

SYNTHESIS AND CHARACTERIZATION OF TELLURIUM(IV) COMPLEXES WITH 2-NAPHTHOL

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ABSTRACT

Compounds of the general formula $\text{TeCl}_{4-n}(\text{OC}_{10}\text{H}_7)_n$ ($n=1-3$) have been prepared by reacting tellurium(IV) chloride with 2-naphthol. The compounds act as Lewis acids and form adducts with pyridine, piperidine, γ -picoline, 2,2'-bipyridyl and 1,10-phenanthroline. The parent compounds and the adducts have been characterized on the basis of elemental analyses, molar conductance and molecular weight determinations and infrared spectroscopic studies, which indicate the existence of bridged structures through naphthoxy group in the parent compounds and a breakdown of structure of the parent compound on adduct formation.

INTRODUCTION

THE chemistry of metal phenoxides has been a subject of interest because of the catalytic, biological and industrial applications of these compounds¹. One of the general methods of preparation of phenoxides involves the reaction of metal halides with phenol, wherein OH group is deprotonated and hydrogen chloride gas is evolved. We have already reported the synthesis of phenoxides of Al(III)², Ti(IV)³, Nb(V) and Ta(V)⁴ by this method. However, in a recent report⁵ on the reaction of tellurium(IV) chloride with phenols, it is claimed that it is not the phenolic proton which takes part in the reaction but that, instead, the proton of the phenol ring is responsible for the evolution of HCl, thereby leading to the formation of hydroxyphenyltellurium(IV) halides. These observations prompted us to undertake the parallel reaction of tellurium(IV) chloride with 2-naphthol and characterize the reaction products.

EXPERIMENTAL

Materials

2-Naphthol (BDH) was recrystallized twice from hot carbon tetrachloride. The sample with melting point 121–122°C was used for various reactions. Tellurium(IV) chloride (Reidel) was used as such without further purification. All the bases were purified by standard methods before use.

Preparation of the complexes

The compounds, which may be formulated as

$\text{TeCl}_3(\text{OC}_{10}\text{H}_7)$, $\text{TeCl}_2(\text{OC}_{10}\text{H}_7)_2$ and $\text{TeCl}(\text{OC}_{10}\text{H}_7)_3$, were prepared by mixing the xylene solutions of tellurium tetrachloride and 2-naphthol in appropriate molar ratios under anhydrous conditions, followed by refluxing on an oil bath till evolution of hydrogen chloride gas ceased. The resulting solution was filtered to remove a very small amount of solid formed during the reaction. Addition of an inert solvent like petroleum ether to the solution resulted in the separation of a solid compound, which was filtered and recrystallized from an ether-THF mixture (2:1).

The adducts with nitrogenous bases were prepared by stirring the xylene solution of the parent naphthoxide with a base (1:1) for about 24 h. Solid compound in each case was isolated by the addition of petroleum ether, and was filtered, washed with petroleum ether, and dried *in vacuo*.

The complexes were analysed for tellurium as tellurium metal, and chlorine was estimated by Volhard's method. Measurements of conductance were carried out on an Elico conductivity bridge, type CM-82T. Infrared spectra of the complexes were recorded in potassium bromide pellets on Perkin Elmer 337 and 621 spectrometers. Molecular weights of all the complexes were determined by cryoscopic method.

RESULTS AND DISCUSSION

The analytical data for the complexes, along with their colour, molar conductances and molecular weights, are given in table 1. These compounds are quite stable in dry air but change their colour when

Table 1 Analytical and IR spectroscopic data for synthesized tellurium (IV) naphthoxides

