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Synthesis and Characterization of Some Group 12 Metal Complexes with Tellurium Containing 10-Membered Tetraazamacrocyclic Ligands

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Abstract: A new series of 10-membered tellurium containing 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 $L^3=10$ -membered tellurium containing tetraazamacrocyclic ligands] have been prepared *via* the template condensation of ethylenediamine 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 measurements, infrared, electronic absorption and proton magnetic resonance spectral studies. IR and PMR spectra confirm the formation of 10-membered tetraazamacrocycle skeleton and their tetradentate nature. An octahedral geometry has been assigned to all the metal complexes on the basis of various physicochemical studies.

Keywords: Tellurium, Tetraazamacrocycles, Diaryltellurium dichlorides, Ethylenediamine, Template condensation.

Introduction

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 behaviour between the hard and soft donors towards a metal center^{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, macrocycle complexes are significant as they have been found to act as possible models for biochemically important proteins and enzymes⁸⁻¹².

Some recent publications¹³⁻¹⁷ exhibit the development of tellurium containing macrocycles. Srivastava *et al.*¹⁸ reported the route of synthesis of metal complexes with tellurium containing

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macrocycles. In continuation of our earlier work^{19,20} on such macrocyclic complexes, we herein report the synthesis and characterization of divalent zinc, cadmium and mercury complexes with three novel tellurium tetraazamacrocycles, (Te_2N_4 system).

Experimental

The chemicals, tellurium tetrachloride (Aldrich), ethylenediamine, $ZnCl_2$, $CdCl_2.2.5$ H₂O, HgCl₂, 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 TeCl₄ with phenol²¹, *o*-cresol²² and anisole²³ respectively as reported in the literature. All the preparations were carried out in dry conditions under an atmosphere of nitrogen.

Preparation of complexes

The 10-membered tellurium tetraazamacrocyclic metal complexes have been synthesized by the template condensation reaction of metal chlorides with diaryltellurium dichlorides and ethylenediamine in 1: 2: 2 molar ratios.

A general method for the preparation of these 1, 6-diaryltellura –2, 5, 7, 10-tetraazacyclodecane metal complexes is given below: 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 ethylenediamine 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 of metal dichloride. An immediate change in colour 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 coloured 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 volumetrically²⁴. 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 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 when condensed with ethylenediamine in presence of metal dichlorides in 2: 2: 1 molar ratios, yield the desired complexes as shown below



Where

L¹ ; R = p-hydroxyphyenyl L² ; R = 3-methyl-4-hydroxyphyenyl L³ ; R = p-methoxyphenyl M = Zn^{II}, Cd^{II} and Hg^{II}

These complexes are coloured, crystalline, air stable solids and are soluble only in polar donor organic solvents. The analytical data and some physical properties of these complexes are given in Table 1.

Conductance studies

The molar conductance values for these complexes (except ZnL^2Cl_2 and HgL^2Cl_2) in DMSO at *ca*. 10⁻³ M are lower than the ranges reported²⁵ for 1:1 type electrolytes, reflecting their partial dissociation in this solvent. The molar conductance for ZnL^2Cl_2 is close to those of 1:1 electrolytes and for HgL^2Cl_2 is higher than those of 1:1 type electrolytes. These two complexes probably ionize into $[\text{ML}^2\text{Cl.DMSO}]^+$ and Cl^- ions due to the solvation process, since DMSO is known to be a good donor²⁵. So, on the basis of conductance studies, these complexes in general may be represented as $[\text{MLCl}_2]$.

Magnetic and electronic spectral studies

As expected, these d¹⁰ metal ion complexes are diamagnetic in nature. No d-d transitions are observed for these complexes consistent with the d¹⁰ configuration. The electronic absorption spectra of these complexes display a broad and intense band in the region 32000-22000 cm⁻¹ due to CT transitions^{26,27}. The n- π^* and π - π^* bands of the ligand may also be mixed with this charge transfer band²⁷. 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 colour of the complexes.

Infra-red spectra

The important IR bands and their assignments are tabulated in Table 2. The spectra are quite complex and an attempt has thus been made to draw the conclusions by comparing the spectra of metal complexes with those of corresponding constituent diarytellurium dichlorides and ethylenediamine.

