39.09; H, 7.34; N, 12.67.

2.1.7. *Trans*-[CoL$_{C\alpha}$Cl(ONO)]ClO$_4$. *trans*-[CoL$_{C\alpha}$Cl$_2$]ClO$_4$ (0.2707 g, 0.5 mmol) and NaNO$_2$ (0.0345 g, 0.5 mmol) were suspended in dry MeOH (30 cm^3). The suspension was heated on a water bath for 15 min until the solution turned brown-yellow. The solution was filtered hot and the filtrate reduced to 4 cm^3 when crystallization set in. After cooling, the yellow-brown product was filtered off, washed with EtOH and Et$_2$O and dried *in vacuo*. Anal. Calcd for $C_{18}H_{40}Cl_2CoN_5O_6$ (%): C, 39.14; H, 7.30; N, 12.68. Found: C, 39.10; H, 7.33; N, 12.68.

2.1.8. *Trans*-[CoL$_{A\beta}$(NCS)$_2$]ClO$_4$. *trans*-[CoL$_{A\beta}$CL$_2$]ClO$_4$ (0.2707 g, 0.5 mmol) and NH$_4$SCN (0.076 g, 1.0 mmol) were suspended in MeOH (20 cm^3). The mixture was heated on water bath for 15 min until the solution turned red-brown. The mixture was filtered hot and the filtrate concentrated to 4 cm^3. After cooling, the red-brown product was filtered off, washed with absolute EtOH and Et$_2$O and dried in a vacuum desiccator over silica gel. Anal. Calcd for $C_{20}H_{40}ClCoN_6O_4S_2$ (%): C, 40.92; H, 6.87; N, 14.32; S, 10.92. Found: C, 40.90; H, 6.91; N, 14.30; S, 10.88.

2.1.9. *Trans*-[CoL$_{B\alpha}$(NCS)$_2$]ClO$_4$. *trans*-[CoL$_{B\alpha}$CL$_2$(ClO$_4$)] (0.2703 g, 0.5 mmol) was suspended in hot dry MeOH (20 cm^3), NH$_4$SCN (0.076 g, 1.0 mmol) was added and treated as above. Anal. Calcd for $C_{20}H_{40}ClCoN_6O_4S_2$ (%): C, 40.92; H, 6.87; N, 14.32; S, 10.92. Found: C, 40.89; H, 6.90; N, 14.33; S, 10.90.

2.1.10. *Trans*-[CoL$_{B\beta}$(NCS)$_2$]ClO$_4$. *trans*-[CoL$_{B\beta}$CL$_2$]ClO$_4$ (0.2707 g, 0.5 mmol) was suspended in hot MeOH (20 cm^3). A solution of NH$_4$SCN (0.076 g, 1.0 mmol) in hot MeOH (20 cm^3) was added to the suspension, the mixture heated on water bath for 15 min and filtered while hot. On further heating on a water bath for 20 min, the volume was reduced to ca 2 cm^3. Since no crystals were produced at this stage, the solution was diluted with 1 cm^3 of EtOH and flushed with Et$_2$O to give a red-brown, sticky material. After decanting off the mother liquor, the sticky material was washed with a little Et$_2$O and a brown powder isolated. Anal. Calcd for $C_{20}H_{40}ClCoN_6O_4S_2$ (%): C, 40.92; H, 6.87; N, 14.32; S, 10.92. Found: C, 40.87; H, 6.89; N, 14.29; S, 10.90.

Table 1. Electronic spectra and conductivity data for the complexes.