Compound	Colour	Found (calcd), %		Λ_M (ohm ⁻¹ cm ² mol ⁻¹)	Molecular weight, found (calcd)	IR			
		Te	Cl			ν_{C-O}	ν_{Te-O}	$Te \begin{array}{c} \diagup O \diagdown \\ \diagdown O \diagup \end{array} Te$	ν_{Te-Cl}
TeCl ₃ (OC ₁₀ H ₇)	Dirty green	33.93 (33.90)	28.25 (28.21)	9.1	745 (377.5)	1200	—	518, 475	368
TeCl ₂ (OC ₁₀ H ₇) ₂	Dirty green	26.38 (26.39)	14.66 (14.64)	8.3	980 (485)	1208	575	525	365
TeCl(OC ₁₀ H ₇) ₃	Light brown	21.64 (21.60)	5.95 (5.99)	6.9	1176 (592.5)	1212	570	520	360, 345

exposed to moist air. Melting points of these compounds could not be determined correctly because of their high sensitivity to moisture. They are fairly soluble in common organic solvents, such as benzene, nitrobenzene, carbon tetrachloride, chloroform, etc. The molar conductance values of millimolar (10⁻³ M) solutions of the compounds in nitrobenzene show that they are slightly dissociated in solution. Molecular weight determinations cryoscopically in nitrobenzene indicate their molecular complexity to be around two, suggesting dimeric character.

Evolution of hydrogen chloride gas during the preparation of these compounds has been attributed to deprotonation of the phenolic OH group rather than to the action of the ring proton, as evidenced by the complete absence of any band in the region 3380–3600 cm⁻¹ assigned to ν_{OH} in pure naphthol⁶ and substantiated by the preliminary negative test of phenolic OH group in organic chemistry. There is a significant lowering of ν_{C-O} observed at 1260 cm⁻¹ in pure naphthol, by about 50–60 cm⁻¹ (table 1), suggesting bonding of oxygen to the metal, which is further confirmed by the appearance of entirely new bands in the region 560–580 cm⁻¹ and 480–520 cm⁻¹ assigned to the terminal ν_{Te-O} ⁷ and bridging

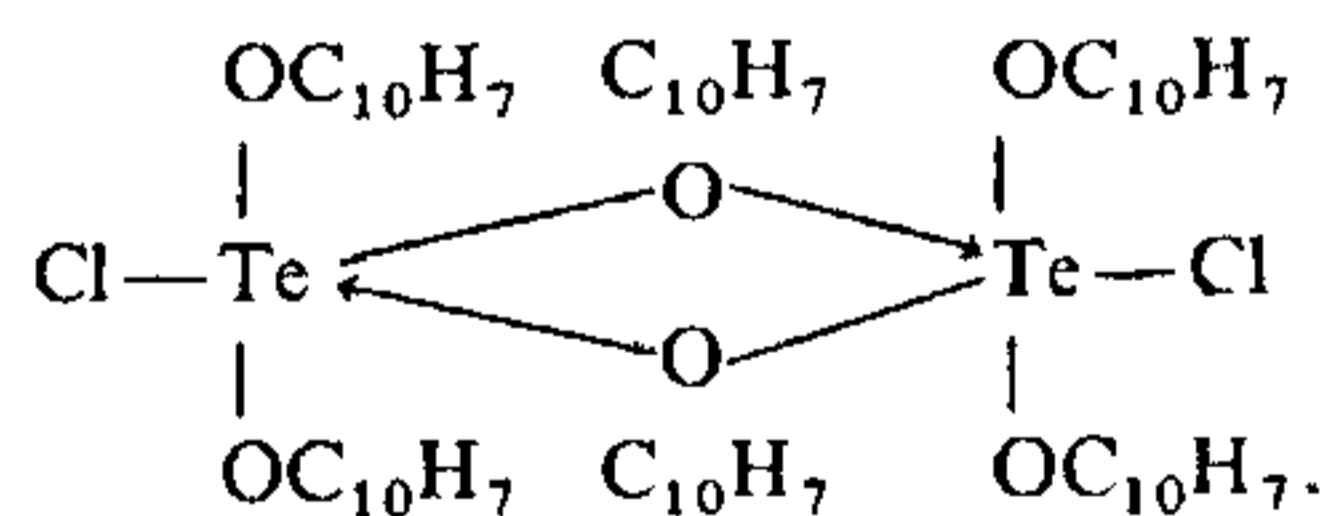
$Te \begin{array}{c} \diagup O \diagdown \\ \diagdown O \diagup \end{array} Te$ modes⁸ respectively. In the case of TeCl₃(OC₁₀H₇), however, only bands due to the bridging $Te \begin{array}{c} \diagup O \diagdown \\ \diagdown O \diagup \end{array} Te$ modes could be observed.

