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STUDY ON PICOLINE COMPLEXES OF p-HYDROXYPHENYLTELLURIUM (IV) TRIHALIDES

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ABSTRACT

Eighteen new complexes of *p*-hydroxphenyltellurium trihalides, *p*-$HOC_6H_4TeX_3$ (X = Cl, Br, I) with α-, β- and γ- picolines, $RTeX_3$. Pic and $RTeX_3$. 2 Pic, have been synthesized and characterized by elemental analyses, conductance, cryoscopy, infrared and proton magnetic resonance studies. Conductance measurements in nitrobenzene, acetone and acetonitrile predict their non-electrolyte to 1 : 1 electrolyte type behaviour in solution, which is well supported by cryoscopic studies in nitrobenzene. Spectral studies indicate the linkage of picoline molecules to the tellurium atom of hydroxyphenyltellurium group through the nitrogen atom. Square-pyramidal and octahedral structures have been suggested for $RTeX_3$. Pic and $RTeX_3$. 2Pic, respectively.

Key words : *p*-Hydroxyphenyltellurium trihalides, α-, β- and γ- Picolines, Picoline complexes

INTRODUCTION

Organyltellurium trichlorides are known to behave as Lewis acids and form molecular complexes with several N-, O- and S- donor bases[1-9]. Some of these are reported[6,7] to posses antimicrobial activity as well. The hydroxyaryltellurium trihalide have two active sites to interact with the Lewis bases, the phenolic OH and the acceptor tellurium atom. In continuation of our earlier work on the complexes of hydroxyaryltellurium trihalides[10-14] with various bases, we hereby report the synthesis and characterization of picoline complexes of p-hydroxyphenyltellurium trihalides.

EXPERIMENTAL

Materials and methods

All the chemicals used were of Anal AR grade. Solvents were purified and dried by conventional methods[15,16]. p-Hydroxyphenyl trichloride was prepared by reaction of tellurium tetrachloride with phenol[17,18] and the corresponding tribromide and triiodide by the halogen-exchange processes[17,18].

Preparation of picoline complexes

$RTeX_3$ .Pic

A solution of 5 mmol of picoline in about 5 mL of dry benzene was added to a saturated solution of 5 mmol of p-hydroxyphenyltellurium trihalide in dry methanol taken in a RB flask. The contents were refluxed for 2 - 3 h under an atmosphere of dry N_2 and then concentrated to about 10 mL under reduced pressure. This was left overnight to get crystals of the product, which was filtered, washed with chloroform and dried in a vacuum desiccator over P_410_{10}.

$RTeX_3$.2Pic

A saturated solution of 5 mmol of $RTeX_3$ in dry methanol was added slowly and with constant stirring to a solution of 10 mmol of picoline in about 10 mL benzene. The contents were stirred for about 2 - 3 h under an atmosphere of dry N_2. This resulted in the separation of a solid product. A second crop was obtained after concentration of filterate to about one third of its original volume. The complex was filtered, washed with chloroform and dried over P_4O_{10} in vacuum desiccator.

All the complexes were recrystallized from dry methanol. The purity was checked by TLC using silica-gel plates. The complexes were analysed for tellurium, halogen, carbon, hydrogen and nitrogen contents. The analytical data are compiled in Table 1.

Physical studies

Conductance studies were performed under dry conditions at 25 ± 2^oC in nitrobenzene, acetone and acetonitrile using a Systronics conductance bridge type 305 and dip-type cell with smooth platinum electrodes. Molecular weights were determined cryoscopically in dry nitrobenzene upto the saturation point. IR spectra were recorded on a Shimazdu FT IR–8300 Infrared spectrophotometer. ^1H NMR spectra were obtained from S.A.I.F, Punjab University, Chandigarh, in DMSO-d_6 using tetramethylsilane as an internal reference.

Table 1: Analytical data, physical properties and yields for picoline complexes of p-hydroxyphenyltellurium trihalides

