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Investigations on some d^{10} metal-ion complexes with 12-membered tellurium containing tetraazamacrocycles

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ABSTRACT

A novel series 12-membered ditellura tetraazamacrocyclic complexes, $[ML^1Cl_2]$, $[ML^2Cl_2]$ *and* $[ML^3Cl_2]$, *where* [M = Zn(II), Cd(II), Hg(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, conductance measurements, infrared, electronic absorption and proton magnetic resonance spectral techniques. The spectral studies confirm the formation of 12-membered tetraazamacrocycle skeletons and their tetra dentate nature involving four nitrogen atoms. A distorted octahedral geometry has been assigned to all the metal complexes on the basis of these studies.*

Keywords: 12-Membered tetraazamacrocycles, Diaryltellurium dichlorides, 1,3-diainopropane, Template condensation.

INTRODUCTION

The ligand chemistry of tellurium has developed quite rapidly during the last decade [1-7]. Also, the coordination chemistry of organotellurium ligands containing *hard* donor atoms such as nitrogen and oxygen along with *soft* tellurium is interesting as such ligand framework can provide 'insight' into competitive coordination behavior between the *hard* and *soft* donors towards a metal center **[**8,9**].** In addition, macrocyclic complexes are significant as they are known to act as possible models for biochemically important proteins and enzymes [10,11]. Srivastava *et al* [12] reported the route of synthesis of metal complexes with tellurium containing macrocycles. In continuation of our earlier work [13,14] on such macrocyclic complexes, we hereby report the synthesis and characterization of divalent zinc, cadmium and mercury complexes with three novel 12-membered ditellura tetraazamacrocycles, Te_2N_4 system.

MATERIALS AND METHODS

Materials

The chemicals, tellurium tetrachloride and 1,3-diminopropane (Aldrich), $ZnCl_2$, $CdCl_2.2.5\ H_2O$, $HgCl_2$, phenol, *o*-cresol and anisole (Loba Chemie) were of reagent grade. All the solvents were purified and dried before use by conventional methods.

Preparation of Diaryltellurium dichlorides

Bis(*p*-hydroxyphenyl), bis(3-methyl-4-hydroxyphenyl) and bis(*p*-methoxyphenyl) tellurium dichlorides were prepared by direct reactions of $TeCl_4$ with phenol [15] , *o*-cresol [16] and anisole [17] respectively as reported in the literature. All the preparations were carried out in dry conditions under an atmosphere of nitrogen.

Preparation of Complexes

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

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

A saturated solution of 4.0 mmol of diaryltellurium dichloride (1.536 g, 1.648 g, 1.648 g respectively, for *p*-hydroxyphenyl, 3-methyl-4-hydroxyphenyl, *p*-methoxyphenyl derivatives) in methanol was added slowly and with constant stirring to a methanolic (~ 5 mL) solution of 0.296 g, 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 a saturated methanolic solution of 2.0 mmol (0.272 g, 0.456 g and 0.540 g respectively for $ZnCl_2$, $CdCl_2.2.5\ H_2O$ and $HgCl_2$) of metal dichloride. An immediate change in color was observed. The solution was then refluxed for 3-4 h and concentrated to about one third of the original volume and cooled. This resulted in the separation of a colored solid. This was filtered, washed with benzene/petroleum ether and dried in a vacuum desiccator over P_4O_{10}.