Complex	Empirical Formula	Colour	M.P. °C Yield <u>A</u>			Analys	Analysis found (calculated), %				$\Lambda_{\rm M}$ at ca.10 ⁻³ M ohm ⁻¹
Complex	(Formula Weight)	Coloui	(dec.)	%	С	Н	Ν	Cl	Te	М	cm ² mol ⁻¹ in MSO
$[ZnL^1Cl_2]$	$C_{28}H_{32}Cl_2N_4$	Bright	100-101	82	38.01	3.16	6.13	8.44	28.93	7.36	26.7
	$O_4 Te_2 Zn (880.1)$	orange			(38.21)	(3.66)	(6.37)	(8.06)	(29.00)	(7.43)	
$[ZnL^2Cl_2]$	$C_{32}H_{40}Cl_2N_4$	Drown	158-160	82	40.80	4.14	5.62	7.62	27.65	6.91	62 /
	$O_4 Te_2 Zn (936.2)$	DIOWII			(41.05)	(4.31)	(5.98)	(7.57)	(27.26)	(6.98)	03.4
$[ZnL^{3}Cl_{2}]$	$C_{32}H_{40}Cl_2N_4$	Pale	118-120	63	40.91	4.21	5.76	7.49	27.35	6.85	20.2
	$O_4 Te_2 Zn (936.2)$	white			(41.05)	(4.31)	(5.98)	(7.57)	(27.26)	(6.98)	
$[CdL^1Cl_2]$	$C_{28}H_{32}Cl_2N_4$	Dark	178-180	48	36.03	3.08	5.82	7.50	27.65	11.55	37.5
	$O_4 Te_2 Cd (927.1)$	red			(36.27)	(3.48)	(6.94)	(7.65)	(27.53)	(12.13)	
$[CdL^2Cl_2]$	$C_{32}H_{40}Cl_2N_4$	Orange	180-185	77	38.62	3.89	5.16	7.39	25.50	10.92	33.6
	$O_4 Te_2 Cd (983.2)$	pink			(39.09)	(4.10)	(5.70)	(7.21)	(25.96)	(11.43)	
$[CdL^{3}Cl_{2}]$	$C_{32}H_{40}Cl_2N_4$	Light	117-121	65	38.91	3.97	5.58	7.02	25.84	11.31	22.5
	$O_4 Te_2 Cd (983.2)$	brown			(39.09)	(4.10)	(5.70)	(7.21)	(25.96)	(11.43)	
[HgL ¹ Cl ₂]	$C_{28}H_{32}Cl_2N_4$	Ded	130-133	52	(22, 12) (2.16)	(2, 10)	(5.50)	6.80	25.14	19.69	60.7
	$O_4 Te_2 Hg (1015.3)$	Red			(33.12)) (3.18)	(5.52)	(6.98)	(25.55)	(19.76)	
[HgL ² Cl ₂]	$C_{32}H_{40}Cl_2N_4$	Dark	120-125 6	(7	67 (35.87)	(3.76)	(5.23)	6.50	23.72	18.26	108.4
	$O_4 Te_2 Hg (1071.4)$	brown		6/				(6.62)	(23.82)	(18.72)	
[HgL ³ Cl ₂]	$C_{32}H_{40}Cl_2N_4$	D	100 110	8-110 51	(35.87)	(3.76)	(5.23)	6.53	23.75	18.55	16 5
	$O_4 Te_2 Hg (1071.4)$	Brown	108-110					(6.62)	(23.82)	(18.72)	46.5
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Table 1. Analytical data, physical properties, yields and molar conductance for metal complexes