S. No.	Complex (Empirical formula)	Colour (Formula wt.)	Analyses found (calculated) %					M.P., (^{o}C) (dec.)	Yield (%)
			Te	X	C	H	N		
1	$RTeCl_3.\alpha$-Pic ($C_{12}H_{12}Cl_3NoTe$)	Cream (420.9)	29.78 (30.37)	24.98 (25.31)	34.10 (34.30)	2.45 (2.88)	2.96 (3.33)	122-125	60
2	$RTeCl_3.2\alpha$-Pic ($C_{18}H_{19}Cl_3N_2OTe$)	Light yellow (513.3)	25.21 (24.86)	20.61 (20.72)	41.65 (42.12)	3.49 (3.73)	5.10 (5.46)	178-180	75
3	$RTeBr_{3.}\alpha$-Pic ($C_{12}H_{12}Br_3NoTe$)	White (552.7)	22.65 (23.05)	42.68 (43.31)	26.00 (26.04)	1.99 (2.19)	2.21 (2.53)	200-203	80
4	$RTeBr_3.2\alpha$-Pic ($C_{18}H_{19}Br_3N_2oTe$)	Dull white (646.7)	18.98 (19.73)	36.80 (37.07)	33.10 (33.43)	3.16 (2.96)	4.57 (4.33)	185-188	85
5	$RTeI_{3.}\alpha$-Pic ($C_{12}H_{12}I_3NoTe$)	Orange (694.5)	18.59 (18.37)	54.65 (54.81)	21.11 (20.75)	1.45 (1.74)	1.79 (2.02)	190-192	70
6	$RTeI_3.2\alpha$-Pic ($C_{18}H_{19}I_3N_2oTe$)	Dark orange (787.7)	15.90 (16.20)	47.85 (48.33)	27.31 (27.45)	2.22 (2.43)	3.30 (3.56)	145-146	50
7	$RTeCl_3.\beta$-Pic ($C_{12}H_{12}Cl_3NoTe$)	White (420.9)	30.05 (30.37)	25.08 (25.31)	33.86 (34.30)	2.45 (2.88)	3.15 (3.33)	180-183	70
8	$RTeCl_3.2\beta$-Pic ($C_{18}H_{19}Cl_3N_2OTe$)	Dull white (513.3)	23.98 (24.86)	20.56 (20.72)	41.69 (42.12)	3.46 (3.73)	5.35 (5.46)	200-203	80
9	$RTeBr_3.\beta$-Pic ($C_{12}H_{12}Br_3NoTe$)	Cream (552.7)	22.56 (23.05)	43.15 (43.31)	25.70 (26.04)	1.87 (2.19)	2.15 (2.53)	175-178	65

S. No.	Complex (Empirical formula)	Colour (Formula wt.)	Analyses found (calculated) %					M.P., (^oC) (dec.)	Yield (%)
			Te	X	C	H	N		
10	$RTeBr_3$. 2β-Pic ($C_{18}H_{19}Br_3N_2oTe$)	Pale yellow (646.70)	19.41 (19.73)	36.61 (37.07)	33.76 (33.43)	2.43 (2.96)	4.67 (4.33)	195-197	50
11	$RTeI_3$.β-Pic ($c_{12}H_{12}I_3NoTe$)	Greenish yellow (694.50)	18.56 (18.37)	54.98 (54.81)	20.35 (20.75)	1.54 (1.74)	2.41 (2.02)	142-144	75
12	$RTeI_3$.2β-Pic ($C_{18}H_{19}I_3N_2oTe$)	Orange (787.70)	16.35 (16.20)	48.17 (48.33)	27.31 (27.45)	2.16 (2.43)	3.67 (3.56)	210-213	60
13	$RTeCl_3$.γ-Pic ($C_{12}H_{12}Cl_3NoTe$)	Light cream (420.90)	29.87 (30.37)	25.01 (25.31)	34.35 (34.30)	2.56 (2.88)	3.02 (3.33)	180-183	65
14	$RTeCl_3$.2γ-Pic ($C_{18}H_{19}Cl_3N_2OTe$)	Dull white (513.30)	24.46 (24.80)	20.11 (20.72)	41.8 (42.12)	3.37 (3.73)	5.86 (5.46)	>240	75
15	$RTeBr_3$.γ-Pic ($C_{12}H_{12}Br_3NoTe$)	Cream (552.70)	23.45 (23.05)	44.1 (43.31)	26.51 (26.04)	1.8 (2.19)	2.87 (2.53)	140-143	85
16	$RTeBr_3$.2γ-Pic ($C_{18}H_{19}Br_3N_2oTe$)	Light yellow (646.70)	19.56 (19.73)	36.5 (37.07)	33.67 (33.43)	2.45 (2.96)	4.02 (4.33)	180-183	65
17	$RTeI_3$.γ-Pic ($C_{12}H_{12}I_3NoTe$)	Dark brown (694.50)	18 (18.37)	54.2 (54.81)	20.47 (20.75)	1.23 (1.74)	1.8 (2.02)	>230	75
18	$RTeI_3$.2γ-Pic ($C_{18}H_{19}I_3N_2oTe$)	Orange (787.70)	15.83 (16.20)	48.53 (48.33)	27.78 (27.45)	2.1 (2.43)	3.31 (3.56)	150-153	85

