

Study on Some Aryltellurium(IV) Complexes of 2,3-Bis(salicylideneamino)-Pyridine Schiff Base

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ABSTRACT

Eight new aryltellurium and diaryltellurium (IV) chelate with dibasic tetradentate schiff base formed by condensation of salicylaldehyde and 2,3-diaminopyridine having formula $ArTeCl.L$ and $Ar_2Te.L$ have been synthesized and characterized by elemental analyses, infrared and proton magnetic resonance studies. The data predict the hexa coordination of tellurium atom by dibasic tetradentate -N, -N', -O, and -O' Schiff base having distorted octahedral geometry.

Keyword: Salicylaldehyde, 2, 3-diaminopyridine, aryltellurium (IV) and Schiff base.

I. INTRODUCTION

The Schiff base involving a pyrimidine ring like pyridoxazole and pyridoxamine have received considerable attention in the literature which play an important role in biological system¹. The condensation products of aminopyridines and o-hydroxy aromatic aldehyde are attractive from several points of view. The anti-inflammatory activity of 2-salicylidene aminopyridine and corresponding complex with metal has been reported². Hadjoudis³ reported photochromic and thermochromic behavior of a series of 2, 3 and 4-salicylideneaminopyridines⁴. The appearance of both phenomena was linked with intramolecular proton transfer. Sustained interest in the characteristic of the aryltellurium complexes of Schiff base derived from condensation of 2,3-aminopyridine and salicylaldehyde. Also, aryltellurium(IV) chlorides are known⁵⁻¹⁵ to act as Lewis acids and form complexes with several N-, O- and S- donor bases. In view of this, we herein report some new complexes derived from aryltellurium(IV) trichlorides, R_1TeCl_3 and diaryltellurium(IV) dichlorides, R_2TeCl_2 with 2,3-bis(salicylideneamino)-pyridine Schiff base.

II. EXPERIMENTAL

All preparations were carried out under an atmosphere of dry N_2 and the solvents used were purified by standard method^{16,17} before use. The purity of compounds was checked by Thin Layer Chromatography using Silica gel-G (Merck). Melting points were determined in open capillary tube and are uncorrected. Carbon, hydrogen and nitrogen analyses were obtained microanalytically from SAIF, Panjab University Chandigarh on a ThermoFinnigan CHNS analyser. IR(4000-400 cm^{-1}) and far IR(400-50 cm^{-1}) spectra were recorded in KBr/polyethylene pellets on a F.T. Infra-Red Spectrophotometer Model RZX (Perkin Elmer) at SAIF, Panjab University Chandigarh. Proton Magnetic Resonance Spectra were recorded in $DMSO-d_6$ using TMS as an internal reference on BRUKER AVANCE II 400 NMR spectrometer.

Preparation of Aryltellurium(IV) Trichlorides and Diaryltellurium(IV) Dichlorides p-Methoxyphenyltellurium(IV) trichloride^{18,19}, bis(p-methoxyphenyl)tellurium(IV) dichloride^{19,20}, p-ethoxyphenyltellurium (IV) trichloride²¹, bis(p-

ethoxyphenyl)tellurium dichloride²¹, p-hydroxyphenyltellurium (IV) trichloride²², bis(p-hydroxyphenyl) tellurium (IV) dichloride²², 3-methyl-4-hydroxyphenyl tellurium (IV) trichloride²³ and bis(3-methyl-4-hydroxyphenyl) tellurium (IV) dichloride²³ were prepared by the reactions of TeCl₄ with anisole, phenetole, phenol, o-cresol respectively, by the methods reported in the literature¹⁸⁻²³.

Preparation of 2, 3-bis(salicylideneamino)-pyridine Schiff Base (L)¹⁰⁻¹⁵

Schiff base was prepared by mixing 2:1 stoichiometric amount of analytically pure salicylaldehyde with 2, 3-diaminopyridine dissolved in ethanol and refluxing for 4 hours on water bath. The evaporation of the resulting solution to half the volume, the separated orange crystal was filtered off and recrystallized from ethanol.