	d–d bands		
Complex	Solvent	λ_{max}/nm(log ε)[a]	Cond. in DMF ($ohm^{-1}\,cm^2\,mol^{-1}$)
trans-$[CoL_{A\alpha}(ONO)_2](ClO_4)$	DMF	530 (1.90)	74
trans-$[CoL_{A\beta}(ONO)_2](ClO_4)$	DMF	540 (1.90)	68
trans-$[CoL_{\beta\alpha}(ONO)_2](ClO_4)$	DMF	540 (1.94)	81
trans-$[CoL_{B\beta}(ONO)_2](ClO_4)$	DMF	531 (2.28)	79
trans-$[CoL_{C\alpha}(ONO)_2](ClO_4)$	Nujol	457	
	DMF	470 (2.27)	81
trans-$[CoL_{B\alpha}Cl(ONO)](ClO_4)$	DMF	500 (1.92)	80
trans-$[CoL_{C\alpha}Cl(ONO)](ClO_4)$	DMF	485 (1.98)	72
trans-$[CoL_{A\beta}(NCS)_2](ClO_4)$	DMF	565 (2.17)	100
trans-$[CoL_{B\alpha}(NCS)_2](ClO_4)$	Nujol	561 (4.12)	
	DMF	563 (2.39)	71
trans-$[Co_{B\beta}(NCS)_2](ClO_4)$	Nujol	432	
	DMF	565 (2.17)	90
trans-$[CoL_{C\alpha}(NCS)_2](ClO_4)$	DMF	560 (2.41)	84
trans-$[CoL_{A\alpha}(H_2O)_2](ClO_4)_3$	Nujol	438	
	DMF	530 sh (1.77)	250
trans-$[CoL_{B\alpha}(H_2O)_2](ClO_4)_3$	Nujol	422	
	DMF	525 sh (1.95)	270
trans-$[CoL_{C\alpha}(H_2O)_2](ClO_4)_3$	DMF	480 sh (1.55)	280
trans-$[CoL_{B\alpha}(OH)_2](ClO_4)$	DMF	530 sh (1.90)	83

[a] ε_{max} = maximum molar extinction coefficient in $M^{-1}\,cm^{-1}$.

2.1.11. *Trans*-$[CoL_{C\alpha}](NCS)_2]ClO_4$. *Tran*s-$[CoL_{C\alpha}Cl_2]ClO_4$ (0.2707 g, 0.5 mmol) and NH_4SCN (0.076 g, 1.0 mmol) were suspended in MeOH (100 cm^3). The mixture was heated until the solution changed colour to green-red and the solution concentrated until the product crystallized out. The dark-red product was filtered off while hot, washed with EtOH and Et_2O and dried *in vacuo*. Anal. Calcd for $C_{20}H_{40}ClCoN_6O_4S_2$ (%): C, 40.92; H, 6.87; N, 14.32; S, 10.92. Found: C, 40.93; H, 6.88; N, 14.28; S, 10.94.

2.1.12. *Trans*-$[CoL_{A\alpha}(H_2O)_2](ClO_4)_3$. *trans*-$[CoL_{A\alpha}Cl_2]ClO_4$ (0.2707 g, 0.5 mmol) was suspended in H_2O (20 cm^3). About 0.3 g (excess) of moist AgOH was added. The mixture was heated on water bath for 30 min until the solution turned red. After cooling, the mixture was filtered to remove AgCl and excess AgOH. The solution was concentrated to about 4 cm^3 and allowed to stand overnight in the dark. The solution was filtered again to remove any Ag_2O. The filtrate was diluted with H_2O, neutralized with dilute $HClO_4$, concentrated to about 1 cm^3 and diluted with 2 cm^3 of EtOH. With the addition of Et_2O, the red-brown product precipitated. It was filtered off, washed with little EtOH, then with excess Et_2O, and dried in a desiccator over silica gel. Anal. Calcd for $C_{18}H_{44}Cl_3CoN_4O_{14}$ (%): C, 30.63; H, 6.28; N, 7.94. Found: C, 30.58; H, 6.31; N, 7.91.

2.1.13. *Trans*-$[CoL_{B\alpha}(H_2O)_2](ClO_4)_3$. *trans*-$[CoL_{B\alpha}Cl_2]ClO_4$ (0.2707 g, 0.5 mmol) and moist AgOH in excess (about 0.3 g) were suspended in MeOH (20 cm^3). The suspension was heated on a water bath for about 30 min until the solution turned red. After cooling, the mixture was filtered to remove AgCl and excess AgOH. After the addition

Table 2. Selected IR data for the complexes.

