



STUDY ON DIVALENT TRANSITION METAL COMPLEXES WITH TELLURIUM CONTAINING 12-MEMBERED TETRAAZAMACROCYCLIC LIGANDS

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ABSTRACT

Nine new complexes of the type, $[ML^1Cl_2]$, $[ML^2Cl_2]$ and $[ML^3Cl_2]$, where $[M = Mn(II), Co(II), Cu(II)]$; L^1 , L^2 and $L^3 = 12$ -membered tellurium containing tetraazamacrocyclic ligands] have been prepared *via* the template condensation of 1,3-diaminopropane and diaryltellurium dichlorides, R_2TeCl_2 , ($R = p$ -hydroxyphenyl, 3-methyl-4-hydroxyphenyl, *p*-methoxyphenyl) in the presence of metal chlorides. These complexes have been characterized by elemental analyses, conductivity, magnetic susceptibility measurements, infrared, electronic absorption and proton magnetic resonance spectra. An octahedral structure has been suggested for all these metal complexes.

Key words: Tellurium, Tetraazamacrocycles, Diaryltellurium dichlorides, 1,3-Diaminopropane, Metal complexes.

INTRODUCTION

The coordination chemistry of organotellurium ligands containing hard donor atoms such as N and O along with soft tellurium is interesting as such ligand framework can provide 'insight' into competitive coordination behaviour between the hard and soft donors towards metal ions^{1,2}. Such molecular systems may be important in transition metal catalyzed asymmetric synthesis^{3,4} and as single source precursors in MOCVD processes⁵⁻⁷. Also, macrocyclic complexes are significant as they have been found to act as possible models for biochemically important proteins and enzymes⁸⁻¹². The development of tellurium containing macrocycles is evidenced in some recent publications¹³⁻¹⁸. In continuation of our work¹⁹ on metal complexes with tellurium containing macrocycles, we hereby report the synthesis and characterization of divalent manganese, cobalt and copper complexes with three novel 12-membered tellurium tetraazamacrocycles, (Te_2N_4 system).

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EXPERIMENTAL

Materials and methods

All the chemicals used were of Analytical Reagent grade. Solvents were purified and dried by conventional methods^{20, 21}.

Bis(*p*-hydroxyphenyl)-bis(3-methyl-4-hydroxyphenyl) and bis(*p*-methoxyphenyl) tellurium dichlorides were prepared by direct reactions of TeCl₄ with phenol²², *o*-cresol²³ and anisole²⁴, respectively. All the preparations were carried in dry conditions under an atmosphere of nitrogen.

Preparation of complexes

The 12-membered tellurium tetraazamacrocyclic transition metal complexes have been synthesized by the template condensation reaction of metal chlorides with diaryltellurium dichlorides and 1, 3-diaminopropane in 1 : 2 : 2 molar ratio.

A general method for the synthesis of these 1, 7-diaryltellura-2, 6, 8, 12-tetraazacyclododecane metal complexes is -

A saturated solution of 4.0 mmol of diaryltellurium dichloride in methanol was added slowly and with constant stirring to a methanolic (~ 5 mL) solution of 4.0 mmol of 1,3-diaminopropane taken in a R.B. Flask. A distinct change in colour with slight turbidity was observed. The contents were refluxed for 2-3 h, followed by addition of 2.0 mmol solution of metal dichloride in about 10 mL methanol. An immediate change in colour was observed. The solution was then refluxed for 3-4 h and concentrated to about one third of original volume and cooled. This resulted in the separation of a coloured solid. Solid product was also obtained in some cases without concentration. This was filtered, washed with benzene/petroleum ether and dried in a vacuum desiccator over P₄O₁₀.

