Studies on Some Tellurium Containing Tetraaza Macrocyclic Complexes of Co(II), Mn(II) and Cu(II)

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ABSTRACT

Nine new 10-membered tellurium containing Tetraaza macrocyclic complexes of Co(II), Mn(II) and Cu(II) have been synthesized by template condensation of diaryltellurium(IV) dichlorides, (aryl = p- methoxyphenyl, 3-methyl-4-hydroxyphenyl and p-hydroxyphenyl) with 1,2-diaminopropane and divalent metal chlorides in 2:2:1 molar ratio in dry methanol. The complexes have been characterized by elemental analyses, molar conductance, IR, proton NMR and electronic absorption spectroscopy. On the basis of these studies, a distorted octahedral structure for these complexes has been suggested and hence these complexes may be formulated as [MLCl$_2$]. The metal complexes have also been evaluated for their antimicrobial activity and Mn(II) complexes are observed to possess substantial activity.

Keywords: Template condensation; 1,2-Diaminopropane; Tellurium containing Tetraaza macrocyclic complexes; *p*-Methoxyphenyl

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INTRODUCTION

The design and study of well-arranged metal containing macrocycles is an interesting field of chemistry [1]. Elegant studies on ligand design and metal ion recognition of macrocyclic complexes have been reported by Lindoy [2-4] *et al.* Synthetic macrocyclic complexes mimic some naturally occurring macrocycles because of their resemblance with many natural macrocycles, such as metalloproteins and metalloenzymes [5]. A wide variety of macrocyclic complexes were reported by Martel and coworkers [6-9] where he added a note on the catalytic activity of Cu complexes [9]. Macrocyclic complexes are also important in coordination chemistry due to applications in biometallic activation and catalysis [10], as dyes and pigments [11] and pharmacological properties [12]. Template synthetic route for transition metal complexes of tellurium containing tetraazamacrocycles [13-18] has been reported. Prompted by these facts and in continuation of our earlier work [19,20], the synthesis, spectral characterization, antibacterial and antifungal activity of some new Co(II), Mn(II) and Cu(II) complexes with three 10-membered tellurium containing tetraazamacrocycles are discussed in this paper.

EXPERIMENTAL SECTION

Materials and methods
The chemicals used for the synthesis, recrystallization and analyses were of reagent grade. The solvents, phenol, anisole and *o*-cresol were purified by standard methods [21,22] before use. Solvents were stored over molecular sieves. Air and moisture sensitive preparations were carried out under an atmosphere of dry N$_2$. IR (4000-400 cm^{-1} using KBr) and far IR (40-500 cm^{-1} using polyethylene) spectra were recorded on F.T. Infra-Red Spectrometer Model Nicolet IS50 (Thermo Scientific). ^{1}HNMR Spectra were recorded at SAIF, Panjab University, Chandigarh in DMSO-d$_6$ using TMS as an internal reference on BRUKER AVANCE II 400 NMR spectrometer. Magnetic mass susceptibility data were obtained from NPL, New Delhi on a Gouy's balance (model Johnson Matthey Alfa products) using glycerin as a calibrant. Melting points were determined in open capillary tube and are uncorrected. The Carbon, Hydrogen and Nitrogen analyses were obtained from SAIF, Panjab University, Chandigarh on a Microprocessor based Thermo Scientific (FLASH 2000) CHNS-O Organic Elemental Analyser. Chlorine and tellurium contents were determined volumetrically [23(a),23(b)] while cobalt and manganese gravimetrically [23(c),23(d)]. Copper was estimated on Atomic Absorption Spectrophotometer

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(ECIL Model No.4129). Electronic spectra were recorded in $BaSO_4$ at 25 ± 2 °C on a UV-VIS-NIR Spectrophotometer; model UV-3600 Plus (SHIMADZU).

Antimicobial evaluation
The complexes were screened for antibacterial and antifungal activity against Gram +ve bacteria: *Staphylococcus aureus* (MTCC 2901), *Bacillus subtilis* (MTCC 2063) and *Bacillus cereus* (MTCC 7350), Gram -ve bacteria: *Escherichia coli* (MTCC 1652) and *Salmonella typhi* (ATCC 15499); fungal strains: *Candida albicans* (MTCC 227), *Aspergillus niger* (MTCC 8189) and *Aspergillus fumigatus* (ITCC 4517) using tube dilution method [24]. The test and standard compound were both serially diluted in double strength nutrient broth- I.P for bacteria and sabouraud dextrose broth –I.P for fungi [25]. Dilutions were made in DMSO. Cefadroxil and fluconazole were taken as standard drugs. The results were stated in terms of minimum inhibitory concentration (MIC).