Complex	ν_{NH}	ν_{CH}	$\nu_{\mathrm{CH_3}}$	ν_{CC}	ν_{MN}	$\nu_{\mathrm{ClO_4}}$	Other bands
trans-$[\mathrm{CoL}_{\mathrm{A}\alpha}(\mathrm{ONO})_2](\mathrm{ClO}_4)$	3185 m	2980 w	1380 m	1190 w	530 w	1085 vs, 615 vs	1480 vs, $\nu_{\mathrm{N=O}}$; 1080 vs, ν_{NO}; 360 w, ν_{NO}
trans-$[\mathrm{CoL}_{\mathrm{A}\beta}(\mathrm{ONO})_2](\mathrm{ClO}_4)$	3180 s	2975 s	1380 s	1190 w	555 b	1085 vs, 620 s	1485 vs, $\nu_{\mathrm{N=O}}$; 1085 vs, ν_{NO}; 355 w, ν_{NO}
trans-$[\mathrm{CoL}_{\beta\alpha}(\mathrm{ONO})_2](\mathrm{ClO}_4)$	3185 s	2975 m	1380 m	1190 w	560 sh	1085 vs, 620 s	1485 vs, $\nu_{\mathrm{N=O}}$; 1085 vs, ν_{NO}; 355 w, ν_{NO}
trans-$[\mathrm{CoL}_{\mathrm{B}\beta}(\mathrm{ONO})_2](\mathrm{ClO}_4)$	3190 s	2980 sh	1375 w	1185 m	570 m	1080 vs, 615 vs	1480 s, $\nu_{\mathrm{N=O}}$; 1080 vs, ν_{NO}; 345 w, ν_{NO}
trans-$[\mathrm{CoL}_{\mathrm{C}\alpha}(\mathrm{ONO})_2](\mathrm{ClO}_4)$	3140 m	2965 w	1370 s	1195 m	560 w	1080 vs, 620 s	1470 s, $\nu_{\mathrm{N=O}}$; 1080 vs, ν_{NO}; 350 w, ν_{NO}
trans-$[\mathrm{CoL}_{\mathrm{B}\alpha}\mathrm{Cl}(\mathrm{ONO})](\mathrm{ClO}_4)$	3180 m	2982 w	1380 s	1175 m	550 m	1080 vs, 610 s	1450 w, $\nu_{\mathrm{N=O}}$; 1080 vs, ν_{NO}; 240 w, $\nu_{\mathrm{Co-Cl}}$, 340 w, ν_{NO}
trans-$[\mathrm{CoL}_{\mathrm{C}\alpha}\mathrm{Cl}(\mathrm{ONO})](\mathrm{ClO}_4)$	3200 w	2978 w	1380 s	1170 w	580 m	1080 s, 1620 s	1450 m, $\nu_{\mathrm{N=O}}$; 1080 s, ν_{NO}; 250 m, $\nu_{\mathrm{Co-Cl}}$, 360 w, ν_{NO}
trans-$[\mathrm{CoL}_{\mathrm{A}\beta}(\mathrm{NCS})_2](\mathrm{ClO}_4)$	3189 s	2960 s	1380 m	1135 sh	560 sh	1100 vs, 620 s	2100 vs, ν_{CN}; 850 m, ν_{CS}; 460 m, ν_{NCS}
trans-$[\mathrm{CoL}_{\mathrm{B}\alpha}(\mathrm{NCS})_2](\mathrm{ClO}_4)$	3185 m	2980 w	1380 m	1190 w	540 sh	1090 vs, 620 s	2100 vs, ν_{CN}; 850 m, ν_{CS}; 460 sh, ν_{NCS}
trans-$[\mathrm{CoL}_{\mathrm{B}\beta}(\mathrm{NCS})_2](\mathrm{ClO}_4)$	3200 w	2965 m	1370 w	1125 m	520 w	1120 vs, 625 s	2100 m, ν_{CN}; 840 m, ν_{CS}; 470 m, ν_{NCS}
trans-$[\mathrm{CoL}_{\mathrm{C}\alpha}(\mathrm{NCS})_2](\mathrm{ClO}_4)$	3190 m	2960 sh	1385 m	1130 m	550 sh	1090 vs, 625 vs	2100 vs, ν_{CN}; 840 s, ν_{CS}; 465 m, ν_{NCS}
trans-$[\mathrm{CoL}_{\mathrm{A}\alpha}(\mathrm{H_2O})_2](\mathrm{ClO}_4)_3$	3200 w	2975 w	1380 s	1175 m	550 b	1070 vs, 620 vs	3460 b, ν_{OH}; 1610 b, ν_{HOH}; 430 w, ν_{MO}
trans-$[\mathrm{CoL}_{\mathrm{B}\alpha}(\mathrm{H_2O})_2](\mathrm{ClO}_4)_3$	3195 s	2960 m	1380 s	1135 m	545 sh	1070 s, 620 s	3440 b, ν_{OH}; 1635 vs, ν_{HOH}; 450 b, ν_{MO}
trans-$[\mathrm{CoL}_{\mathrm{C}\alpha}(\mathrm{H_2O})_2](\mathrm{ClO}_4)_3$	3180 m	2980 w	1380 s	1140 m	510 b	1070 m, 615 m	3440 b, ν_{OH}; 1630 b, ν_{HOH}; 425 m, ν_{MO}
trans-$[\mathrm{CoL}_{\mathrm{B}\alpha}(\mathrm{OH})_2](\mathrm{ClO}_4)$	3195 m	2960 m	1370 m	1170 m	480 sh	1070 m, 620 m	3560 b, ν_{OH}; 480 sh, ν_{MO}