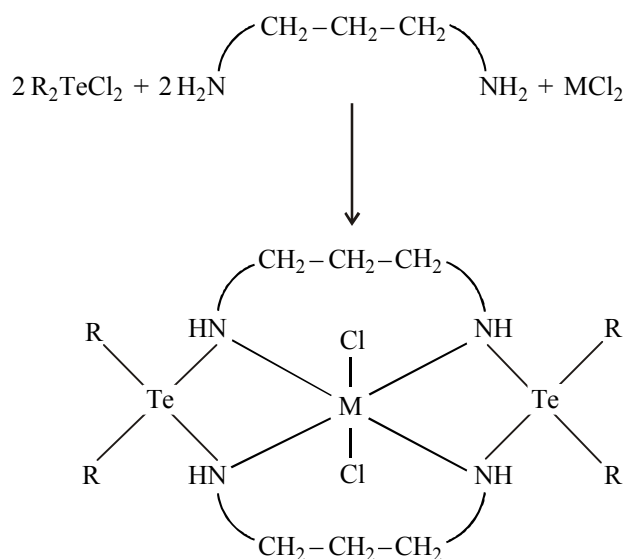
Physical studies

The conductance studies were performed in acetonitrile under dry conditions at 25 ± 2°C using a Systronics Type 305 conductivity bridge and a dip type cell with smooth platinum electrodes. The electronic spectra were recorded in dimethylsulphoxide at 22 ± 2°C on a Thermo Spectronic UV-1 spectrophotometer. The magnetic susceptibility data were obtained from National Physical Laboratory, New Delhi on a Gouy's balance (Model Johnson Matthey Alfa Products) using glycerin as a calibrant. The IR spectra (4000-400 cm⁻¹) were recorded as KBr pellets on a Perkin-Elmer Model 2000 FTIR Spectrometer at SAIF, Panjab University, Chandigarh. ¹H NMR spectra were recorded in DMSO - d₆ on

BRUKER XWIN - NMR AVANCE 300 operating at 300.13 MHz, using tetramethylsilane as an internal reference. The NMR spectra were obtained from Kurukshetra University, Kurukshetra.

RESULTS AND DISCUSSION

Diaryltellurium dichlorides and 1, 3-diaminopropane, when refluxed in the presence of metal dichlorides, yield the complexes of 12-membered tellurium containing tetraazamacrocycles as per **Scheme 1**.



where

L^1 ; R = *p*-Hydroxyphenyl

L^2 ; R = 3-Methyl-4-hydroxyphenyl

L^3 ; R = *p*-Methoxyphenyl

M = Mn^{II} , Co^{II} and Cu^{II}

Scheme 1

The molecular formulae of the complexes $[ML^1Cl_2]$, $[ML^2Cl_2]$ or $[ML^3Cl_2]$ have been assigned on the basis of the results of their elemental analyses (Table 1). These complexes are coloured, crystalline, air stable solids and are soluble only in polar donor organic solvents.

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

Complex	Empirical formula (Formula weight)	Colour	M.P. (°C) (dec.)	Yield (%)	Analysis found (calculated) %					Λ_M at ca. $10^{-3} \text{ M ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$	
					C	H	N	Cl	Te		M
[MnL ¹ Cl ₂]	C ₃₀ H ₃₆ Cl ₂ N ₄ O ₄ Te ₂ Mn (897.7)	Dark orange	150-155	64	39.87 (40.14)	3.80 (4.04)	5.97 (6.24)	8.05 (7.90)	28.54 (28.43)	5.91 (6.12)	112.0
[MnL ² Cl ₂]	C ₃₄ H ₄₄ Cl ₂ N ₄ O ₄ Te ₂ Mn (953.8)	Brown orange	200-202	92	42.39 (42.82)	4.25 (4.65)	5.30 (5.87)	7.57 (7.43)	26.27 (26.76)	5.61 (5.76)	15.5
[MnL ³ Cl ₂]	C ₃₄ H ₄₄ Cl ₂ N ₄ O ₄ Te ₂ M (953.8)	Dark brown	175-180	67	42.62 (42.82)	4.42 (4.65)	5.59 (5.87)	7.21 (7.43)	27.02 (27.76)	5.64 (5.76)	61.0
[CoL ¹ Cl ₂]	C ₃₀ H ₃₆ Cl ₂ N ₄ O ₄ Te ₂ Co (901.7)	Brown pink	160-165	68	39.46 (39.96)	3.79 (4.02)	6.01 (6.21)	7.92 (7.86)	28.36 (28.30)	6.26 (6.54)	62.7
[CoL ² Cl ₂]	C ₃₄ H ₄₄ Cl ₂ N ₄ O ₄ Te ₂ Co (957.8)	Brown grey	193-195	94	42.11 (42.64)	4.17 (4.63)	5.22 (5.85)	7.43 (7.40)	26.99 (26.65)	5.83 (6.15)	25.6
[CoL ³ Cl ₂]	C ₃₄ H ₄₄ Cl ₂ N ₄ O ₄ Te ₂ Co (957.8)	Blue green	140-145	66	42.20 (42.64)	4.26 (4.63)	5.53 (5.85)	7.26 (7.40)	26.52 (26.65)	5.91 (6.15)	30.8
[CuL ¹ Cl ₂]	C ₃₀ H ₃₆ Cl ₂ N ₄ O ₄ Te ₂ Cu (906.3)	Purple brown	89-93	59	39.29 (39.76)	3.74 (4.00)	5.94 (6.18)	8.00 (7.82)	28.22 (28.16)	6.88 (7.82)	90.6
[CuL ² Cl ₂]	C ₃₄ H ₄₄ Cl ₂ N ₄ O ₄ Te ₂ Cu (962.4)	Red brown	195-197	96	42.12 (42.43)	4.05 (4.61)	5.27 (5.82)	7.44 (7.37)	26.40 (26.52)	6.25 (6.60)	14.0
[CuL ³ Cl ₂]	C ₃₄ H ₄₄ Cl ₂ N ₄ O ₄ Te ₂ Cu (962.4)	Light green	130-135	60	42.20 (42.43)	4.33 (4.61)	5.63 (5.82)	7.13 (7.37)	26.27 (26.52)	6.54 (6.60)	69.9

The molar conductances of soluble complexes in acetonitrile at *ca* 10^{-3} M show their non-electrolyte to weak-electrolyte nature²⁵ and hence, suggest their formulation as $[\text{MLCl}_2]$.

