Synthesis and characterization of 2-[2-aryltelluroethyl] -3-methyl pyridines (Te,N) and 2-[2-(3-methyl pyridoethyltelluro) ethyl]-3-methyl pyridine (N,Te,N)

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ABSTRACT

The potentially bidentate hard and soft acid containing (Te,N) compounds, 2-(2-aryltelluroethyl)-3-methyl pyridines (L) [$C_{14}H_{15}NTe$] and tridentate(N,Te,N) 2-[2-(3-methyl pyridoethyltelluro)ethyl]-3-methyl pyridine (L') [$C_{16}H_{20}N_2Te$] have been synthesized in good yield (> 75%) and characterized by physical, analytical and spectroscopic [^1H, $^{13}C\{^1H\}$ and $^{125}Te\{^1H\}$ NMR and IR] methods. The reaction of methyl iodide with L [$C_{14}H_{15}NTe$] results in the formation of the salt of the type ArTe $(CH_2)_2$-2-$(C_5H_4N)^+$. CH3I with affecting the tellurium moiety.

Key words: Ligands (Te, N) and (N, Te, N); IR spectra, NMR spectra.

INTRODUCTION

There has been a recent interest in the ligand chemistry of tellurium[1,2] but despite this growth of activity the literature contains few reports of bi-or multidentate ligands containing tellurium. Incorporation of the ditelluride group into a cyclic system may be expressed to enhance the reactivity at the Te-Te bond as a result of strain involving both entropic and enthalpic effect[3]. Here we report synthesis and characterization of 2-(2-aryltelluroethyl)-3-methyl pyridines (L) [$C_{14}H_{15}NTe$], where Ar = Phenyl (La) [$C_{14}H_{15}NTe$], 4-methylphenyl (Lb) [$C_{15}H_{17}NTe$], 4-methoxyphenyl (Lc) [$C_{15}H_{17}ONTe$], 4-ethoxyphenyl (Ld) [$C_{16}H_{19}ONTe$], and 2-[2-(3-methyl pyridoethyltelluro) ethyl]-3-methyl pyridine (L') [$C_{16}H_{20}N_2Te$].

MATERIAL AND METHODS

Tellurium tetrachloride, aryl tellurium trichlorides, diarylditellurides, diphenyldiselenides, 2-(2-chloroethyl) pyridine are the main starting materials used in this work. The methods of conductance and magnetic moment measurement are given. The instruments and techniques used to record IR and NMR [^1H, ^{13}C {^1H}]. Chemicals were obtained from BDH, Aldrich, Strem and Sigma are used without purification. Organic solvents (BDH, Merck and Glaxo) were used after purification and drying (whenever required) by standard methods[4-5].

EXPERIMENTAL

2-(2-chloroethyl) pyridine and

diarylditellurides (aryl= phenyl, 4-methylphenyl, 4-methoxyphenyl, 4-ethoxyphenyl) prepared by the literature methods[6-7]. The detailed procedure for the synthesis of L and L' are given below.

Synthesis of 2-[2-aryltelluroethyl]-3-methyl pyridines (La-d)

To the hot ethanolic (25cm^3) solution of appropriate ditelluride (3 mmol), solution of sodium boro hydride (1.0 gm, 10 cm^3 of 10% NaOH), added slowly in nitrogen atmosphere, till colourless solution of sodium aryl telluride formed. To this 2-(2-chloroethyl)-3-methyl pyridine (6 mmol dissolved in 5 cm^3 ethanol) was added drop wise with vigorous stirring and the resulting solution further refluxed for one hour. The ligand (La-Ld) thus formed were extracted into chloroform (250 cm^3). After removing the excess of chloroform, liquid form of the compound separated out, which was purified by column chromatography, using silica column and chloroform: hexane (5: 95; 10: 90) as elutent.

Synthesis of 2-[2-(3-methyl pyridoethyltelluro) ethyl]-3-methyl pyridine (l')

In a round bottom (100 ml) flask Tellurium powder (2 gm, 16 mmol) and sodium borohydride (5 gm dissolved in 10 cm^3 of 10% NaOH) were refluxed in water (50 cm^3) until the colourless solution of Na_2Te was obtained. To this 2-(2-chloroethyl)-3-methyl pyridine (4.9 gm, 32 mmol) in 5 cm^3 of ethanol was added drop wise and the content further refluxed for two hours with vigorous stirring. The compound extracted into chloroform (250 cm^3), after removal of excess of chloroform, red colour liquid was obtained, washed with water and dried over anhydrous calcium chloride under vacuum.

