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Studies on Some Diorganotellurium (IV) Complexes with a N_4 Donor Macrocyclic Ligand; 1,4,8,11-tetraazatetradeca 5,7,12,14-tetraene

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Eight complexes of diorganotellurium(IV) with general formulae $[R_2Te(L)]X_2$ where R = phenyl or methyl and L = 1, 4, 8, 11 tetra-azatetradeca 5, 7, 12, 14 tetraene and X = Cl^-, ClO_4^-, NO_3^-, BF_4^- have been prepared and their structures have been assigned on the basis of elemental analyses, molar conductance and spectral studies. The macrocycle, which is a N_4 donor is found to behave as tridentate in nature, coordinating to organotellurium(IV) through only three of its nitrogens as confirmed by ir and ^1H nmr data. The resulting complexes are thus assigned distorted octahedral geometries.

INTRODUCTION

A large number of macrocyclic complexes of different transition metals have been reported from this laboratory[1–4], and during our attempts to prepare the corresponding organometallic derivatives of macrocyclic ligands, some complexes of diorganotin(IV) have also been prepared and reported[5,6]. The present paper reports the synthesis followed by structural assignment of some diorganotellurium(IV) complexes using a macrocycle derived from ethylenediamine and acetyl acetone.

EXPERIMENTAL

$TeCl_4$, Ph_4Sn and Te powder were obtained from M/s Aldrich Chemicals (USA), Ethylenediamine; acetylacetone. Nickel chloride and Potassium cyanide were BDH reagents. Other commercially available reagents were purified by standard methods and all the reactions were carried out under dry nitrogen. Ph_2TeCl_2[7] and Me_2TeI_2[8] were prepared by reported methods and simple metathetical reactions of these with AgX (where X = ClO_4^- and NO_3^-) and with $NaBF_4$ in dry methanol have been used to prepare perchlorate, nitrate and tetrafluoroborate derivatives. All the macrocyclic complexes have been prepared by non-template method as detailed below:

Preparation of Macrocyclic Ligand (L)

The free macrocyclic ligand has been obtained by a 2 : 2 intramolecular condensation reaction between ethylene-diamine and acetylacetone in the

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presence of $NiCl_2 \cdot 6H_2O$[9] followed by extrication of nickel(II) using potassium cyanide[10].

Preparation of Complexes

To a dry methanolic solution containing R_2TeX_2 (0.01 mol) (where $R = Ph$ or Me and $X = Cl^-$, NO_3^-, BF_3^-, ClO_4^-) was added the extricated macrocycle (0.01 mol) and the resulting solution was stirred at room temperature under dry nitrogen. After 6 hrs the stirring was stopped and the yellow complex which had settled down was filtered, washed repeatedly with solvent ether and dried over P_4O_{10} in vacuum.

The elemental analyses were carried out at semi-microscale at CDRI Lucknow. Molar conductance of the 10^{-3} molar solutions of complexes in anhydrous DMSO were measured at 30°C by Philip magic eye conductivity bridge Model PR 9500 using dip type conductivity cell. The IR spectra were recorded in CsI on a Perkin Elmer model 521 spectrophotometer. ^{1}HNMR spectra of the complexes were recorded in DMSO-D^6 using TMS as internal standard on a Varian A 90 D spectrometer.

RESULTS AND DISCUSSION

The above synthesis has resulted in eight new complexes, the analytical data (Table 1) for which correspond to molecular formulae $[R_2Te(L)]X_2$ where R = phenyl or methyl. $L = C_{14}H_{24}N_4$ and $X = Cl^-$, ClO_4^-, NO_3^- and BF_4^-. The complexes are yellow crystalline solids and their molar conductances in DMSO are in the range 40–60 $ohm^{-1}\ cm^2\ mol^{-1}$ corresponding to 1 : 2 electrolyte.

In the IR spectra of the free macrocyclic ligand, recorded in the range 4000–200 cm^{-1}, the NH— and $>C=O$ stretchining frequencies at 3300 and 1740 cm^{-1} disappear and in their place a strong band is observed at 1600 cm^{-1} corresponding to the formation of Schiffs base macrocyclic ligand. This frequency undergoes a significant lowering corresponding to coordination and is observed in the spectra of complexes at 1590 ± 5 cm^{-1} and hence the band is assigned to be due to coordinated $>C=N$ group. Two very weak absorptions at 450 ± 5 cm^{-1} and 395 ± cm^{-1} identified in the spectra of complexes but absent in the free ligand may be assigned to be due to Te–N stretching[11]. In addition two other weak bands identified at 250 ± 4 in $[Ph_2Te(L)]X_2$ complexes and at 534 ± 5 cm^{-1} in $[Me_2Te(L)]X_2$ complexes are attributed to Te–C(Ph) and Te–C(Me) stretches[12, 13]. In the IR spectra of all the complexes vibrations associated with anions are observed at 1090, 635, 415 cm^{-1} for perchlorate[14], 1048, 620, 435 cm^{-1} for tetrafluoroborate[15]. 1351, 825 cm^{-1} for nitrate[16] and 648 cm^{-1} for chloride[17] and these correspond to uncoordinated anions.