Magnetic and electronic spectral studies

The Mn^{II} complexes show magnetic moments (Table 2) corresponding to five unpaired electrons (5.40 – 5.69 B.M.) at room temperature, close to the spin-only value of 5.92 B.M. Electronic spectra of these complexes display two weak absorption bands as shown in Table 2, which are characteristic of octahedral geometry^{18,26,27}.

Table 2: Magnetic moment and electronic spectral data for metal complexes

Complex	Magnetic moment (B.M.)	Electronic absorption, cm^{-1} assignment		
$[\text{MnL}^1\text{Cl}_2]$	5.50	29730 ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g(\text{D})$	31645 ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P}) \& (\text{CT})$	
$[\text{MnL}^2\text{Cl}_2]$	5.40	25350 ${}^6\text{A}_{1g} \rightarrow {}^4\text{A}_{1g}(\text{G})$	32495 ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P}) \& (\text{CT})$	
$[\text{MnL}^3\text{Cl}_2]$	5.69	27950 ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{D})$	35390 ${}^6\text{A}_{1g} \rightarrow {}^4\text{A}_{2g}(\text{F}) \& (\text{CT})$	
$[\text{CoL}^1\text{Cl}_2]$	2.68	9630 ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{F})$	16370 ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}(\text{F})$	31550 ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P}) \& (\text{CT})$
$[\text{CoL}^2\text{Cl}_2]$	5.09	9299 ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{F})$	16490 ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}(\text{F})$	32050 ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P}) \& (\text{CT})$
$[\text{CoL}^3\text{Cl}_2]$	4.40	9680 ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{F})$	16778 ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}(\text{F})$	32573 ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P}) \& (\text{CT})$
$[\text{CuL}^1\text{Cl}_2]$	2.10	10753 ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$	18299 ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$	31847 [CT]
$[\text{CuL}^2\text{Cl}_2]$	2.15	11200 ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$	18520 ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$	31042 [CT]
$[\text{CuL}^3\text{Cl}_2]$	2.18	11180 ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$	18656 ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$	30864 [CT]

The magnetic moment values of cobalt (II) complexes lie in the range 4.40 – 5.09 B.M. corresponding to three unpaired electrons. The low value (2.68 B.M.) in $[\text{CoL}^1\text{Cl}_2]$ may be due to spin-cross over phenomenon²⁸. The electronic absorption spectra of all the Co (II) complexes exhibit absorption in the region 9299-9680 cm^{-1} , 16370-16778 cm^{-1} and around 32000 cm^{-1} , which may tentatively be assigned as shown in Table 2. These transitions suggest an octahedral environment^{26,29} around the cobalt ion.

The magnetic moments of copper (II) complexes at room temperature lie in the range 2.10 – 2.18 B.M. corresponding to one unpaired electron. Electronic spectra of these complexes display bands in the range 10753 – 11200 cm^{-1} (${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$), 18299 – 18656 (${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$) and 30864 – 31847 (CT). Jahn-Teller distortion expected in d^9 configuration actually disturbs the degeneracy; thus, causing a split in energy level due to tetragonal distortion in geometry. This electronic spectral pattern of copper (II) complexes under study suggests^{18,26,30,31} a distorted octahedral or tetragonal geometry.

IR spectra

The important IR bands and their assignments are tabulated in Table 3. The spectra are quite complex and an attempt has therefore been made to draw the conclusions by comparing the spectra of metal complexes with those of corresponding constituent diarytellurium dichlorides and 1, 3-diaminopropane.

Table 3: IR data (cm^{-1}) for metal complexes

Complex	$\nu_{\text{N-H}}$	N-H def.	N-H out of plane bending	$\nu_{\text{C-N}}$
$[\text{MnL}^1\text{Cl}_2]$	3171 m	1627 m	828 s	1173 s
$[\text{MnL}^2\text{Cl}_2]$	3230 m	1626 m	871 m, 813 s	1177 m
$[\text{MnL}^3\text{Cl}_2]$	3190 m	1635 m	822 vs	1177 s
$[\text{CoL}^1\text{Cl}_2]$	3240 m	1640 m	828 s	1172 s
$[\text{CoL}^2\text{Cl}_2]$	3195 m	1626 s	871 m, 813 s	1176 m
$[\text{CoL}^3\text{Cl}_2]$	3210 m*	1653 m	822 s	1175 vs
$[\text{CuL}^1\text{Cl}_2]$	3200 m	1650 vs	811 m	1173 m
$[\text{CuL}^2\text{Cl}_2]$	3160 m	1625 m	871 m, 812 s	1176 m
$[\text{CuL}^3\text{Cl}_2]$	3250 m*	1652 m	822 s	1176 s