RESULTS AND DISCUSSION

Synthesis of 2-(2-Aryltelluroethyl)-3-methyl pyridines (L) and 2-[2-(3-methyl pyridoethyltelluro) ethyl]-3-methyl pyridine (L') in schematic reaction shown as:

$$(C_5H_3N.CH_3)\text{-}2\text{-}CH_2CH_2Cl \xrightarrow[\text{EtOH-}H_2O]{2\text{ArTeNa}} \text{ArTe}CH_2CH_2\text{-}2\text{-}(C_5H_3NCH_3) \quad (L)$$

$$(C_5H_3N.CH_3)\text{-}2\text{-}CH_2CH_2Cl \xrightarrow[\text{EtOH-}H_2O]{Na_2Te} [(C_5H_3N.CH_3)\text{-}2\text{-}CH_2CH_2]_2Te \quad (L')$$

$$Ar = C_6H_5\ (La),\ 4\text{-}CH_3C_6H_4\ (Lb),\ 4\text{-}CH_3OC_6H_4\ (Lc),\ 4\text{-}C_2H_5OC_6H_4\ (Ld),$$

The high boiling liquids L [$C_{14}H_{15}NTe$] and L' [$C_{16}H_{20}N_2Te$] are pale yellow to red in colour, soluble in nonpolar and polar organic solvents. On exposure to air they change their colour from yellow to dark red. The various physical and spectroscopic properties of L and L' are discussed below:

Conductance and molecular weight measurements

The molar conductance (Λ_m) values of ligand L [$C_{14}H_{15}NTe$] and L' [$C_{16}H_{20}N_2Te$] (Table 1) determined in acetonitrile and nitro methane (1mM), reveals their nonelectrolytic behaviour. Molecular weights (Table 1) of L [$C_{14}H_{15}NTe$] and L' [$C_{16}H_{20}N_2Te$] determined in chloroform have been found close to the molecular formulations arrived at by analytical data.

IR spectra

The important IR bands along with their assignments and are presented in table 2. The assignments of the bands have been made on the

Table 1: Physical properties of ligands La-Ld and L'

Compound	Color (Liquid)	Yield %	Bpt. (°C)	Solubility		Mol.wt. (Calcd.)	Te % (Calcd.) In $CHCl_3$	($/\backslash_M$) In $Ch_3cn/C_6h_5no_2$ $Ohm^{-1}cm^2mol^{-1}$
				Good	Moderate			
La [$C_{14}H_{15}NTe$]	Pale yellow	85	172	Hexane, $CHCl_{3,}CH_3CN$	_	310 (324.6)	38.20 (39.3)	16.30/2.6
Lb [$C_{15}H_{17}NTe$]	Yellow	82	180	Hexane, $CHCl_{3,}CH_3CN$	_	303 (338.6)	37.50 (37.68)	14.2/3.4
Lc [$C_{15}H_{17}ONTe$]	Orange yellow	85	178	$CHCl_{3,}CH_3CN$	Hexane	325 (354.6)	35.93 (35.98)	15.2/2.9
Ld [$C_{16}H_{19}ONTe$]	Pale yellow	90	184	$CHCl_{3,}CH_3CN$	Hexane,	375 (368.6)	34.0 (34.61)	15,6/2.8
L' [$C_{16}H_{20}N_2Te$]	Red	90	136	Hexane, $CHCl_{3,}CH_3CN$	_	325 (367.6)	33,60 (34.71)	14.0/2.6

For 1:1 electrolyte $/\backslash_m$ inacetonitrile = 100-160 and in nitrobenzene = 20-30 $ohm^{-1}cm^2mol^{-1}$

La = $C_6H_5TeCH_2CH_2$-2-($C_5H_3NCH_3$) Ld = 4-$C_2H_5OC_6H_4TeCH_2CH_2$-2-($C_5H_3NCH_3$)

Lb = 4-$CH_3C_6H_4TeCH_2CH_2$-2-($C_5H_3NCH_3$) L' = [($C_5H_3N.CH_3$)-2-$CH_2CH_2]_2Te$

Lc = 4-$CH_3OC_6H_4TeCH_2CH_2$-2-($C_5H_3NCH_3$)

Table 2: Important ir bands (Cm^{-1}) of L and L'