RESULTS AND DISCUSSION

p-Hydroxyphenyltellurium trihalides, $RTeX_3$ (X = Cl, Br, I), when reacted with isomeric picolines, form 1 : 1 as well as 1 : 2 molecular complexes.

$$RTeX_3 + Pic \rightarrow RTeX_3 \cdot Pic$$

$$RTeX_3 + 2\,Pic \rightarrow RTeX_3 \cdot 2\,Pic$$

These complexes are coloured solids in dry air and soluble in polar organic solvents.

Conductance and cryoscopic studies

The molar conductance data of these complexes in nitrobenzene, acetone and acetonitrile and the cryoscopic data in nitrobenzene are given in Table 2.

The molar conductance, Λ_M values for picoline complexes reflect their non-electrolyte to weak-electrolyte type behaviour in solutions except $RTeBr_3$. 2β-Pic, $RTeI_3$. β-Pic, $RTeBr_3$. γ-Pic and $RTeBr_3$. 2γ-Pic where the Λ_M values in nitrobenzene lie within or close to the expected ranges[19] for 1 : 1 electrolytes. This may be due to the dissociation of these complexes into $[RTeX_2 \cdot Pic/ RTeX_2 \cdot 2\,Pic]^+$ and X^- ions (Pic = β- or γ-picoline ; X = Br or I). The conductance behaviour of picoline complexes is well supported by the conductance data in nitrobenzene.

Infrared spectral studies

The infrared spectra of picoline complexes of *p*-hydroxyphenyltellurium trihalides show the presence of bands pertaining to hydroxyl group indicating thereby the non interaction of phenolic OH group with the picolines. The most important band of picolines, which upon complexation undergoes a distinct positive shift is $\nu_{C=N}$, which in parent picolines appear around 1574 –1578 cm^{-1}, and in the complexes, it is shifted[3,6,8,20,21] by about +50 cm^{-1}. All the picoline complexes of *p*-hydroxyphenyltellurium trihalides show new band around 1635 cm^{-1}, which suggests the linkage of picoline molecules to tellurium through the nitrogen atom.

Proton magnetic resonance spectral studies

The ^1H NMR data for some picoline complexes are presented in Table 3.

Table 2. Molar conductance, cryoscopic and IR data for picoline complexes of p-hydroxyphenyltellurium

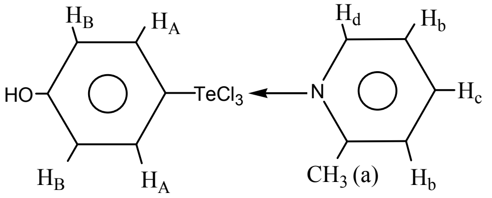
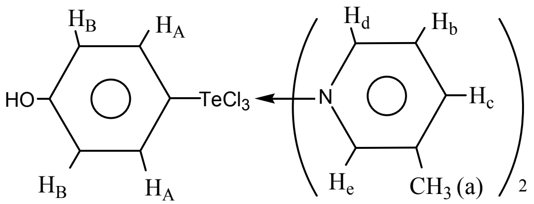
S. No.	Complex	Λ_M at ca. 10^{-3} M, ohm^{-1} cm^2 mol^{-1}			Formula weight	Conc. range, (mmol/L)	Average mol. wt. found in nitrobenzene	$\nu_{C=N}$ (cm^{-1})
		Nitrobenzene	Acetone	Acetonitrile				
1	$RTeCl_3.\alpha$-Pic	2.01	36.50	63.21	420.9	2.34 - 5.46	394.9	1632 w
								1618 w
2	$RTeCl_3.2\alpha$-Pic	2.31	42.50	67.27	513.3	1.73 - 3.45	495.1	1648 m
								1635 m
3	$RTeBr_3.\alpha$-Pi c	4.31	43.47	72.16	552.7	2.47 - 3.72	539.2	1650 m
								1612 m
4	$RTeBr_3.2\alpha$-Pic	4.52	52.51	82.11	646.7	3.45 - 5.74	628.4	1635 m
5	$RTeI_3.\alpha$-Pic	7.20	80.37	25.30	694.5	1.54 - 3.94	682.5	1651 m
								1635 w
6	$RTeI_3.2\alpha$-Pi c	8.35	59.67	15.74	787.7	2.74 - 9.02	785.0	1638 mb
								1615 w
7	$RTeCl_3.$ β-Pic	*	*	*	420.9	*		1625 w
8	$RTeCl_3.2\beta$-Pic	*	*	*	513.3	*		1645 vw
								1630 vw
9	$RTeBr_3.$ β-Pic	3.08	66.04	*	552.7	1.34 - 3.42	516.3	1635 w
10	$RTeBr_3.2\beta$-Pic	18.83	53.22	*	646.7	1.46 - 2.87	555.7	1635 vw
								1610 vw