**Preparation of Diaryltellurium(IV) dichlorides**
Bis(*p*-hydroxyphenyl)tellurium(IV) dichloride [26], bis(3-methyl-4-hydroxyphenyl)tellurium(IV) dichloride [27] and bis(*p*-methoxyphenyl) tellurium(IV) dichloride [28,29] were prepared by direct reactions of $TeCl_4$ with phenol, *o*-cresol and anisole respectively, by reported methods.

Preparation of metal complexes with 10-membered Ditellura Tetraaza macrocycles
A saturated solution of 5.0 mmol of diaryltellurium(IV) dichloride in dry methanol was added dropwise with constant stirring to a methanolic (~ 5 mL) solution of 5.0 mmol of 1, 2-diaminopropane taken in a round bottom flask. An immediate change in colour was observed. The contents were refluxed for 3-4 h followed by the addition of saturated methanolic solution of metal chlorides (2.5 mmol). This resulted in a distinct change in colour. The mixture was then again refluxed for 7-8 h and cooled to room temperature. The filtrate was concentrated and kept in refrigerator to obtain the crystalline product. This was filtered, washed with petroleum-ether and dried in a vacuum desiccator over P_4O_{10}.

RESULTS AND DISSCUSSION

Diaryltellurium(IV) dichlorides when refluxed with 1, 2-diaminopropane in presence of $CoCl_2$. $6H_2O$/ $MnCl_2$ $4H_2O$/ $CuCl_2$ in 2:2:1 molar ratios yield the desired complexes as shown in Scheme-1.
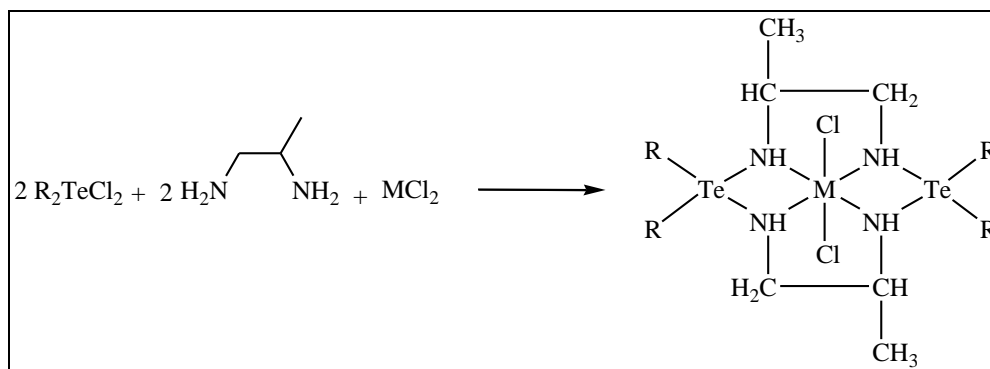
where L^1; R = *p-hydroxyphenyl,* L^2; R = *3-methyl-4-hydroxyphenyl,* L^3; R = *p-methoxyphenyl,* M= Co(II), Mn(II) and Cu(II).

Scheme 1: Formation of the Co(II), Mn(II) and Cu(II) Complexes

These complexes are crystalline, colored solids and are soluble in polar donor organic solvents. The physical properties and analytical data of these complexes are presented in Table 1.

Conductance studies
Molar conductance, $\wedge_M$ values for soluble metal complexes in acetonitrile at *ca*.10^{-3} M are compiled in table 1. The observed $\wedge_M$ values, which are much less than those reported[30] for 1:1 electrolyte predict non electrolyte type behavior of these complexes and hence suggest their formulation as $[MLCl_2]$.