*mixed with moisture band, s = strong, m = medium, vs = very strong

The metal complexes under study did not show bands characteristic of free NH_2 group, instead the entire complexes exhibit a single sharp absorption band at around $3160\text{--}3250\text{ cm}^{-1}$ (sometimes mixed with O-H) attributed to $\nu_{\text{N-H}}$ stretching vibration. The assignment of this sharp band is based on the fact that macrocyclic ligands, which have coordinated secondary amino group have bands in the vicinity^{18,32-34} of 3200 cm^{-1} . This contention finds support³² from appearance of bands of medium to strong intensity at $\sim 1625\text{--}1650\text{ cm}^{-1}$ and $\sim 812\text{--}871\text{ cm}^{-1}$ assigned as N-H deformation coupled with N-H out of the plane bending vibrations. Bands at $\sim 1175\text{ cm}^{-1}$ may be reasonably assigned to C-N stretching vibration^{18,35,36}. The above observations strongly suggest^{18,32,35,36} that proposed macrocyclic framework is formed. The formation of tellurium containing macrocyclic ring is also supported by appearance of new weak intensity bands around $420\text{--}410\text{ cm}^{-1}$ due to Te-N^{18,37}. Evidence for formation of proposed macrocycles and coordination through N atoms is further supported by new medium to weak intensity bands around $480\text{--}450\text{ cm}^{-1}$ assignable to M-N stretching.³⁸ The $\nu_{\text{M-Cl}}$; however, could not be ascertained due to non-availability of far infrared data.

¹H NMR spectra

The proton chemical shifts for some representative complexes, having sufficient solubility in $\text{DMSO}-d_6$, are compiled in Table 4.

Table 4: ¹H NMR data (δ ppm) for metal complexes in $\text{DMSO}-d_6$

Complex	-NH-	-CH ₂ - (middle)	-CH ₂ - (adjacent to N)	-CH ₃ *	Phenyl	-OH
[MnL ² Cl ₂]	1.91 ^s (4H)	2.07 ^m (4H)	2.89 ^m (8H)	2.49 ^s (8H)	6.92 ^d (4H) 7.30 ^s , 7.61 ^d (8H)	8.01 ^b (4H)
[CoL ² Cl ₂]	1.93 ^s (4H)	2.09 ^m (4H)	2.97 ^t (8H)	2.49 ^s (12H)	6.91 ^d (4H) 7.33 ^s , 7.64 ^d (8H)	8.36 ^b (4H)
[CuL ² Cl ₂]	1.95 ^s (4H)	2.11 ^m (4H)	2.93 ^m (8H)	2.49 ^s (12H)	6.93 ^d (4H) 7.33 ^s , 7.62 ^d (8H)	8.09 ^b (4H)

*May be mixed with solvent peak, s = singlet, d = doublet, t = triplet, m = multiplet, b = broad

The phenyl protons in metal complexes resonate at slightly up field side ($6.92\text{--}7.64\text{ }\delta$ ppm) as compared to parent diaryltellurium dichlorides²³, due to increase in electron density at the tellurium atom as a result of replacement of 2 Cl by 2 N atoms. 1, 3-diaminopropane, $\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2$, exhibits³⁹ protons resonances at 1.15 (4H), 2.76 (4H) and 1.59 (2H) δ ppm due to amino, methylene (adjacent to N) and middle methylene groups, respectively.

The metal complexes do not show any signal due to free amino group. Instead, a broad singlet at 1.91-1.95 δ ppm assignable to coordinated secondary amino group⁴⁰, confirms the formation of 12-membered tellurium containing tetraazamacrocycles skeleton. The middle methylene protons and those adjacent to N-atoms resonate at 2.07-2.11 and 2.89-2.97 δ ppm, respectively. This behavior of complexes under study is quite similar to those of other tetraazamacrocycles^{18,41,42} derived from 1, 3-diaminopropane. Further, the independence of aryl proton chemical shifts on the metal ions, hints at the non-involvement of tellurium atoms of the macrocycle in coordination with the metal ions. Thus, ¹H NMR studies on these metal complexes support the formation of 12-membered tellurium tetraazamacrocycles and their tetradentate ligation behaviour as predicted by IR studies.

Based on analyses, conductance, magnetic, electronic, infrared and proton magnetic resonance spectral studies, a distorted octahedral geometry involving four N atoms of tetraazamacrocycle and 2 Cl may be proposed for these metal complexes.

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