Apart from these bands due to the tellurium–oxygen bond, sharp bands in the region 350–370 cm⁻¹ can be assigned to the ν_{Te-Cl} modes^{9–11}. No band that

could be assigned to the bridging $Te \begin{array}{c} \diagup Cl \diagdown \\ \diagdown Cl \diagup \end{array} Te$ mode expected to fall well below 300 cm⁻¹ has been observed, thus suggesting that bridging in these compounds is through naphthoxy groups and not through chlorines. All important bands are given in table 1.

Apart from these bands, it is quite significant that no band was observed in the region 200–250 cm⁻¹, which otherwise could have been assigned to ν_{Te-C} modes¹², thus excluding the formation of organometallic hydroxyphenyltellurium(IV) halides. These observations are in contrast to those of Khandelwal *et al.*⁵, who have reported involvement of ring proton and not of phenolic OH in evolution of HCl gas in the reaction of phenol with TeCl₄ thereby giving hydroxyphenyltellurium(IV) halides. But we are aware, in view of limited evidence, that the possibility of formation of hydroxynaphthyltellurium(IV) chloride cannot be completely ruled out, because there was always a very small amount of solid left in the solution after the reaction was over, which could not be analysed properly because of limited resources and was therefore rejected.

Thus, based on limited IR spectroscopic observations coupled with conductance and cryoscopic studies, dimeric structures bridging through naphthoxy groups may be proposed. The structure, of TeCl(OC₁₀H₇)₃ may therefore be written as



Similar structures may be written for other compounds.

The five-atom coordination around tellurium attained through naphthoxy bridges has changes to six-atom coordination when these naphthoxides are allowed to react with strong bases such as pyridine, piperidine, γ -picoline, 2,2'-bipyridine and 1,10-phenanthroline. These bases react exothermally with the naphthoxides of tellurium(IV) forming compounds of composition TeCl_{4-n}(OC₁₀H₇)_n.2L and TeCl_{4-n}(OC₁₀H₇)_n.B with monodentate (L) and bidentate

Table 2 Analytical data for the adducts of tellurium (IV) naphthoxides

Compound	Colour	Found (calcd), %		Λ_M (ohm ⁻¹ cm ² mol ⁻¹)	Molecular weight, found (calcd)
		Te	Cl		
TeCl ₃ (OC ₁₀ H ₇) ₂ .2 py	Dirty green	23.92 (23.90)	19.83 (19.88)	15.2	528 (535.5)
TeCl ₃ (OC ₁₀ H ₇) ₂ .2 pip	Light green	23.33 (23.37)	19.39 (19.45)	12.6	537 (547.5)
TeCl ₃ (OC ₁₀ H ₇) ₂ .2 γ -pic	Light brown	22.69 (22.71)	18.93 (18.89)	14.1	569 (563.5)
TeCl ₃ (OC ₁₀ H ₇) ₂ .bipy	Light green	23.93 (23.94)	19.92 (19.96)	16.3	539 (533.5)
TeCl ₃ (OC ₁₀ H ₇) ₂ .phen	Light green	22.99 (22.95)	19.07 (19.10)	16.9	552 (557.5)
TeCl ₂ (OC ₁₀ H ₇) ₂ .2 py	Light green	19.88 (19.90)	11.08 (11.04)	13.2	642 (643)
TeCl ₂ (OC ₁₀ H ₇) ₂ .2 pip	Light green	19.58 (19.54)	10.79 (10.83)	11.7	658 (655)
TeCl ₂ (OC ₁₀ H ₇) ₂ .2 γ -pic	Light brown	19.12 (19.07)	10.55 (10.58)	12.5	622 (671)
TeCl ₂ (OC ₁₀ H ₇) ₂ .bipy	Light green	20.00 (19.96)	11.11 (11.07)	—	648 (641)
TeCl ₂ (OC ₁₀ H ₇) ₂ .2 phen	Light green	19.30 (19.24)	10.68 (10.67)	—	671 (665)
TeCl(OC ₁₀ H ₇) ₃ .2 py	Dirty green	17.00 (17.05)	4.70 (4.73)	11.0	744 (750.5)
TeCl(OC ₁₀ H ₇) ₃ .2 pip	Light green	16.72 (16.78)	4.68 (4.65)	10.8	763 (762.5)
TeCl(OC ₁₀ H ₇) ₃ .2 γ -pic	Light brown	16.49 (16.44)	4.52 (4.56)	9.7	771 (778.5)
TeCl(OC ₁₀ H ₇) ₃ .bipy	Light green	17.03 (17.10)	4.75 (4.74)	13.2	756 (748.5)
TeCl(OC ₁₀ H ₇) ₃ .phen	Light green	16.59 (16.56)	4.64 (4.59)	13.4	766 (772.5)