TABLE 1

ANALYTICAL DATA OF $[(R_2Te(L)]X_2$

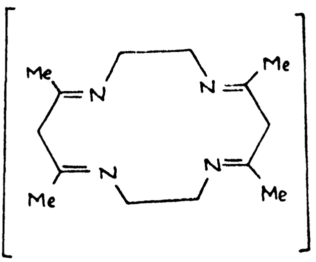
Complexes	Colour	M.Pt. (°C)	Elemental analysis Found (Calc) %				Molar conductance in ohm^{-1} cm^2 mol
			Te	C	H	N	
$C_{14}N_{24}N_4$	brownish yellow	85	—	66.7 (66.8)	9.6 (9.8)	22.5 (22.8)	—
$[Ph_2Te(C_{14}H_{14}N_4)]Cl_2$	light yellow	205	21.24	51.94 (51.83)	3.99 (3.04)	9.32 (9.07)	46.2
$[Ph_2Te(C_{14}H_{24}N_4)](ClO_4)_2$	light yellow	*	17.52 (16.91)	**	**	7.69 (8.07)	46.8
$[Ph_2Te(C_{14}H_{24}N_4)](NO_3)_2$	yellowish white	>240	19.54 (19.78)	47.78 (47.18)	3.68 (3.42)	8.58 (8.79)	56.0
$[Ph_2Te(C_{14}H_{24}N_4)](BF_4)_2$	whitish yellow	>240	21.70 (21.86)	**	**	9.52 (9.23)	52.4
$[Me_2Te(C_{14}H_{24}N_4)]Cl_2$	light yellow	195	26.80 (26.32)	40.33 (41.22)	5.04 (5.72)	11.76 (12.18)	54.1
$[Me_2Te(C_{14}H_{24}N_4)](ClO_4)_2$	light yellow	*	21.12 (21.28)	**	**	9.27 (9.85)	51.2
$[Me_2Te(C_{14}H_{24}N_4)](NO_3)_2$	white yellow	>240	24.12 (24.48)	36.29 (36.88)	4.54 (4.58)	10.59 (10.77)	44.3
$[Me_2Te(C_{14}H_{24}N_4)](BF_4)_2$	white yellow	>240	27.44 (28.12)	**	**	12.04 (12.43)	58.2

*Explodes before melting.

**Due to explosive character and presence of fluorine C, H analysis were not possible.

In the ^1H NMR spectrum of free ligand L, all the CH_3 protons, as these are equivalent, are observed as a singlet at δ 1.75 (12H). The methylene protons are of two types, the ones corresponding to acetyl acetone are observed at δ 2.30 (4H) as singlet while the ones due to ethylenediamine which is a part of the macrocycle, are observed at δ 2.70 (8H) also as singlet. In the ^1H NMR spectrum of complex $[Ph_2Te(L)](NO_3)_2$ two multiplets centered at δ 7.90 and δ 7.50 (8H) are observed which correspond to the phenyl protons. The signals due to methyl protons are split into three singlets centred at δ 1.87 (6H), δ 1.93 (3H) and δ 2.15 (3H) while all thc CH_2 protons are observed as a broad signal at δ 3.60 (12H). The complex $|Me_2Te(L)|(NO_3)_2$ gives similar spectra except that phenyl protons disappear and a broad doublet at δ 2.05 (3H) corresponding to methyl protons of Me_2Te is observed.

The shift of the signals to low field is indicative of the coordination of macrocycle. The splitting of methyl proton signals into three singlets suggests that the macrocycle (L) is coordinated to organotellurium (IV) through only three of its nitrogens, as coordination through all four nitrogens will give rise to equivalent methyl groups. This type of tridentate coordination is also expected to result in five types of CH_2 protons, which are not observed as five individual signals but merge together to give a broad signal at δ 3.60 (12 H). The complexes are thus assigned octahedral structure in which the macrocycle occupies three equatorial positions, organic group two axial position and the lone pair of tellurium occupies the forth vacant equatorial position.



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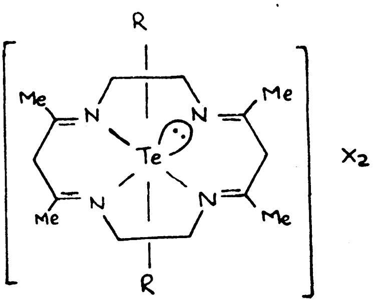

Ib

$X = Cl_2^-, ClO_4^-, NO_3^-. BF_4^-$

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