Physical Measurements

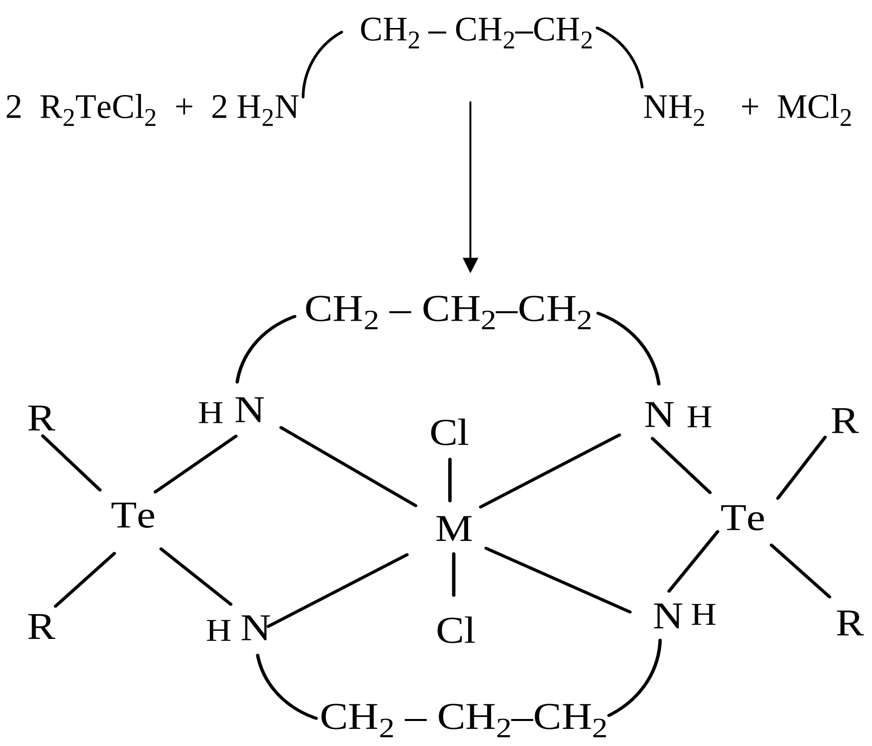
Elemental analysis for C, H, N for the zinc and cadmium complexes were obtained from SAIF, Panjab University, Chandigarh on a CARLO ERBA Model 1106. Tellurium and chlorine contents were determined volumetrically [18]. Metals were estimated on Atomic Absorption Spectrophotometer (ECIL Model No. 4129). The conductance measurements in DMSO were performed on a Systronic Type 305 conductivity bridge at 25 ± 2° C using a dip type cell with smooth platinum electrodes. The electronic spectra were recorded in dimethylsulphoxide at 25 ± 2°C on a Thermo Spectronic UV-1 Spectrophotometer. 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 at Kurukshetra University, Kurukshetra in DMSO – d_6 on BRUKER XWIN – NMR AVANCE 300 operating at 300.13 MHz, using tetramethylsilane as an internal reference.

RESULTS AND DISCUSSION

Tellurium tetrachloride when heated with arene, R-H (phenol, *o*-cresol, anisole) gives diaryltellurium dichlorides [15-17] as per equation:

$$2\,R{-}H \;+\; TeCl_4 \;\rightarrow\; R_2TeCl_2 \;+\; 2\,HCl$$

These 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 = Zn^{II}, Cd^{II} and Hg^{II}