Ligands	υ{Te-C(aliphatic)}	υ{Te-C(aromatic)}	δ (C-N)
La [$C_{14}H_{15}NTe$]	480	262,292	410
Lb [$C_{15}H_{17}NTe$]	482	248,288	408
Lc [$C_{15}H_{17}ONTe$]	480	250,290	410
Ld [$C_{16}H_{19}ONTe$]	484	256,298	408
L' [$C_{16}H_{20}N_2Te$]	497	-	410

Table 3. ^1H and ^{125}Te {^1H} NMR data for 2-(2-chloroethyl) pyridine, La-Ld, and L' in $CdCl_3$ at25°c (δ, ppm)

Compound	H_6 (d)	Aryl and pyridyl protons (m)	H_7 & H_8 (m)	H (R) ^1H	$^{125}Te\{^1H\}$
(C_5H_4N)-2-(CH_2)$_2$Cl	8.45	7.20(H_3,H_5);7.58(H_4)	3.9t,3.2t	-	-
La [$C_{14}H_{15}NTe$]	8.56	7.00-7.60	3.2	-	-
Lb [$C_{15}H_{17}NTe$]	8.51	6.95-7.70	3.2	2.38s	-
Lc [$C_{15}H_{17}ONTe$]	8.50	6.70-7.70	3.2	2.75s	481
Ld [$C_{16}H_{19}ONTe$]	8.55	6.70-7.70	3.2	3.97q, 1.40t	-
L' [$C_{16}H_{20}N_2Te$]	8.55	7.39(H_3,H_5);7.58(H_4)	3.3	-	167

(s = singlet; d = doublet; t = triplet; q = quartet; m =multiplet)
La = 2-(2-Aryltelluroethyl)-3-methyl pyridine
Lb = 2-[2-(4-methylaryl) Telluroethyl]-3-methyl pyridine
Lc = 2-[2-(4-methoxyaryl) Telluroethyl]-3-methyl pyridine
Ld = 2-[2-(4-ethoxyaryl) Telluroethyl]-3-methyl pyridine
L' = 2-[2-(3-methyl pyridoethyltelluro) ethyl]-3-methyl pyridine

Table 4: ^{13}C {^1H} NMR chemical shifts for ligands La-Ld and L' IN $CDCl_3$ (δ, ppm)

Ligand	C_7	C_8	Aryl and Pyridyl	C(R)
La*	40.0	6.5	137.8(C_2), 121.4(C_3), 136.2(C_4), 122.7(C_5), 149.5(C_6), 112.6(C_9), 138.3(C_{10}), 129.0(C_{11}), 127.3(C_{12})	-
Lb	40.1	3.2	134.0(C_2), 117.7(C_3), 135.0(C_4), 119.0(C_5), 149.5(C_6), 105.6(C_9), 132.5(C_{10}), 126.5(C_{11}), 121.3(C_{12})	17.6
Lc	40.3	6.8	140.0(C_2), 121.3(C_3), 136.3(C_4), 122.7(C_5), 149.5(C_6), 101.2(C_9), 141.0(C_{10}), 115.1(C_{11}), 160.1(C_{12})	55.1
Ld	40.2	6.8	140.0(C_2), 121.4(C_3), 136.4(C_4), 122.2(C_5), 149.5(C_6), 101.2(C_9), 141.1(C_{10}), 115.8(C_{11}), 159.3(C_{12})	63.5,14.9
L'*	40.3	2.2	136.5(C_2), 120.2(C_3), 135.6(C_4), 122.3(C_5), 148.2(C_6)	-

* = Not Observed.
La = 2-(2-Aryltelluroethyl)-3-methyl pyridine [$C_{14}H_{15}NTe$]
Lb = 2-[2-(4-methylaryl) Telluroethyl]-3-methyl pyridine [$C_{15}H_{17}NTe$]
Lc = 2-[2-(4-methoxyaryl) Telluroethyl]-3-methyl pyridine [$C_{15}H_{17}ONTe$]
Ld = 2-[2-(4-ethoxyaryl) Telluroethyl]-3-methyl pyridine [$C_{16}H_{19}ONTe$]
L' = 2-[2-(3-methyl pyridoethyltelluro) ethyl]-3-methyl pyridine [$C_{16}H_{20}N_2Te$]

basis of earlier reports[8,10]. The IR spectra of L [$C_{14}H_{15}NTe$] and L' [$C_{16}H_{20}N_2Te$] show characteristic band at 410 cm^{-1} due to δ(C-N) vibration (out of plane ring deformation) [(8)]. Two medium to low intensity υ [Te-C (aromatic)] bands appear between 240-260 and 280-295 in the IR spectra of L [$C_{14}H_{15}NTe$] concurring with earlier observations[9]. A band of medium to strong intensity at around 480 cm^{-1} in the IR spectra of L [$C_{14}H_{15}NTe$] and L' [$C_{16}H_{20}N_2Te$] attributed to υ[Te-C(aliphatic)] vibration[(9)].

