Synthesis and Characterization of [(RR'Te)2L1], [(RR'Te)2L2] and [(RR'Te)L3] Compounds with Macrocyclic Ligands: A Photoelectron Spectroscopic Study

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ABSTRACT

[(RR'Te)2L1], [(RR'Te)2L2] and [(RR'Te)L3] compounds (where \( R = R' = C_6H_5CH_2; p-MeOC_6H_4; R = p-MeOC_6H_4 \) & \( R' = p-Me_2NC_6H_4; R = p-EtOC_6H_4 & R' = p-Me_2NC_6H_4; R = R' = C_6H_5C_6H_4 \) and \( L = L^1 = 3, 6, 9, 12, 20, 23, 26, 29, 35, 36\)-decaazatricyclo[29.3.1.1] hexatriaconta-1(34), 14, 16, 18(36), 31(35), 32-hexaene-2, 13, 19, 30-tetraene; \( L^2 = 3, 6, 9, 17, 20, 23, 29, 30\)-octaazatricyclo[23.3.1.1] triaconta-1(28), 11, 13, 15(30), 25(29), 26-hexaene-2, 10, 16, 24–tetraene and \( L^3 = 3, 7, 15, 19, 25, 26\)-hexaazatricyclo[19.3.1.1]hexacosa-1(24), 9, 11, 13(26), 21(25), 22–hexaene–2, 8, 14, 20–tetraene have been synthesized and characterized by elemental analysis, molar conductance, I.R. and X-ray photoelectron spectra (XPS) data and an distorted octahedral geometry were established.

Keywords: Macrocyclic Ligands, Organotellurium (II), XPS.

I. INTRODUCTION

Macrocyclic ligands and their metal complexes have attracted extensive research interest in the past decades, due to its applications and their importance in coordination chemistry and bioinorganic chemistry. Many macrocyclic ligands such as crown ethers, porphyrins, saturated and unsaturated polyamines, polyazamacrocycles, donor macrocyclic, Robson type tetraimino diphenol macrocyclic ligands have been synthesized and characterized in last few decades. The studies on complexes of Schiff base macrocyclic ligands with different size, number and donor atoms for coordination with a variety of metal centres have been studied. Moreover, the template condensation reaction lies in the heart of macrocyclic chemistry. Many transition metal ions are found in living systems in macrocyclic ligand environment and work as enzymes or carriers.

Macrocyclic metal complexes have been used as detecting tumor lesions, as in labeling monoclonal antibodies with radioactive models, as metal ion separation, as cancer diagnosis, as radiotherapeutic and therapeutic, as catalyst, as pharmacological agents, as biological process such as photosynthesis and dioxygen transport, as photosensitizer, as versatile coordination behaviour, as toxicity against bacterial fungal growth, as anticancerous, as environment importance, as potential medicinal applications such as magnetic resonance imaging (MRI), as N.M.R. shift and relaxation agents; as catalysts; as RNA cleavage catalysts. The different type of macrocyclic ligands and their metal complexes discoveries have created supramolecular chemistry and its enormous diversity. Very recently few comprehensive reviews on macrocyclic ligands and their metal complexes with their applications have been also appeared. Very recently the development of compartmental macrocyclic Schiff bases and related polyamine derivatives have been also published. Recently, the electron donor properties of organotellurium (IV) and (II) of macrocyclic compounds i.e. as Lewis base are well known, but the electron acceptor i.e. as Lewis acid properties of organotellurium (II) of macrocyclic compounds are less known. This paper deals with the acceptor
properties of organotellurium (II) macrocyclic compounds.

II. METHODS AND MATERIAL

Experimental

Te powder and TeCl₄; all chemicals and solvents were of A R Grade and purchased from Aldrich and BDH and were used after distillation and further purification. (C₆H₅CH₂)₂Te; (C₆H₄)₂Te; (p-MeOC₆H₄)₂Te; (p-MeOC₆H₄) (p-Me₂NC₆H₄)Te and (p-EtOC₆H₄) (p-Me₂NC₆H₄)Te were prepared, purified and characterized as reported in literature¹¹³⁻¹¹⁷.

Preparation of Metal Compounds

A. Preparation of [(RR'Te)₂L₁] compounds with macrocyclic ligand (L₁) i.e. 3, 6, 9, 12, 20, 23, 26, 29, 35, 36-decaazatricyclo [29.3.1.1] hexatriaconta-1 (34), 14, 16, 18(36), 31(35), 32-hexaene-2, 13, 19, 30-tetraone ligands:

Triethylenetetraamine (1 mmol) was mixed with RR’Te (1 mmol) in dry ethanol and refluxed for 1 hr. and then put dropwise pyridine 2,6-dicarboxylic acid into this solution (2mmol : 2mmol ratio) and again refluxed this solution for 2 hrs. The resulting precipitate was filtered and recrystallized into ether : ethanol ( 9: 1 ratio ). (Fig. 01).

Figure 1. Proposed mechanism of [(RR Te)₂L₁] compounds i.e. Homobimetallic compounds where L₁= 3, 6, 9, 12, 20, 23, 26, 29, 35, 36-decaazatricyclo [29.3.1.1] hexatriaconta-1(34), 14, 16, 18(36), 31(35), 32-hexaene-2, 13, 19, 30-tetraone.

B. The preparation of [( RR’Te). L₂ ] compounds with macrocyclic ligand (L₂) i.e. 3, 6, 9, 17, 20, 23, 29, 30- octaazatricyclo [ 23.3.1.1] triaconta -1 (28), 11, 13, 15(30), 25(29), 26- hexaene -2, 10, 16, 24-tetraone.