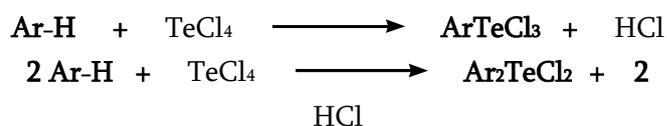
Preparation of Schiff base Complexes of Aryltellurium(IV) Trichlorides and Diaryltellurium(IV) Dichlorides

Aryltellurium(IV) trichlorides, ArTeCl₃ and diaryltellurium(IV) dichlorides Ar₂TeCl₂ (Ar = p-methoxyphenyl, p-ethoxyphenyl, p-hydroxyphenyl and 3-methyl-4-hydroxyphenyl), when reacted with sodium salt of schiff base in equimolar ratio, yield ArTeCl.L and Ar₂Te.L type complexes. Sodium salt of the ligand was prepared by reacting equimolar (2:1) quantity of sodium metal and Schiff base in methanol. The solvent was distilled off to obtain sodium salt of Schiff base. Then a methanolic saturated solution of 2 mmol of aryltellurium(IV) trichloride or diaryltellurium(IV) dichloride was added dropwise to suspension of 2 mmol of sodium salt of Schiff base in about 50 mL benzene under reflux. The reaction mixture was further refluxed for 3-4 hours, cooled and precipitated sodium chloride was filtered off. The filtrate was then concentrated to about one third of original volume under reduced pressure and cooled in an ice bath to obtain coloured product. This was

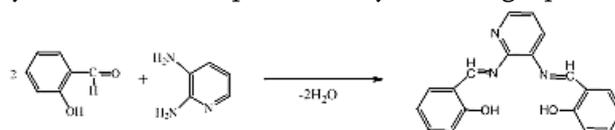
filtered, washed with benzene + methanol (1:1) and dried in vacuum desiccator over P₄O₁₀.

III. RESULTS AND DISCUSSION

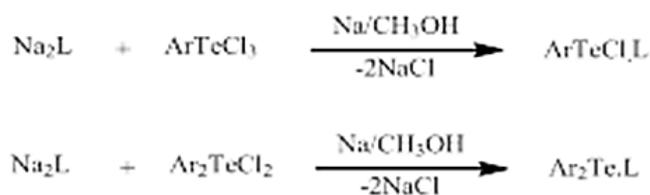
TeCl₄ when heated with anisole, phenetole, phenol, o-cresol (Ar-H) appears to undergo Friedel-Crafts type condensation reaction whereby TeCl₃⁺ unit attacks a position para to the methoxy/ethoxy/hydroxy groups in the aromatic rings, thus resulting in the formation of aryltellurium(IV) trichlorides and diaryltellurium(IV) dichlorides.



Preparation of Pyridoxylidene-trimethoprim Schiff base (L) by the reaction of trimethoprim drug and Pyridoxal can be represented by following equations.



Sodium salt of 2,3-bis(salicylideneamino)-pyridine Schiff base (Na₂L) reacts with aryltellurium (IV) trichlorides and diaryltellurium (IV) dichlorides in 1:1 molar ratio to yield the corresponding aryltellurium(IV) complexes.



All the tellurium(IV) complexes are coloured, crystalline solids, stable at room temperature and non-hygroscopic in nature. The complexes have been analysed for their tellurium, chlorine, carbon, hydrogen and nitrogen contents and the data along with their physical properties and yields are presented in Table 1.

Table1. Analytical Data and Physical Properties of 2,3-bis(salicylideneamino)-pyridine Complexes of Tellurium(IV)