S. No.	Complex	Λ_M at ca. 10^{-3} M, ohm^{-1} cm^{2} mol^{-1}			Formula weight	Conc. range, (mmol/L)	Average mol. wt. found in nitrobenzene	$\nu_{C=N}$ (cm^{-1})
		Nitrobenzene	Acetone	Acetonitrile				
11	$RTeI_3$. β-Pic	18.91	28.83	*	694.5	2.64 - 4.98	581.7	1625 w
12	$RTeI_3$.2β-Pic	12.42	25.06	27.21	787.7	2.11 - 3.16	687.1	1625 w
13	$RTeCl_3$. γ-Pic	1.28	12.02	*	420.9	1.23-2.87	422.4	1638 m
14	$RTeCl_3$.2 γ –Pic	6.71			513.3	2.46-4.26	507.1	1635 w
15	$RTeBr_3$. γ -Pic	23.10	78.34	*	552.7	1.34-3.47	391.8	1638 w
16	$RTeBr_3$.2 γ -Pic	20.31	45.83	*	646.7	2.15-5.32	458.3	1645 m
17	$RTeI_3$. γ –Pi c	17.20	49.21	*	694.5	1.11-5.66	633.7	1635 m
18	$RTeI_3$.2 γ -Pic	15.43	45.34	*	787.7	2.34-4.84	636.6	1650 m

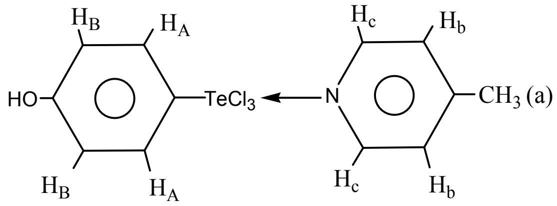
Λ_M reported for 1 : 1 electrolyte : nitrobenzene = 20 - 30, acetone = 100 - 140 and acetonitrile = 120 - 160.

* Not soluble ; w = weak , m = medium , v = very

Table 3. ^{1}H NMR data (δ ppm) for picoline complexes of p-hydroxyphenyl tellurium trihalides in DMSO-d_6.

Complex	Chemical shift (δ ppm)	Assignment
$RTeCl_3$. α-Pic	2.79^{s} (3H)	-CH_3, H_a
	6.91^{d} (*9Hz*, 2H)	H_B
	7.76^{m} (3H)	H_b and H_c
	7.80^{d} (*9Hz*, 2H)	H_A
	8.73^{d} (*5Hz*, 1H)	H_d
	9.97^{b} (1H)	-OH
$RTeI_3$. α-Pic	2.89^{s} (3H)	-CH_3 (H_a)
	6.96^{d} (*9Hz*, 2H)	H_B
	7.77^{m} (3H)	H_b and H_c
	7.83^{d} (*9Hz*, 2H)	H_A
	8.65^{d} (*5Hz*, 1H)	H_d
	9.96^{b} (1H)	-OH
$RTeCl_3$. 2α-Pic	2.94^{s} (6H)	-CH_3 (H_a)
	6.98^{d} (*9Hz*, 2H)	H_B
	7.72, 8.30^{m} (6H)	H_b and H_c
	7.82^{d} (*9Hz*, 2H)	H_A
	8.66^{d} (*5Hz*, 2H)	H_d
	9.85^{b} (1H)	-OH
$RTeCl_3$. 2β-Pic	2.58^{s}, 2.59^{s} (6H)	-CH_3 (H_a)
	6.94^{d} (*9Hz*, 2H)	H_B
	7.58, 7.62^{m} (4H)	H_b and H_c
	7.81^{d} (*9Hz*, 2H)	H_A
	8.52^{d} (2H)	H_d
	8.62^{s} (2H)	H_e
	9.90^{b} (1H)	-OH

Cont…

RTeCl$_3$. γ-Pic 	2.51^s (3H)	-CH$_3$ (H$_a$)
	6.86^d (*9Hz*, 2H)	H$_B$
	7.96^d (*9Hz*, 2H)	H$_A$
	7.73^d (*8.8Hz*, 2H)	H$_b$
	8.61^d (*6.5Hz*, 2H)	H$_c$
	9.80^b (1H)	-OH

s = singlet, d = doublet, m = multiplet, b = broad.