The diethylenetriamine (2mmol) was mixed with [RR Te] (1mmol) in dry ethanol and refluxed for 1 hr. and then pyridine- 2,6-dicarboxylic acid (2mmol :1mmol ratio ) is mixed into above solution and refluxed for 2 hrs. The resulting precipitate was filtered and recrystallized by benzene-pet-ether (9:1 ratio) solution (Fig. 02).
**C. Preparation of [(RRTe)\(L^3\)] compounds with macrocyclic ligand (\(L^3\)) i.e.3, 7, 15, 19, 25, 26–hexaaazatricyclo[19.3.1.1]hexacosa1(24), 9, 11, 13(26), 21(25), 22–hexaene – 2, 8, 14, 20 –tetraone**

The 1,3 – diaminopropane (2mmol) was mixed with [ RRTe ] (1mmol) in dry ethanol and refluxed for 1 hr. and then pyridine 2,6- dicarboxylic acid (2mmol : 1mmol ratio ) was mixed into the above solution and again refluxed for 2 hrs.. The resulting precipitate was filtered and recrystallized by benzene-pet-ether (9:1 ratio) solution (Fig. 03).

**Characterization of the Complexes**

The elemental analysis for C, H, N and Te metal were determined on a semi micro scale at Central Drug Research Institute, Lucknow, U.P. India. Molar conductance of all the complexes were measured at room temperature in acetone by Digisum Electronic Conductivity Bridge. Infra-Red spectra of all these complexes were recorded in KBr and CsI on Perkin-Elmer 457 spectrometer.The X-ray photoelectron spectra i.e. XPS were recorded on a VG scientific ESCA-3 MK II electron spectrometer. The Mg kα X-ray line (1253.6 eV) was used for photo excitation. The Cu 2p\(\frac{3}{2}\) (BE = 932.8 ± 0.2 eV) and Au 4f\(\frac{7}{2}\) (BE = 83.8 ± 0.1 eV) lines were used to calibrate the instrument and Ag 3d\(\frac{5}{2}\) (BE = 368.2 eV) was used for cross-checking. All the spectra were recorded using the same spectrometer parameter of 50 eV pass energy and 4mm slit width. The reduced full width at half maximum (FWHM) at the Au 4f\(\frac{7}{2}\) (BE = 83.8 eV) level under these conditions was 1.2 eV.The powdered sample was mixed with high purity silver powder to reduce the charging effect. A thin layer of such a sample was pressed on a gold metal gauge which was welded to a nickel sample holder. The Ag 3d\(\frac{5}{2}\) (BE = 368.2 eV) level obtained from this sample was sharp and did not show any observable shift. Thus the charging of the samples if present at all was negligible. The spectra were recorded in triplicate in the region of the interest. In most of the cases the binding energies were reproducible within ±0.1 eV. The usual least square fitting procedure of determining peak positions, line width and areas was used.

**III. RESULTS AND DISCUSSION**

All these newly synthesized compounds are soluble in common organic solvent and stable towards atmospheric oxygen and moisture. The element analysis for C, H, N and Te were found within range ± 0.5%. The molar conductance of 10\(^{-3}\) M solution of the compounds was determined at room temperature were observed in range from 20-30 ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\) in acetone and 0.82 to 1.02 ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\) in nitrobenzene indicating absence of ionic species. Both
elemental analysis and molar conductance suggested the composition of prepared compounds as [(RRTe)$_2$L]$; [RR TeL$_2$] and [RR TeL$_3$].

Infrared frequencies associated with fundamental modes of vibration of v$_{Te-C}$ and v$_{Te-N}$ was observed in the range 230 - 260 cm$^{-1}$ and 410 - 420 cm$^{-1}$.120

The binding energies (eV) of [(RR Te)$_2$L]$; [RR TeL$_2$] and [RR TeL$_3$] for Te 3d$_{3/2,5/2}$ and N1s photoelectron peaks are listed in table. 1 (Fig. 4 to 5). It was observed that the binding energies of Te 3d$_{3/2,5/2}$ in the starting material RR Te was higher than their prepared molecular adducts [(RR Te)$_2$L]$; [RR TeL$_2$] and [RR TeL$_3$]. These observations suggested that electron density on tellurium metal ion has increased due to coordination of ligand with tellurium metal ion.118(Fig.4). Moreover, N1s photoelectron spectra in [(RRTe)$_2$L]$] compounds have shown two N1s photoelectron with intensity ratio of 6:4 at binding energies ~401 & ~404 eV suggested that six nitrogen atoms are uncoordinated while four are coordinated. Similarly, in [RR TeL$_2$] and [RR TeL$_3$] N1s photoelectron spectra have shown two N1s photoelectron peak, one at ~401 and another at ~404 eV with 6:2 and 4:2 intensity ratio respectively, suggesting six nitrogen atoms are uncoordinated and two nitrogen atoms are coordinated in [RR TeL$_2$] compounds while in [RR TeL$_3$] four nitrogen atoms are uncoordinated and two nitrogen atoms are coordinated (Fig.5).118

Thus elemental analysis, molar conductance, I.R. and X-ray photoelectron spectra (XPS) data suggested that all these molecular adducts are having distorted octahedral geometry.

Table 1: Te 3d$_{3/2,5/2}$ and N1s binding energies (eV) in [RR Te] and [(RR Te)$_2$L]$], [RR TeL$_2$], [RR TeL$_3$] compounds

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IV. ACKNOWLEDGEMENT

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V. REFERENCES