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

Compound	% Inhibition of mycelial growth			
	Alternaria alternata	*Curvularia lunata*	*Macrophomina phaseolina*	Reference
L_A	27.78	11.36	14.60	19
trans-$[CoL_{A\alpha}Cl_2](ClO_4)$	5.00	2.55	3.05	this work
trans-$[CoL_{A\alpha}(ONO)_2](ClO_4)$	4.90	1.98	2.99	this work
trans-$[CoL_{A\alpha}(H_2O)_2](ClO_4)_3$	4.50	2.20	2.90	this work
trans-$[CoL_{A\beta}Cl_2](ClO_4)$	5.45	2.65	3.25	this work
Trans-$[CoL_{A\beta}(NCS)_2](ClO_4)$	4.98	2.25	3.00	this work
trans-$[CoL_{A\beta}(ONO)_2](ClO_4)$	5.13	1.88	3.09	this work
L_B	25.92	9.94	13.53	19
trans-$[CoL_{B\alpha}Cl_2](ClO_4)$	3.31	2.13	5.25	this work
trans-$[CoL_{B\alpha}(NCS)_2](ClO_4)$	3.09	2.82	4.83	this work
trans-$[CoL_{B\alpha}(ONO)_2](ClO_4)$	2.99	2.83	4.95	this work
trans-$[CoL_{B\alpha}Cl(ONO)](ClO_4)$	2.67	2.17	5.20	this work
trans-$[CoL_{B\alpha}(H_2O)_2)(ClO_4)_3$	2.90	2.13	4.43	this work
trans-$[CoL_{B\alpha}(OH)_2](ClO_4)$	3.30	2.77	5.61	this work
trans-$[CoL_{B\beta}Cl_2](ClO_4)$	2.79	3.01	5.09	this work
trans-$[CoL_{B\beta}(NCS)_2](ClO_4)$	3.00	2.92	4.78	this work
trans-$[CoL_{B\alpha}(ONO)_2]ClO_4)$	3.50	2.95	4.33	this work
L_C	25.00	12.77	16.65	19
trans-$[CoL_{C\alpha}Cl_2](ClO_4)$	4.07	3.16	5.04	this work
trans-$[CoL_{C\alpha}(NCS)_2](ClO_4)$	3.40	3.01	5.77	this work
trans-$[CoL_{C\alpha}(ONO)_2](ClO_4)$	3.03	2.76	5.26	this work
trans-$CoL_{C\alpha}Cl(ONO)_2](ClO_4)$	2.97	2.99	4.53	this work
trans-$[CoL_{C\alpha}(H_2O)_2](ClO_4)_3$	3.19	2.18	4.37	this work