^{1}H and $^{125}Te\{^{1}H\}$ NMR spectra

The ^{1}H NMR spectra of Ligands 2-(2-aryltelluroethyl)-3-methyl pyridines (L) and 2-[2-(3-methyl pyridoethyltelluro) ethyl]-3-methyl pyridine (L') were recorded in $CDCl_3$ [(11-13)]. The various chemical shifts along with their assignments are given in table 3.

The ^{1}H NMR spectra of L [$C_{14}H_{15}NTe$] and L' [$C_{16}H_{20}N_2Te$] show multiplet at ~δ,3.2for H_7 and H_8 rather than two triplets (centered at δ, 3.9 and 3.2 ppm respectively) as observed in the precursor, 2-(2-chloroethyl)-3-methyl pyridine. The up field shift (0.7ppm) of H_8 in the ligand with respect to their precursor may be attributed to replacement of chlorine atom by tellurium, an atom of much lower electro negativity. This shielding of H_8 protons result in their merger with H_7 signals[14-16].

The atomic ring protons in La [$C_{14}H_{15}NTe$] appear as multiplet and merged with the pyridine ring protons between δ 7.00-7.60 ppm. The aromatic ring protons of Lb-Ld [$C_{15}H_{17}NTe$], [$C_{15}H_{17}ONTe$], [$C_{16}H_{19}ONTe$], do not appear as two doublets as expected for a 1, 4-disubstituted benzene ring having substituents of different electro negativities[(19)] but merge with the pyridine ring protons and appear as a multiplet between δ 6.70-7.70 ppm.

In L [$C_{14}H_{15}NTe$] and L' [$C_{16}H_{20}N_2Te$] the proton linked to the carbon ortho to nitrogen (H_6) appears most downfield as compare to other ring protons and appears at δ, 8.5ppm as a doublet. The nitrogen being electronegative in nature deshields the adjacent carbon most, and consequently the proton linked to it, is deshielded most[17,18].

In L', [$C_{16}H_{20}N_2Te$] H_4 appear at δ, 7.25ppm, and H_3 and H_5 appear at ä, 7.08 ppm as multiplet as expected for ortho substituted alkyl pyridine[20].

The ^{125}Te {^{1}H} NMR spectra of Lc [$C_{15}H_{17}ONTe$] and L' [$C_{16}H_{20}N_2Te$] show a sharp singlet at ä, 481 and 167 ppm respectively which are in concordance with the values reported for asymmetric alkyl aryltellurides and symmetric dialkyltelluride[(21-23)].

^{13}C {^{1}H} NMR spectra

The assignment of the signals (Table 4) in the ^{13}C {^{1}H} NMR spectra of L [$C_{14}H_{15}NTe$] and L' [$C_{16}H_{20}N_2Te$] recorded in $CDCl_3$ have been made on the basis of literature reports on the related compounds and addivity principle [24-26]. The C_8 appears between δ, 2.2 and 6.8 ppm and C_7 around δ, 40.0 ppm. The C_8 have been found to be shielded because of the presence of a lone pair of electrons on the less electronegative tellurium atom in the ligand concurring with the earlier reports[27] on such compounds.

This observation supports the shielding of CH_2Te protons and consequently their merger with the C_7 protons in ^{1}H NMR spectra. The phenyl ring carbon linked to tellurium (i.e. C_9) appears around δ, 100 ppm in the ^{13}C {^{1}H} NMR spectra of L [$C_{14}H_{15}NTe$] because it experiences greatest shielding among the phenyl carbons due to lone pair of electrons of the tellurium[28]. The carbons of the pyridine ring appear as expected for the ortho substituted alkyl pyridine. The carbon ortho to nitrogen (C_6) appears at δ, 149.5 ppm, most downfield as compared to the other carbons of the ring. This is because of the greater electro negativity of the nitrogen which deshields C_6 most; consequently it appears at most downfield[29-31].

REFERENCES

1. H.J.Gysling. *coord. chem. rev.* **42**: 133 (1982).
2. H.J.Gysling in F.J.Berry and W.R. Mcwhinnine (Eds.), 4th Inter. Conf. org.chem. Selenium and Tellurium Univ. Aston.