Infrared spectra
The preliminary identification of the metal complexes has been obtained from infrared spectra. The important IR bands along with their assignments are presented in Table 2. The spectra of the metal complexes are quite complex and thus an attempt has been made to identify the donor sites by comparing the spectra of the complexes with those of corresponding constituents; 1,2-diaminopropane and diaryltellurium dichlorides

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Table 1: Analytical data, physical properties and molar conductance values for the metal complexes

Complex	Empirical formula (FW)	Color	M.P. °C	Yield %	Analysis found (calculated),%						Λ_M at *ca*.10^{-3} M S cm^2 mol^{-1} in acetonitrile
					C	H	N	Cl	Te	M	
[CoL^{1}Cl$_2$]	C$_{30}$H$_{36}$Cl$_2$N$_4$O$_4$Te$_2$Co (901.67)	Green	136-138	74	39.64	3.79	6.04	7.58	28.03	6.34	**
					- 39.96	- 4.02	- 6.21	- 7.86	-28.3	- 6.54	
[CoL^{2}Cl$_2$]	C$_{34}$H$_{44}$Cl$_2$N$_4$O$_4$Te$_2$Co (957.78)	Dark green	122-124	78	42.42	4.89	5.6	7.25	26.39	5.89	21.4
					- 42.64	- 4.63	- 5.85	-7.4	- 26.65	- 6.15	
[CoL^{3}Cl$_2$]	C$_{34}$H$_{44}$Cl$_2$N$_4$O$_4$Te$_2$Co (957.78)	Dark green	128-130	74	42.31	4.39	5.2	7.16	26.49	5.87	22.5
					- 42.64	- 4.63	- 5.85	-7.4	- 26.65	- 6.15	
[MnL^{1}Cl$_2$]	C$_{30}$H$_{36}$Cl$_2$N$_4$O$_4$Te$_2$Mn (897.68)	Light pink	176-178*	82	39.79	3.78	6.02	7.74	28.28	5.81	**
					- 40.14	- 4.04	- 6.24	-7.9	- 28.43	- 6.12	
[MnL^{2}Cl$_2$]	C$_{34}$H$_{44}$Cl$_2$N$_4$O$_4$Te$_2$Mn (953.78)	Cream	182-184*	72	42.58	4.88	5.61	7.23	26.45	5.49	17.1
					- 42.82	- 4.65	- 5.87	- 7.43	- 26.76	- 5.76	
[MnL^{3}Cl$_2$]	C$_{34}$H$_{44}$Cl$_2$N$_4$O$_4$Te$_2$Mn (953.78)	Light brown	178-180*	71	42.63	4.48	5.61	7.33	26.6	5.51	29
					- 42.82	- 4.65	- 5.87	- 7.43	- 26.76	- 5.76	
[CuL^{1}Cl$_2$]	C$_{30}$H$_{36}$Cl$_2$N$_4$O$_4$Te$_2$Cu (906.28)	Blue	156-158	72	39.52	3.84	5.87	7.69	28.02	6.88	**
					- 39.76	-4	- 6.18	- 7.82	- 28.16	- 7.01	
[CuL^{2}Cl$_2$]	C$_{34}$H$_{44}$Cl$_2$N$_4$O$_4$Te$_2$Cu (962.39)	Blue	168-170*	65	42.11	4.94	5.6	7.18	26.22	6.49	16.5
					- 42.43	- 4.61	- 5.82	- 7.37	- 26.52	-6.6	
[CuL^{3}Cl$_2$]	C$_{34}$H$_{44}$Cl$_2$N$_4$O$_4$Te$_2$Cu (962.39)	Blue	172-174	63	42.21	4.44	5.57	7.08	26.22	6.35	20.5
					- 42.43	- 4.61	- 5.82	- 7.37	- 26.52	-6.6	

ΛM reported [30] for 1:1 electrolyte in acetonitrile= 120-160 S cm2 mol-1, *decomposition temperature, **insoluble in acetonitrile.

Table 2: Important IR Data (cm-1) for metal complexes

Complex	ν_{N-H}	N-H def.	N-H out of plane bending	ν_{X-N}	ν_{M-N}	$\nu_{M-X\lambda}$	ν_{Te-N}
[CoL^{1}Cl$_2$]	3212 m	1620 m	827 s	1173 s	441 m	317 m	418 w
[CoL^{2}Cl$_2$]	3225 m	1612 m	814 m	1177 m	462 m	314 m	421 w
[CoL^{3}Cl$_2$]	3202 m	1640 s	816 m	1173 m	446 m	308 w	418 w
[MnL^{1}Cl$_2$]	*	1610 m	829 s	1169 s	511 m	331 m	422 w
[MnL^{2}Cl$_2$]	3200* m	1620 m	806 m	1158 m	486 m	325 m	423 w
[MnL^{3}Cl$_2$]	3180 m	1652 m	818 m	1175 m	510 m	325 m	414 w
[CuL^{1}Cl$_2$]	3226 m	1610 m	825 s	1172 s	447 m	311 m	426 w
[CuL^{2}Cl$_2$]	3250* m	1630 m	812 s	1174 m	467 m	313 m	424 w
[CuL^{3}Cl$_2$]	3189 m	1620 m	823 m	1178 m	466 w	315 m	420 w