of H_2O (20 cm^3) to the filtrate, it was concentrated to about 4 cm^3 and allowed to stand overnight in the dark. The solution was filtered again to remove any Ag_2O, the filtrate diluted with distilled H_2O and neutralized with $HClO_4$. The red solution was dried on a water bath to yield an oily product that was treated with EtOH and dried on a water bath. Addition of EtOH and drying on a water bath was repeated three times to give the red-brown product. Anal. Calcd for $C_{18}H_{44}Cl_3CoN_4O_{14}$ (%): C, 30.63; H, 6.28; N, 7.94. Found: C, 30.60; H, 6.30; N, 7.93.

2.1.14. *Trans*-$[CoL_{C\alpha}(H_2O)_2](ClO_4)_3$. *trans*-$[CoL_{C\alpha}Cl_2]ClO_4$ was suspended in MeOH (40 cm^3) and about 0.3 g AgOH was added. The mixture was heated on a water bath for 30 min when the solution turned red. After cooling, the mixture was filtered to remove unreacted AgOH and AgCl. The red solution was allowed to stand overnight in the dark and filtered again. The solution was neutralized with dilute $HClO_4$ and concentrated to 5 cm^3, when dark-brown crystals precipitated. After cooling, the product was filtered off, washed with EtOH and Et_2O and dried *in vacuo*. Anal. Calcd for $C_{18}H_{44}Cl_3CoN_4O_{14}$ (%): C, 30.63; H, 6.28; N, 7.94. Found: C, 30.59; H, 6.31; N, 7.94.

2.1.15. *Trans*-$[CoL_{B\alpha}(OH)_2]ClO_4$. *trans*-$[CoL_{B\alpha}Cl_2]ClO_4$ (0.2707 g, 0.5 mmol) was suspended in MeOH (30 cm^3) and about 0.3 g (excess) of moist AgOH was added. The solution turned red after heating the mixture for 30 min. After cooling, the mixture was filtered to remove AgCl and AgOH. To the filtrate, H_2O (20 cm^3) was added. The solution was then concentrated to about 4 cm^3 and allowed to stand overnight in the dark. The solution was filtered again to remove Ag_2O and dried on the water bath to yield a dark-red product. The product was collected immediately in a sample tube and dried in a desiccator over silica gel. Anal. Calcd for $C_{18}H_{42}ClCoN_4O_6$ (%): C, 42.82; H, 8.38; N, 11.10: Found: C, 42.00; H, 8.40; N, 11.09.

2.2. *Physical measurements*

Visible spectra were recorded on a Shimadzu UV-visible spectrophotometer. Conductance measurements were carried out on a Hanna Instruments HI-8820 conductivity bridge at 25 ± 0.1°C. IR spectra were recorded on a Perkin Elmer 883 infrared spectrophotometer (KBr disks). Magnetochemical measurements were recorded on a Sherwood Scientific magnetic susceptibility balance. C,H,N,S analyses were performed in the Department of Chemistry, University of Hamburg, Hamburg, Germany.

2.3. *Antifungal activities*

In vitro antifungal activities of the complexes against a range of phytopathogenic fungi were assessed by the poisoned food technique. Potato dextrose agar (PDA) was used as the growth medium and DMF as the solvent to prepare solutions of the complexes. 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 solidified, a 5 mm mycelial growth disc for each fungus was placed in the centre of each assay plate against the control. The mean growth of the fungus was measured (in mm) after five days incubation at 25 ± 2°C.