Compound No.	Complex	Empirical Formula (Formula Wt.)	Colour (Yield, %)	M. Pt. (°C) dec.	Analyses % Found (Calculated)				
					C	H	N	Te	Cl
Schiff Base	2,3-bis(salicylideneamino)-pyridine(L)	C ₁₉ H ₁₅ N ₃ O ₂ (317.34)	Orange (80)	134-136	71.79 (71.91)	4.44 (4.78)	13.07 (13.24)	-	-
1	ArTeClL (p-methoxyphenyl)	C ₂₆ H ₂₀ ClN ₃ O ₃ Te (585.5)	Pale yellow (84)	180-182	53.28 (53.33)	3.99 (3.44)	7.01 (7.18)	21.59 (21.79)	5.97 (6.06)
2	ArTeClL (p-ethoxyphenyl)	C ₂₇ H ₂₂ ClN ₃ O ₃ Te (599.53)	Cream (82)	198-200	47.41 (54.09)	4.02 (3.70)	9.13 (7.18)	16.58 (21.28)	9.13 (5.91)
3	ArTeClL (p-hydroxyphenyl)	C ₂₅ H ₁₈ ClN ₃ O ₃ Te (571.48)	Brown (88)	192-194	45.98 (52.54)	3.95 (3.17)	9.50 (7.35)	17.39 (22.33)	9.23 (6.20)
4	ArTeClL (3-methyl-4-hydroxyphenyl)	C ₂₆ H ₂₀ ClN ₃ O ₃ Te (585.5)	Dark brown (72)	210-212	53.25 (53.33)	3.78 (3.44)	7.07 (7.18)	21.64 (21.79)	5.93 (6.06)
5	Ar ₂ Te.L (p-methoxyphenyl)	C ₃₃ H ₂₇ N ₃ O ₄ Te (657.19)	Yellow (80)	170-172	60.27 (60.31)	4.81 (4.13)	6.01 (6.39)	19.59 (19.42)	-
6	Ar ₂ Te.L (p-ethoxyphenyl)	C ₃₅ H ₃₁ N ₃ O ₄ Te (685.24)	Light cream (85)	188-190	61.27 (61.35)	4.43 (4.56)	6.07 (6.13)	18.59 (18.62)	-
7	Ar ₂ Te.L (p-hydroxyphenyl)	C ₃₁ H ₂₃ N ₃ O ₄ Te (629.13)	Dark red (78)	182-184	59.07 (59.18)	3.57 (3.68)	6.59 (6.68)	20.19 (20.28)	-
8	Ar ₂ Te.L (3-methyl-4-hydroxyphenyl)	C ₃₃ H ₂₇ N ₃ O ₄ Te (657.19)	Red (70)	150-152	60.17 (60.31)	4.88 (4.13)	6.06 (6.39)	19.49 (19.42)	-

Infrared Spectra

The IR spectra of Schiff base and its complexes with aryltellurium(IV) are compared in order to determine the coordination sites involved in the chelation. The position or intensities of some guide peaks in the spectrum of ligand are changed upon chelation. The characteristic peaks are listed in Table 2.

Upon comparison it is found that

1. IR spectra of Schiff base spectrum shows the presence of a weak broad band at 2730 cm⁻¹ due to intramolecular hydrogen bonding between hydrogen atom of hydroxyl group present on salicylidene part and lone pair on nitrogen atom of two azomethine groups by forming six membered conjugate chelate ring^{24,25}. This band disappears on the complexation, which indicates that these hydroxyl groups coordinate to tellurium after deprotonation^{26,27}.
2. The involvement of deprotonated -OH group of salicylidene part in chelation is confirmed by the shift of the phenolic C-O stretching band

toward higher frequency, observed at 1285 cm⁻¹ in the free ligand, to the extent of 20-55 cm⁻¹ in the complexes²⁴.

3. In addition to this a spectra of Schiff base ligand, a strong band in the region 1630 cm⁻¹ as well as the band at 1580 cm⁻¹ are assigned to azomethine groups. This band is shifted to higher and lower wavenumbers²⁴⁻²⁷ (± 30 cm⁻¹) in the complexes indicating the participation of the two azomethine group nitrogens in coordination⁹⁴.
4. New bands are found in spectra of complexes in the region 273-298 cm⁻¹, which are assigned to ν_{Te-O} stretching vibration²⁸ for Schiff base tellurium complexes. The bands at 408-420 cm⁻¹ in complexes have been assigned to ν_{Te-N} of the azomethine mode¹⁰⁻¹⁵.

From IR studies, it is conclude that Schiff base behave as a dibasic tetradentate ligand with -N, N', -O and -O' donor sites coordinating to aryltellurium(IV) chloride via two azomethine N and also by two deprotonated phenolic -O atom.

Table 2. Important Infrared Absorption Bands (cm^{-1}) of Schiff Base and Complexes.

Complex	V(O-H) intramolecular Hydrogen bonding	V(CH=N) Azomethine groups	V(C-O) phenolic group	V(Te-N)	V(Te-O)
Schiff base(L)	2730 vw	1630 vs 1580 s	1285	-	-
1	-	1620 vs 1560 s	1310	408 m	298 w
2	-	1610 vs 1565 s	1320	410 m	284w
3	-	1612 vs 1570 s	1315	415 s	272 w
4	-	16318 vs 1579 s	1305	420 s	282 w
5	-	1621 vs 1572 s	1318	418 s	288 w
6	-	1614 vs 1576 s	1313	412 m	273 w
7	-	1612 vs 1566 s	1340	414 m	286 w
8	-	1620 vs 1571 s	1333	420 m	274 w

^1H NMR Spectra

The proton chemical shift data of Schiff base and its complexes are given in Table 3.