(m= medium, b= broad, s= strong, w= weak) * mixed with ν_{O-H} band

Absence of bands corresponding to free amino group in the metal complexes and appearance of a new single sharp band in the region 3180-3250 cm^{-1} (sometimes mixed with O-H) assignable to ν_{N-H} vibration [18,31-33], provide an evidence for the skeleton of the macrocyclic moiety. This is also supported by the presence of medium to strong intensity band at ~1610 – 1652 cm^{-1} and 806-829 cm^{-1} attributed to N-H deformations coupled with N-H out of plane bending vibrations [30]. Occurrence of medium to weak intensity bands at ~1175 cm^{-1} and 441 – 511 cm^{-1} may be assigned to C-N stretching vibration [16,34,35] and M-N stretching [14,36-39] respectively. Presence of new weak intensity bands near 418-426 cm^{-1} corresponding to Te-N vibration also supports the formation of tellurium containing macrocyclic ring [16,40]. Further medium to weak intensity bands in the region 308-331 cm^{-1} may be assigned to ν(M-Cl) vibration [37,38,41].

Proton NMR spectra
The proton chemical shifts for the metal complexes which are sufficiently soluble in DMSO–d$_6$ are presented in table 3. 1, 2-diaminopropane, H$_2$N-CH(CH$_3$)-CH$_2$-NH$_2$, exhibit protons resonance at 0.45 (4H), 1.25 (3H), 1.67(2H) and 1.83(1H) δ ppm due to amino, methyl, methylene and methanetriyl/ methine groups, respectively [42,43]. Absence of signal due to primary amino group and appearance of a broad singlet at 1.76 - 2.13 δ ppm assignable to coordinated secondary amino group [17] supports the formation of macrocyclic skeleton. Signals at 1.24-1.39 and 2.16 -2.52 δ ppm appears due to the methyl protons of the propylenic chain and phenyl ring respectively to give a singlet. Signals due to methylene and methanetriyl protons appears slightly downfield as a multiplet at ~2.70 to 3.50 δ ppm thereby confirming deshielding of these protons due to metal-nitrogen

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coordination. In comparison to the parent diaryltellurium dichlorides [44], the phenyl protons in the metal complexes resonate at slightly upfield side (6.74-7.84 δ ppm) as 2Cl are replaced by 2 nitrogen atoms causing flow of electron density from nitrogen to tellurium. Further, the independence of chemical shifts of aryl protons on the metal ions, depicts the non-involvement of Te atoms of the macrocycle in coordination with the metal ions. Thus, proton NMR studies on these metal complexes also support the formation of 10- membered ditellura tetraaza macrocycles and their tetra dentate ligation behaviour as predicted by IR studies.

Table 3: ^{1}H-NMR Spectral Data (δ ppm) for the metal complexes in DMSO-d6

Complex	Chemical Shift, δ ppm
[CoL[1]Cl$_2$]	1.78 (s, 4H, -NH-), 1.37 (d, 6H, aliphatic –CH$_3$) 2.70-3.22 (m, 6H, -CH$_2$-, -CH- , propylenic chain), 6.74[d] & 7.65[d] (16H , phenyl), 7.86 (s, 4H,OH)
[CoL[2]Cl$_2$]	2.04 (s, 4H, -NH-), 1.33 (d, 6H, aliphatic –CH$_3$) 2.70-3.00 (m, 6H, -CH$_2$-, -CH-, propylenic chain), 2.17 (s, 12H, Ar-CH$_3$), 6.93[d], 7.57[d] & 7.66[s] (12H, phenyl) 7.73 (s, 4H,OH)
[CoL[3]Cl$_2$]	2.12 (s, 4H, -NH-), 1.24 (d, 6H, aliphatic –CH$_3$) 2.89-3.29 (m, 6H, -CH$_2$-, -CH-, propylenic chain), 3.35 (s, 12H, -OCH$_3$), 6.82[d] &7.84[d] (16H, phenyl)
[MnL[1]Cl$_2$]	2.13 (s, 4H, -NH-), 1.36 (d, 6H, aliphatic –CH$_3$) 2.88-3.37 (m, 6H, -CH$_2$-, -CH-, propylenic chain), 6.63[d] & 7.47[d] (16H, phenyl), 8.5 (s, 4H,OH)
[MnL[2]Cl$_2$]	2.10 (s, 4H, -NH-), 1.35 (d, 6H, aliphatic –CH$_3$) 3.01-3.50 (m, 6H, -CH$_2$-, -CH- , propylenic chain), 2.52* (s, 12H, Ar -CH$_3$), 6.96[d], 7.60[d] & 7.76[s] (12H, phenyl), 8.30 (s, 4H,OH)
[CuL[1]Cl$_2$]	1.76 (s, 4H, -NH-), 1.39 (d, 6H, aliphatic –CH$_3$) 3.03-3.24 (m, 6H, -CH$_2$-, -CH-, propylenic chain), 6.77[d] & 7.77[d] (16H , phenyl), 8.9 (s, 4H,OH)
[CuL[2]Cl$_2$]	1.99 (s, 4H, -NH-), 1.37 (d, 6H, aliphatic –CH$_3$) 2.94-3.31 (m, 6H, -CH$_2$-, -CH-, propylenic chain), 2.16 (s, 12H, Ar -CH$_3$), 6.93[d], 7.57[d] & 7.66[s] (12H, phenyl), 7.77 (s, 4H,OH)