3. Results and discussion

Trans-$[CoLCl_2]ClO_4$ complexes undergo axial ligand substitution to give *trans*-$[CoLCl_xX_y](ClO_4)_z$, where $L = L_{A\alpha}$, $L_{A\beta}$, $L_{B\alpha}$, $L_{B\beta}$ or $L_{C\alpha}$, X = SCN, NO_2, H_2O or OH, $x = 0$ or 1, $y = 1$ or 2; and $z = 1$ or 3 as detailed above. Physical data are summarized in table 1. Although the exact stereochemistries could not be determined with absolute certainty, except in the case of *trans*-$[CoL_{A\alpha}(ONO)_2]ClO_4$, for which a crystal structure analysis has been reported [23], assignments are made on the assumption that axial substitution [21] takes place with retention of configuration and conformation as in the precursor *trans*-dichloro complexes [8, 24]. Characterization of the complexes was achieved by electronic (table 1) and IR (table 2) spectroscopy, and magnetochemical and conductance measurements (table 1). All complexes are diamagnetic.

3.1. *Dinitritocobalt(III) complexes*

The diastereoisomeric *trans*-dichloro complexes, *trans*-$[CoLCl_2]ClO_4$ ($L = L_{A\alpha}$, $L_{A\beta}$, $L_{B\alpha}$ or $L_{C\alpha}$), produce corresponding yellow-brown or yellow *trans*-$[CoL(ONO)_2]ClO_4$ derivatives by reaction with $NaNO_2$ in MeOH. IR spectra display $\nu(ClO_4)$ bands at around 1100 and $620\,cm^{-1}$. Also characteristic of these, and other complexes described herein, is the presence of $\nu(NH)$, $\nu(CC)$, $\nu(CH_3)$ and $\nu(Co–N)$ bands, in their expected ranges. In the nitrito complexes, two well separated $\nu(NO_2)$ bands are evident, one in the region $1410–1490\,cm^{-1}$ due to $\nu(N{=}O)$ and the other in the region $1080–1085\,cm^{-1}$

(overlapped with $\nu(ClO_4^-)$ bands) assigned to ν(NO), as expected for O-bonded nitrito complexes [25]. In addition, bands in the region 340–360 cm^{-1} can be assigned to ν(Co–O) [25]. Coordination of NO_2 through the O atom has been confirmed by an X-ray analysis of *trans*-$[CoL_{A\alpha}(ONO)_2]ClO_4$ [23]. Molar conductivity values of 68–81 $ohm^{-1}\,cm^2\,mol^{-1}$ of the complexes correspond to 1 : 1 electrolytes and are in excellent agreement with the assigned molecular formulas in which the ClO_4 anions are uncoordinated. The d–d bands in the electronic spectra in the region 457–540 nm are in good agreement with other cobalt(III) complexes with NO_2 groups in axial positions [7, 22, 26]. These bands can be assigned to the $^1A_{1g} \rightarrow ^1T_{Ig}$ transition as expected for $[CoN_4Y_2]^{n+}$ (Y = SCN or NO_2) complexes, where the tetragonal splitting is not too large [26]. Bands at around 270 nm or below are due to charge transfer transitions.

3.2. *Monochloronitritocobalt(III) complexes*

Reaction of *trans*-$[CoLCl_2]ClO_4$ ($L = L_{B\alpha}$ or $L_{C\alpha}$) with $NaNO_2$ in MeOH solution resulted in dark-brown *trans*-$[CoL_{B\alpha}(ONO)Cl]ClO_4$ and light-brown *trans*-$[CoL_{C\alpha}(ONO)Cl]ClO_4$. In the IR spectra, the appearance of two well separated $\nu(NO_2)$ bands, as described above, are consistent with O-bonded nitrito ligands [25]. Molar conductivity values are consistent with 1 : 1 electrolytes. Electronic spectra exhibit d–d bands at 485–500 nm, as expected for the CoN_4OCl chromophore [22].