1. In the ^1H NMR spectra of Schiff base shows two singlets at 13.38 δ ppm and 12.85 δ ppm are attributed to phenolic OH groups present in salicylidene parts²⁹ indicates strong intramolecular hydrogen bonding³⁰⁻³¹. The absence of these peaks in all complexes is as a result of enolization followed by deprotonation, indicates phenolic OH groups of salicylidene takes part in coordination³².
2. In Schiff base ligand the azomethine protons³¹ resonate as two singlets of methine protons at 9.622 δ ppm and 8.561 δ ppm which shift to downfield in complexes as compared to the free ligand, suggesting deshielding³² of azomethine

proton due to coordination³³⁻³⁵ to metal ion through the two azomethine nitrogen atom.

Thus, on the basis of IR and ^1H NMR spectral studies, it may be concluded that Schiff base act as a dibasic tetradentate ligand. The IR and NMR peaks of Schiff base shown in figure are as below:

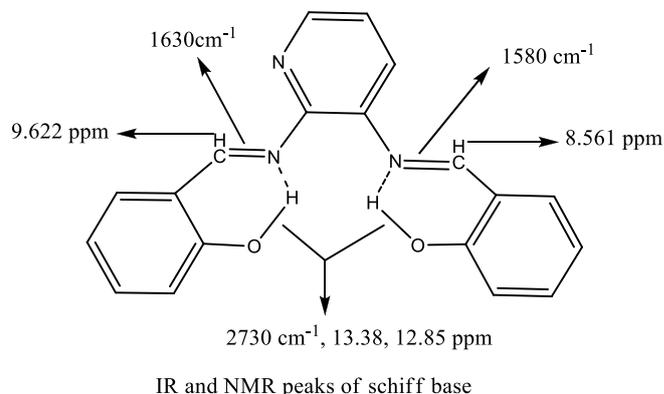


Table 3. ^1H NMR Spectral Data of Schiff Base and Complexes in DMSO-d_6 .

Compound	(O-H) intramolecular Hydrogen bonding	Azomethines-H		Aromatic proton-H
Schiff base(L)	13.38 s, 12.85 s	9.622 s	8.561 s	6.82-8.42 m
1	-	9.753 s	8.664 s	6.13-8.12 m
2	-	9.761 s	8.695 s	6.42-8.18 m
3	-	9.733 s	8.701s	6.57-8.09 m
4	-	9.784 s	8.715 s	6.47-8.81 m
5	-	9.766 s	8.612 s	6.72-8.18 m
6	-	9.781 s	8.656 s	6.82-8.25 m
7	-	9.718 s	8.711 s	6.36-8.33 m
8	-	9.739s	8.716 s	6.43-8.53 m

s = singlet, m = multiplet

On the basis of these studies, the proposed structures for the complexes are as below (Figure 1).

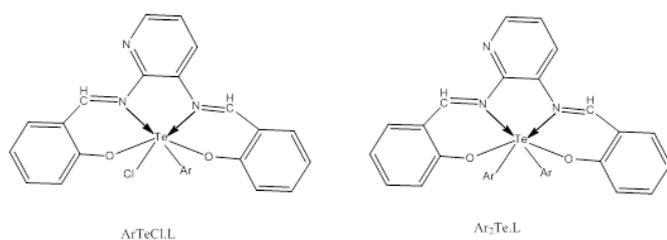


Figure:1 Proposed diagram of complexes

IV. CONCLUSION

Schiff base has been synthesized by condensation of salicylaldehyde with 2,3-diaminopyridine in 2:1 molar ratio. Sodium salt of this Schiff base when reacted with aryltellurium(IV) chlorides in 1:1 molar ratios yield ArTeCl.L and $\text{Ar}_2\text{Te.L}$ ($\text{Ar} = \text{p-methoxyphenyl}$, p-ethoxyphenyl , p-hydroxyphenyl and $\text{3-methyl-4-hydroxyphenyl}$) type complexes. The data predict the hexa coordination of tellurium atom by dibasic tetradentate $-\text{N}$, $-\text{N}'$, $-\text{O}$, and $-\text{O}'$ Schiff base having distorted octahedral geometry.

V. ACKNOWLEDGEMENT

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