Scheme 1. Formation of Metal Complexes

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

Complex	Empirical Formula (Formula Weight)	Color	M.P °C (dec.)	Yield %	Analysis found (calculated) %						Λ_M at *ca.*10^{-3} M Ω^{-1} cm^2 mol^{-1}
					C	H	N	Cl	Te	M	
$[ZnL^1Cl_2]$	$C_{30}H_{36}Cl_2N_4O_4Te_2Zn$ (908.1)	Dark pink	180-182	78	39.28 (39.68)	3.77 (4.00)	5.86 (6.17)	8.05 (7.81)	27.17 (28.10)	7.11 (7.20)	Insoluble
$[ZnL^2Cl_2]$	$C_{34}H_{44}Cl_2N_4O_4Te_2Zn$ (964.2)	Brown	118-120	95	41.90 (42.35)	4.25 (4.60)	5.56 (5.81)	7.33 (7.35)	26.15 (26.47)	6.65 (6.78)	32.4
$[ZnL^3Cl_2]$	$C_{34}H_{44}Cl_2N_4O_4Te_2Zn$ (964.2)	Off white	128-130	68	42.04 (42.35)	4.39 (4.60)	5.63 (5.81)	7.29 (7.35)	26.09 (26.47)	6.26 (6.78)	25.9
$[CdL^1Cl_2]$	$C_{30}H_{36}Cl_2N_4O_4Te_2Cd$ (955.2)	Light orange	150-152	55	37.43 (37.72)	3.56 (3.80)	5.61 (5.87)	7.45 (7.42)	26.58 (26.72)	11.72 (11.77)	Insoluble
$[CdL^2Cl_2]$	$C_{34}H_{44}Cl_2N_4O_4Te_2Cd$ (1011.3)	Dark pink	197-200	72	40.13 (40.38)	4.07 (4.39)	5.13 (5.54)	6.91 (7.01)	24.70 (25.24)	10.95 (11.12)	Insoluble
$[CdL^3Cl_2]$	$C_{34}H_{44}Cl_2N_4O_4Te_2Cd$ (1011.3)	Brown	120-122	67	40.26 (40.38)	4.29 (4.39)	5.36 (5.54)	6.90 (7.01)	25.08 (25.24)	10.85 (11.12)	91.0
$[HgL^1Cl_2]$	$C_{30}H_{36}Cl_2N_4O_4Te_2Hg$ (1043.3)	Purple	169-173	51	(34.54)	(3.48)	(5.37)	6.78 (6.80)	24.20 (24.46)	19.03 (19.23)	Insoluble
$[HgL^2Cl_2]$	$C_{34}H_{44}Cl_2N_4O_4Te_2Hg$ (1099.4)	Dark brown	137-140	76	(37.14)	(4.03)	(5.10)	6.21 (6.45)	23.39 (23.21)	18.05 (18.24)	41.2
$[HgL^3Cl_2]$	$C_{34}H_{44}Cl_2N_4O_4Te_2Hg$ (1099.4)	Cream	190-194	59	(37.14)	(4.03)	(5.10)	6.36 (6.45)	23.16 (23.21)	17.99 (18.24)	56.5

Λ_M *reported[19] for 1 : 1 electrolyte in acetonitrile = 120 – 160.*

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 colored, crystalline, air stable solids and are soluble only in polar donor organic solvents.

The molar conductance of soluble complexes in acetonitrile at *ca.* 10^{-3} M **(**Table 1) show their non-electrolyte to weak-electrolyte nature as the observed Λ_M values are much less than those reported for 1 : 1 type electrolytes [19] and hence suggest their formulation as [$MLCl_2$].

Magnetic and Electronic Spectral Studies
As expected, these d^{10} metal - ion complexes are diamagnetic in nature. No d-d transitions are observed for these complexes consistent with the d^{10} configuration. The electronic absorption spectra of these complexes display a broad and intense band in the region 29850-32467 cm^{-1} due to CT transitions [20,21]. The $n-\pi^*$ and $\pi-\pi^*$ bands of the ligand may also be mixed with this charge transfer band [21]. This band sweeps the near UV portion of electromagnetic radiation and extends in the visible region, with successively diminishing absorbance up to 500 nm. This is responsible for the color of the complexes.

IR Spectra
The important IR bands and their assignments are compiled in Table 2. 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 diaryltellurium dichlorides and 1, 3-diaminopropane.

Table. 2: Important IR data (cm^{-1}) for metal complexes

Complex	ν_{N-H}	N-H def.	N-H out of the plane bending	ν_{C-N}
[ZnL^1Cl_2]	3160 s	1630 m	809 m	1172 m
[ZnL^2Cl_2]	3166 m	1628 m	815 m	1183 m
[ZnL^3Cl_2]	3200 mb	1654 s	823 s	1176 s
[CdL^1Cl_2]	3260 s	1645 m	835 m	1168 s
[CdL^2Cl_2]	*	1623 m	813 s	1185 m
[CdL^3Cl_2]	3180 m	1653 m	823 s	1175 s
[HgL^1Cl_2]	3220 s	1640 m	829 s	1174 vs
[HgL^2Cl_2]	3200 m	1628 m	813 s	1187 m
[HgL^3Cl_2]	3205 m	1653 m	823 s	1176 vs