	Table 2. 1	mportant IR d	lata (cm ²) for metal complexes	
Complex	$\nu_{\rm N-H}$	N-H def.	N-H out of the plane bending	$\nu_{\rm C-N}$
$[ZnL^1Cl_2]$	3145 m	1625 sh	825 s	1174 s
$[ZnL^2Cl_2]$	3160 m	1640 m	813 s	1174 m
$[ZnL^{3}Cl_{2}]$	3240 m	1651 m	822 s	1176 s
$[CdL^1Cl_2]$	3155 m	1631 m	828 s	1172 s
$[CdL^2Cl_2]$	3190 m	1635 m	813 s	1174 m
$[CdL^{3}Cl_{2}]$	3260 m	1652 m	822 s	1176 vs
$[HgL_1^1Cl_2]$	*	1635 m	825 vs	1172 s
$[HgL^2Cl_2]$	3165 m	1640 sh	813 m	1175 m
[HgL ³ Cl ₂]	3250 m	1654 m	821 s	1176 s

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

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The metal complexes under study did not show bands characteristics of free NH₂ group, instead the entire complexes exhibit a single sharp absorption band at around 3145-3260 cm⁻¹ (sometimes mixed with O-H) attributed to v_{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^{18,28-30} in the vicinity of 3200 cm⁻¹. This contention finds support²⁸ from appearance of bands of medium to strong intensity at ~1640 cm⁻¹ and ~825 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^{18,31,32}. The above observation strongly suggest^{18,28,31,32} 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^{18,33}. 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 stretching³⁴. The M-Cl, Cd-N and Hg-N vibrations could not be ascertained due to non-availability of far infrared data.

Proton magnetic resonance spectra

The proton chemical shifts for some representative complexes which are soluble in DMSO-d₆ are compiled in Table 3. The phenyl protons in metal complexes resonate at slightly up field side (6.92-7.65 δ ppm) as compared to parent diaryltellurium dichlorides^{21,22,35}, due to increase in electron density at the tellurium atom as a result of replacement of 2 Cl by 2 N atoms. Ethylenediamine, $H_2^{(a)}$ –($CH_2^{(b)}$)– $NH_2^{(a)}$ shows³⁶ two sets of four equivalent protons each at (a) = 1.19 δ ppm and (b) = 2.74 δ ppm. Metal complexes do not show any signal attributable to free – NH₂, instead a broad singlet at around 1.50-2.05 δ ppm, which may be assigned to coordinated secondary amino group³⁷ is observed. This confirms the formation of proposed macrocycle skeleton. The deshielding of –NH– protons further suggests the donation of electron density to the metal-ions. The methylene protons in these metal complexes resonate at 2.05-2.50 δ ppm, as a multiplet as reported^{18,30,32} for other tetraazamacrocyles derived from ethylenediamine. Also, the independence of aryl proton chemical shifts on the nature of metal-ion precludes the possibility of Te-M bond. Thus, PMR studies on these metal complexes support the formation of 10-membered tellurium tetraazamacrocycles and their tetra dentate ligation behaviour as predicted by IR studies.

Complex	-NH-	$-CH_3^*$	-OCH ₃	CH2	Phenyl	–OH
[ZnL ² Cl ₂]	2.05 ^s (4H)	2.42 ^s (12H)		2.14 ^m (8H)	6.92 ^d (4H) 7.59 ^d ,7.56 ^s (8H)	$9.95^{b} (4H)$
[CdL ² Cl ₂]	1.50 ^s (4H)	2.49 ^s (12H)		2.05 ^m (8H)	6.94 ^d (4H) 7.47 ^s , 7.56 ^d (8H)	8.17 ^b (4H)
[HgL ² Cl ₂]	1.60 ^s (4H)	2.50 ^s (12H)		2.12 ^m (8H)	6.92^{d} (4H) 7.56 ^d , 7.65 ^s (8H)	10.19 ^b (4H)
$[ZnL^{3}Cl_{2}]$	1.79 ^s (4H)		3.79 ^s (12H)	2.50 ^m (8H)	7.16 ^d (8H) 7.41 ^d (8H)	
$[CdL^{3}Cl_{2}]$	1.75 ^s (4H)		3.78 ^s (12H)	2.50 ^m (8H)	7.16 ^d (8H) 7.74 ^d (8H)	
[HgL ³ Cl ₂]	1.75 ^s (4H)		3.81 ^s (12H)	2.50 ^m (8H)	7.16 ^d (8H) 7.52 ^d (8H)	

Table 3. PMR data (δ ppm) for metal complexes in DMSO-d₆

*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 d¹⁰ metal complexes.

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