(s = singlet, d = doublet, t = triplet, m = multiplet, Ar = aromatic); * may be mixed with solvent peak,

Electronic absorption spectra and magnetic studies

The electronic absorption and magnetic moment data for the complexes are presented in table 4.

Table 4: Magnetic moment and electronic spectral data for the complexes

Complex	Band Position (cm^{-1})	Assignments	Observed magnetic moment, μ_B
[CoL[1]Cl$_2$]	9345	$^4T_{1g} \rightarrow {}^4T_{2g}$ (F)	5.17
	14970	$^4T_{1g} \rightarrow {}^4A_{2g}$ (F)	
	23094	$^4T_{1g}$ (F) $\rightarrow {}^4T_{1g}$ (P)	
[CoL[2]Cl$_2$]	10460	$^4T_{1g} \rightarrow {}^4T_{2g}$ (F)	4.8
	15037	$^4T_{1g} \rightarrow {}^4A_{2g}$ (F)	
	33112	$^4T_{1g}$ (F) $\rightarrow {}^4T_{1g}$ (P) & CT	
[CoL[3]Cl$_2$]	9845	$^4T_{1g} \rightarrow {}^4T_{2g}$ (F)	4.79
	14972	$^4T_{1g} \rightarrow {}^4A_{2g}$ (F)	
	32370	$^4T_{1g}$ (F) $\rightarrow {}^4T_{1g}$ (P) & CT	
[MnL[1]Cl$_2$]	18867	$^6A_{1g} \rightarrow {}^4T_{1g}$ (G)	5.86
	31250	$^6A_{1g} \rightarrow {}^4T_{1g}$ (P) & CT	
[MnL[2]Cl$_2$]	23809	$^6A_{1g} \rightarrow {}^4A_{1g}$ (G)	5.9
	35200	$^6A_{1g} \rightarrow {}^4A_{2g}$ (F) & CT	
[MnL[3]Cl$_2$]	24990	$^6A_{1g} \rightarrow {}^4A_{1g}$ (G)	5.71
	34249	$^6A_{1g} \rightarrow {}^4A_{2g}$ (F) & CT	
[CuL[1]Cl$_2$]	10833	$^2B_{1g} \rightarrow {}^2A_1g$	1.87
	17561	$^2B_{1g} \rightarrow {}^2B_{2g}$	
	32448	CT	
[CuL[2]Cl$_2$]	11122	$^2B_{1g} \rightarrow {}^2A_1g$	1.96
	22172	$^2B_{1g} \rightarrow {}^2B_{2g}$	
	32258	CT	
[CuL[3]Cl$_2$]	10772	$^2B_{1g} \rightarrow {}^2A_1g$	1.79
	17636	$^2B_{1g} \rightarrow {}^2B_{2g}$	
	33256	CT	