Birmingham 32-82 (1983).

3. M. Raves croft, R.M.G.Roberts and J.G.Tillett, *J. chem.soc.Perkin Trans.II* 1569 (1982).
4. A.I.Vogel-practical organic chemistry, 3rd edn. (Longmans, London, 1975).
5. J.A.Riddick and W.B.Bunger in organic solvents, vol.2, Techniques of chemistry, 3rd edn; Eds; Arnold Weissberger, (Wiley Interscience, New York) (1970).
6. K.J. Irgolic and R.A. Zingaro-Reactions of organotellurium compounds in organometallic synthesis, vol. 2, Eds; E.Becker and M.Tsutsui (John Wiley and sons, Inc.1971).
7. S.Okio and Y.Noike-J.*pham.soc.Japan*, **72**: 490 (1952).
8. V.K. Jain-Inorg.chem.Acta133 (1987)261, V.K. Jain, R.P. Patel, K.V. Muralidhara and R. Bohra. *Polyhedron*, **8**: 2151(1989).
9. A.K. Patra, M. Ray and R.N. Mukherjee-*Inorg. chem*. **39**: 652 (2000).
10. S. Chatel, Chauvin Anne-S, Ttuchagues, P. Jean, P. Leduc, E. Bill, C. Jean Chattard, D. Mansuy and J. Artaud- *Inorg. chem. Acta* **33:** 19 (2002).
11. H.C. Clark, V.K. Jain and G.S.Rao-J.*organomet, chem*., **279**: 181 (1985).
12. V.K. Jain and G.S.Rao*, Inorg.chim.Acta,* **127**: 161 (1987).
13. V.K. Jain, R.P. Patel, K.Venkatasubramanian-*Polyhedron*, **10**: 851 (1991).
14. C.E. Briant, C.J. Gardener, T.S. Andy Hor, N.D. Howells an D.M.P. Mingos- *J.chem.soc. Dalton Trans*. 2645 (1984).
15. H.J. Gysling. *Coord. chem. Rev.***,** **42**: 133 (1982), H.J. Gysling in S. Patai and Z. Rappaport(Eds.)- The chemistry of organo-selenium and Tellurium compounds, vol.1, Wiley, New York (1986).
16. B.L. khandelwal, K. Kundu and S.K. gupta-*Inorg.chim.Acta* **154**: 183 (1988).
17. E.G. Hope, T. Kemmitt and W. Levason-*Organometallics,* **7**: 78 (1988).
18. T. Kemmitt and W. Levason- *Organometallics,* **8**: 1303 (1989).
19. P.K. Mascharak and D.S. Martin- *Chem. soc. Rev*., **29**: 69 (2000).
20. S.L. Jain, J.A. Crayto, D.T. Richen and J.A. Woollina-*Inorg.chem.commun.* **5**: 853 (2002).
21. S.K. Mandal and L. Que-Jr.*Inorg.chem.* **36**: 5424 (1997).
22. L.M. Barreaw, M.M. Makowaska, Grzyska and A.M. Arif- *Inorg.chem*. **39**: 4390 (2000).
23. T. Kiss, K. Petrohan, P. Buglyo, D. sanna, G. Micera, J.C. Pessoa and C. Maderia-*Inorg.chem.* **37**: 6384 (1988).
24. W.R. Mcwhinnie and M.C. Patel. *J.chem.soc.Dalton Trans*. 199 (1972).
25. J.P. Renault, C. Verchere-Beaur and I. Morgenstern-Badarau. *Inorg.chem*. **39**: 2666 (2000).
26. H.M.K.K. Pathirana and W.R. Mchinnie-J.chem.soc. Dalton Trans. 2003 (1986).
27. R.K. Chaddha and J.M. Miller-*J.chem.soc. Dalton Trans*. 117 (1982).
28. W.J.Le Noble-*J.Am.chem. soc*.**87**: 2434 (1965).
29. G. Petragnani and G. Schill-*Chem.Ber.***103**: 2271 (1971).
30. Sumit Bali, Ajai K. Singh, Pankaj Sharma, J.E. Drake, M.B. Hursthouse and M.E. Light, *Inorganic Chemistry Communications*, **6**(11): 1378-1381 (2003).
31. Garima Singh, Ajai K. Singh, Pankaj Sharma, John E. Drake, Michael B. Hursthouse, Mark E. Light, *Journal of Organometallic Chemistry,* **688**(1-2): 20-26 (2003).