The methyl protons resonating at δ 2.57, 2.33 and 2.36 ppm for α-, β- and γ-picolines, respectively[22], are shifted towards downfield side in the complexes. Similar effect is observed for the other ring protons of the picolines. This down field shift of ligand protons upon complexation suggests the deshielding of these protons due to donation of pair of electrons from nitrogen of picoline to the tellurium atom of RTeX$_3$. The aryl protons (H$_A$ and H$_B$) of hydroxyaryltellurium moiety, which appear[17,18] at δ$_A$ 7.99, δ$_B$ 6.99 ppm in parent *p*-hydroxyphenyltellurium trichloride and at δ$_A$ 7.98, δ$_B$ 6.90 ppm in triiodide, are upfield shifted in the complexes due to shielding of these protons upon accepting the electron from the ligand. The hydroxyl protons resonate separately at around 9.9 δ ppm suggesting its non-involvement in bonding with the ligand.

Also, this shift of ligand protons towards lower field side and aryl protons of RTeX$_3$ towards higher field side indicates the non-dissociative nature of Te-N bond in these complexes. The ratio of methyl protons to hydroxyl protons (and also others) confirms the stoichiometry of complexes.

Thus, tellurium is pentacoodinated in 1 : 1 complex of picolines and it acquires a hexacoordination in 1 : 2 complexes. A square pyramidal structure for RTeX$_3$.Pic and octahedral for RTeX$_3$. 2Pic complexes have been suggested.

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REFERENCES

1. K. J. Wynne and P. S. Pearson, Inorg. Chem., **10**, 2735 (1971).

2. K. J. Wynne and P. S. Pearson, J. Chem. Soc. Chem. Commun., 556 (1970).
3. K. J. Wynne, A. J. Clark and M. Berg, J. Chem. Sec. Dalton, 2370 (1972).
4. E. R. Clark, A. J. Collet and D. G. Naik, J. Chem. Soc. Dalton, 1961 (1973).
5. M. C. Berg, Diss. Abstr. Int. B, **33(7**), 2982 (1972).
6. T. N. Srivastava, M. Singh and H. B. Singh, Indian J. Chem., **21A**, 307 (1982).
7. T. N. Srivastava, R. C. Srivastava and M. Srivastava, Indian J. Chem., **21A**, 539 (1982).
8. T. N. Srivastava, R. C. Srivastava and V. K. Srivastava, J. Indian Chem. Soc., **60**, 891 (1983).
9. M. V. Garad, Polyhedron, **4** , 1353(1985).
10. K. K. Verma and Reena, Synth. React. Inorg. Met. -Org. Chem., **29**, 499 (1999).
11. K. K. Verma, Reena Dahiya and Daya Soni, Synth. React. Inorg. Met. -Org. Chem., **29**, 1033 (1999).
12. K. K. Verma and Reena Dahiya, Synth. React. Inorg. Met.-Org. Chem., **29**, 1299 (1999).
13. K. K. Verma and Reena, Phosphorus, Sulfur and Silicon and the Related Elements, **148**, 227 (1999).
14. Reena, Ph.D. Thesis, M. D. University Rohtak (1999).
15. A. I. Vogel, A Text Book of Practical Organic Chemistry, 3rd Edn., Longmans, London (1975).
16. A. Weissberger, Ed., Techniques of Organic Chemistry, Vol. VII, Interscience Publishers, Inc., NY (1967).
17. B. L. Khandelwal, Krishan Kumar and F. J. Berry, Inorg. Chim. Acta, **47**, 135 (1981).
18. Krishan Kumar, Ph. D. Thesis, IIT, Delhi (1981).
19. W. J. Geary, Coord. Chem. Rev., **7**, 81 (1971).
20. Denys Cook, Can. J. Chem., **42**, 2523 (1964).
21. S. S. Singh and C. B. S. Sengar, Indian J. Chem., **7**, 812 (1969).
22. Academic Press Hand Book Series – Hand Book of Proton NMR Spectra and Data, Ed. Asani Research Centre. Vol. 1, p. 47, Vol. 2, pp. 41, 42.

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