3.3. *Diisothiocyanatocobalt(III) complexes*

Reaction of methanolic suspensions of *trans*-$[CoLCl_2]ClO_4$ ($L = L_{A\alpha}$, $L_{B\alpha}$, $L_{B\beta}$ or $L_{C\alpha}$) with NH_4SCN produced red-brown to dark-red *trans*-$[CoL(NCS)_2](ClO_4)$. The appearance of distinct and sharp ν(CN) bands at 2100 cm^{-1}, ν(CS) at 840–850 cm^{-1}, and ν(NCS) at 460–470 cm^{-1} in their IR spectra is consistent with the coordination of NCS and, further, the positions of the bands support N-bonded thiocyanate groups [25, 27–30]. This assignment is in good agreement with the fact that, generally, first row transition metal complexes of thiocyanate form M–N bonds [21]. Molar conductivity values of 70–100 $ohm^{-1}\,cm^2\,mol^{-1}$ in DMF solution demonstrate that these complexes are 1 : 1 electrolytes, i.e., both thiocyanate ions are coordinated to cobalt and perchlorate is not. Electronic spectra of these complexes display d–d bands at around 560–565 nm, as expected for *trans*-diisothiocyanatocobalt(III) complexes [30].

3.4. *Diaquocobalt(III) complexes*

Reaction of *trans*-$[CoLCl_2]ClO_4$ ($L = L_{A\alpha}$, $L_{B\alpha}$, or $L_{C\alpha}$) with AgOH yielded red dihydroxo complexes in solution. On neutralization with $HClO_4$, these gave red-brown diaquo complexes, *trans*-$[CoL(H_2O)_2](ClO_4)_3$. In addition to the expected bands IR spectra are characterized by the appearance of a distinct and broad ν(OH) band at 3440–3460 cm^{-1} that can be assigned to coordinated water [31], and bands around 1610–1630 cm^{-1}, that are attributed to the HOH bending mode. The spectra also display medium intensity bands around 430–480 cm^{-1}, that can be safely assigned to M–O stretching as expected for aquo complexes [25]. In some complexes, ν(NH) bands are overlapped with ν(OH) bands. Conductance values (250–280 $ohm^{-1}\,cm^2\,mol^{-1}$) are consistent with 1 : 3 electrolytes as expected for the proposed formulations. The positions of d–d bands at around 540 nm in electronic spectra are fully consistent with *trans*-diaquocobalt(III) complexes [7, 22].

3.5. *Dihydroxocobalt(III) complex*

The complex *trans*-$[CoL_{B\alpha}Cl_2]ClO_4$ was allowed to react with AgOH to yield a red solution that on evaporation gave a dark-red product formulated as $[CoL_{B\alpha}(OH)_2]ClO_4$. IR spectra exhibit a sharp band at around $3500\,cm^{-1}$ assigned to ν(OH) [25]. The hydroxo group can be distinguished from the aquo group as the former lacks the HOH bending mode expected near $1600\,cm^{-1}$ [25]. Furthermore, the hydroxo complex exhibits a Co–OH bending mode below $1200\,cm^{-1}$ [25]. The complex also displays a ν(CoOH) band at about $1120\,cm^{-1}$, which indicates that the OH^- groups are coordinated to cobalt. The conductivity value ($83\,ohm^{-1}\,cm^2\,mol^{-1}$) in DMF solution corresponds to a 1 : 1 electrolyte as expected for $[CoL_{B\alpha}(OH)_2](ClO_4)$. In the electronic spectrum, the d–d band at 530 nm is in good agreement with the CoN_4O_2 chromophore [22].

3.6. *Toxicity study*

Antifungal activities of the complexes are summarized in table 3. Screens have been conducted against three phytopathogenic fungi, *Alternaria alternata*, *Curvularia lunata* and *Macrophomina phaseolina*. Complexes of L_B and L_C were found to show higher values, i.e., greater fungitoxicity, against *Macrophonina phaseolina* compared to the other two fungi, whereas complexes of L_A show higher values against *Alternaria alternata*. This observation is in good agreement with results for corresponding copper(II) complexes [19]. Nevertheless, the results show that the new complexes reported herein exhibit low activities in comparison with their corresponding copper(II) [19] and nickel(II) [32] complexes and indeed in comparison with the uncoordinated ligands [19]. A similar phenomenon was observed previously for copper(II) [21] and cobalt(III) [33] complexes of L_1. These observations suggest that the nature of metal ion plays a significant role on the inhibition of mycelial growth.

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