(B) ligands respectively, as evidenced by the elemental analysis data given in table 2. Molar conductance values of millimolar solutions of these compounds in nitrobenzene are comparable with the values reported for 1:1 electrolytes. Interestingly, the values of conductance of these addition compounds are a little higher than those of the parent naphthoxides, which suggests that the coordination of the additional monodentate or bidentate nitrogen ligand promotes ionization of the tellurium-halogen bond, thereby causing an increase in conductance. The molecular weights of these adducts in nitrobenzene suggest that they are nearly monomeric.

Coordination of the ligands to the central metal has been ascertained from the shifts of the $\nu_{C=C}$ and $\nu_{C=N}$ modes¹³⁻¹⁶, observed usually in the region 1400-1600 cm⁻¹ in the pure ligands, towards higher regions on adduct formation, in agreement with the earlier reports. Coordination of piperidine to tellurium was indicated by lowering of the band

present at 3291 cm⁻¹ due to ν_{N-H} by 50-60 cm⁻¹ on adduct formation¹³. Another significant band at 822 cm⁻¹, due to the H-N-C deformation mode¹⁰, is shifted to higher regions, by about 30-40 cm⁻¹. The appearance of new bands in the region 270-280 cm⁻¹ in these adducts may be assigned to the ν_{Te-N} modes, which confirms the coordination of nitrogen of the ligand to the metal.

In the IR spectra of these adducts, it is significant that bands due to the bridging $Te \begin{array}{c} \diagup O \diagdown \\ \end{array} Te$ modes in the parent naphthoxides disappear on adduct formation and, instead, sharp bands in the region 540-580 cm⁻¹ assigned to the terminal ν_{Te-O} modes are observed. This suggests that there is a rupturing of naphthoxy bridging followed by coordination of the ligand, forming hexacoordinated tellurium compounds. Similar observations have been made earlier also in the case of adducts of phenoxides of niobium(V) and tantalum(V) with nitrogenous bases⁴.

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ANNOUNCEMENTS

Training Course in Ethnobotany

Place: Lucknow
 Date: March 1990
 Contact: Dr S. K. Jain
 Course Director
 National Botanical Research Institute
 Lucknow 226 001

2-Day Scientific Communication Teaching Courses

Place: Patna
 Date: 17-18 March 1990
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 Dept of Gastroenterology
 IGIMS, Sheikhpura
 Patna 800 014

Place: Srinagar
 Date: 20-21 March 1990
 Contact: Dr A. H. Durrani
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 Dept of Medicine
 Srinagar Medical College
 Srinagar 190 010

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 Date: 11-13 December 1989
 Contact: Dr Kunthala Jayaraman
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 Anna University
 Madras 600 025

National Symposium on Recent Advances in Digital Signal Processing (DSP) and its Impact on the Development of Electronic Instrumentation

Place: Bombay
 Date: 10-12 January 1990
 Contact: Sri A. M. Patankar
 Convener
 Electronics Division
 Bhabha Atomic Research Centre
 Bombay 400 085