Co(II) complexes shows magnetic moment at 4.79- 5.17 B.M. corresponding to three unpaired electrons. Electronic spectrum shows bands at 9345–10460 cm^{-1}, 14970–15037 cm^{-1} and 23094–33112 cm^{-1}, which may be assigned to the transitions from $^4T_{1g} \rightarrow {}^4T_{2g}$ (F), $^4T_{1g} \rightarrow {}^4A_{2g}$ (F) and $^4T_{1g}$ (F) $\rightarrow {}^4T_{1g}$ (P) & CT, respectively. These position of band suggest octahedral geometry [18,45-47] of Co(II) complexes. The Mn(II) complexes show magnetic moment corresponding to five unpaired electrons (5.71-5.90 B.M.) at room temperature close to the spin only value of 5.92 B. M. Electronic spectra exhibit two weak absorption bands as shown in table 4, which are characteristics of octahedral geometry [17,45,47]. Cu(II) complexes show magnetic moment in the range 1.79-1.96 B.M. at room temperature corresponding to one unpaired electron. In these complexes, bands in the region 10772-11172 cm^{-1}, 17561-22172 cm^{-1} and 32248-33256 cm^{-1} may be assigned to $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2B_{2g}$ and CT bands respectively corresponding to a distorted octahedral or tetragonal geometry [18,45,48-52].

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Antimicrobial studies

The minimum inhibitory concentration (MIC) values shown by the metal complexes against the studied fungal and bacterial strains were compared with those of the standard antibiotics cefadroxil and fluconazole (Table 5 and 6). The results indicate that most of the complexes possess moderate antimicrobial activity as compared to the standard bactericide and fungicide but all the complexes are more active than their precursors. The complex, MnL^2Cl_2 is found to have good activity against *Staphylococcus aureus, Escherichia coli and Candida albicans.*

Table 5: Minimum inhibitory concentration (MIC) of metal complexes against test bacteria

Complex	MIC (μg mL^{-1})				
	S. aureus	*B. Subtilis*	*E. coli*	*B. cereus*	*S. typhi*
R_2TeCl_2 (p-methooxyphenyl)	25	25	25	25	25
R_2TeCl_2 (p-hydroxyphenyl)	25	25	12.5	25	25
R_2TeCl_2 (3-methyl-4-hydroxyphenyl)	12.5	25	25	25	25
1, 2-diaminopropane	25	25	25	12.5	25
$[CoL^1Cl_2]$	12.5	12.5	25	12.5	12.5
$[CoL^2Cl_2]$	12.5	12.5	12.5	12.5	25
$[CoL^3Cl_2]$	12.5	12.5	12.5	12.5	12.5
$[MnL^1Cl_2]$	12.5	12.5	12.5	25	25
$[MnL^2Cl_2]$	**6.25**	12.5	**6.25**	12.5	25
$[MnL^3Cl_2]$	12.5	12.5	12.5	12.5	12.5
$[CuL^1Cl_2]$	12.5	12.5	12.5	12.5	12.5
$[CuL^2Cl_2]$	12.5	12.5	12.5	12.5	12.5
$[CuL^3Cl_2]$	12.5	12.5	12.5	12.5	12.5
Cefadroxil	**3.12**	**1.56**	**3.12**	**1.56**	**3.12**

Table 6: Minimum inhibitory concentration (MIC) of metal complexes against test fungi

Complex	MIC (μg mL^{-1})		
	A. niger	*A. fumigatus*	*C. albicans*
R2TeCl2 (*p*-methooxyphenyl)	25	25	25
R2TeCl2 (*p*-hydroxyphenyl)	25	25	25
R2TeCl2 (3-methyl-4-hydroxyphenyl)	25	25	12.5
1,2-diaminopropane	25	25	25
$[CoL^1Cl_2]$	12.5	25	12.5
$[CoL^2Cl_2]$	12.5	12.5	12.5
$[CoL^3Cl_2]$	12.5	12.5	12.5
$[MnL^1Cl_2]$	25	12.5	12.5
$[MnL^2Cl_2]$	12.5	12.5	**6.25**
$[MnL^3Cl_2]$	12.5	12.5	12.5
$[CuL^1Cl_2]$	12.5	12.5	12.5
$[CuL^2Cl_2]$	12.5	12.5	12.5
$[CuL^3Cl_2]$	12.5	12.5	12.5
Fluconazole	**3.12**	**3.12**	**1.56**

CONCLUSION

The synthesis, characterization and antimicrobial activity of tellurium containing macrocyclic complexes of divalent cobalt, manganese and copper has been described. Synthesis have been carried out by template condensation of diaryltellurium(IV) dichlorides with 1,2-diaminopropane and divalent metal chlorides in 2:2:1 ratio. A distorted octahedral structure has been proposed for Co(II), Mn(II) and Cu(II) complexes on the basis of molar conductance, magnetic, analytic and spectral data. The Mn(II) complex shows good antibacterial and antifungal activities against some pathogenic bacteria and fungi in comparison to other complexes.

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