**mixed with υ_{O-H}, s = strong, m = medium, vs = very strong, sh = shoulder .*

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 3160-3260 cm^{-1} (sometimes mixed with O-H) attributed to ν_{N-H} 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 [12, 22-24] of 3200 cm^{-1}. This contention finds support [22] from appearance of bands of medium to strong intensity at 1623-1654 cm^{-1} and 809-835 cm^{-1} assigned as N-H deformation coupled with N-H out of the plane bending vibrations. Bands at ~1175 cm^{-1} may be reasonably assigned to C-N stretching vibration [12,25,26]. The above observations strongly suggest [12, 22,25,26] that proposed macrocyclic framework is formed.

The formation of tellurium containing macrocyclic ring is also supported by appearance of new weak intensity bands around 420-410 cm^{-1} due to Te-N [12,27]. Evidence for formation of proposed macrocycles and coordination through N atoms is further supported by new medium to weak intensity bands around 480-450 cm^{-1} assignable to M-N stretching [28]. The ν_{M-Cl}, however could not be ascertained due to non-availability of far infrared data.

^{1}H NMR Spectra

The proton chemical shifts for some representative complexes which have sufficient solubility in DMSO –d_6 are presented in Table 3.

The phenyl protons in metal complexes resonate at slightly up field side (6.91-7.85 δ ppm) as compared to parent diaryltellurium dichlorides [15,16], 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, NH_2-CH_2-CH_2-CH_2-NH_2, exhibits [29] 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 1.69-1.93 δ ppm assignable to coordinated secondary amino group [30], confirms the formation of 12-membered tellurium containing tetraazamacrocycles skeleton. The middle methylene protons and those adjacent to N-atoms resonate at 2.08 -2.16 and 2.76 -3.06 δ ppm, respectively. This behavior of complexes under study is quite similar to those of other tetraazamacrocycles [12,31,32] 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, ^{1}H NMR studies on these metal complexes support the formation of 12-membered tellurium tetraazamacrocycles and their tetra dentate ligation behavior as predicted by IR studies.

Table.3: 1H NMR Data (δ ppm) for Metal Complexes in DMSO – d_6

Complex	–NH–	–CH$_2$– (middle)	–CH$_2$– (adjacent to N)	$-CH_3^*$	–OCH$_3$	Phenyl	–OH
[ZnL^1Cl_2]	1.85^s (4H)	2.16^m (4H)	3.06^m (8H)	---	---	6.91^d (8H) 7.85^d (8H)	9.69^b (4H)
[HgL^1Cl_2]	1.87^s (4H)	2.11^m (4H)	2.87^m (8H)	---	---	6.95^d (8H) 7.39^d (8H)	6.73^b (4H)
[ZnL^2Cl_2]	1.93^s (4H)	2.08^m (4H)	2.92^m (8H)	2.49^s (12H)	---	6.94^d (4H) 7.38^s , 7.64^d (8H)	7.98^b (4H)
[ZnL^3Cl_2]	1.69^s (4H)	*	2.83^m (8H)	---	3.80^s (12H)	7.15^d (8H) 7.74^d (8H)	---
[CdL^3Cl_2]	1.72^s (4H)	2.09^m (4H)	2.76^m (8H)*	---	3.79^s (12H)	7.16^d (8H) 7.58^d (8H)	---
[HgL^3Cl_2]	1.80^s (4H)	2.09^m (4H)	2.80^m (8H)	---	3.80^s (12H)	7.15^d (8H) 7.54^d (8H)	---

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

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.

CONCLUSION

Zinc(II), cadmium(II) and mercury(II) complexes have been prepared by condensation of diaryltellurium dichlorides with 1,3-diaminopropane in presence of metal chlorides. These complexes have been characterized using elemental analyses, conductance measurements, electronic absorption, infra-red and proton magnetic resonance spectral techniques. All the metal complexes have been assigned a distorted octahedral stereochemistry.

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