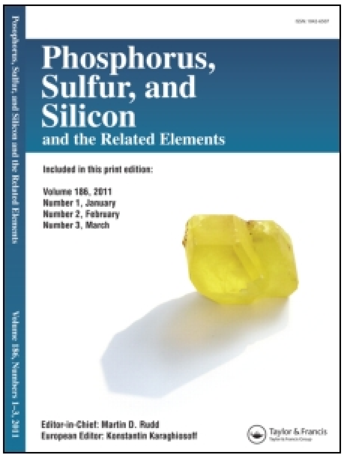

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PENTACOORDINATED MOLECULAR COMPLEXES OF ARYLTELLURIUM(IV) AND DIARYLTELLURIUM(IV) CHLORIDES WITH THIOSEMICARBAZONES

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The molecular complexes of the type $ArTeCl_3.XTSC$ (I) and Ar_2TeCl_2. XTSC (II), where $Ar = C_6H_5$, p-MeC_6H_4 or p-$MeOC_6H_4$ and XTSC = benzaldehyde, acetophenone, salicylaldehyde or 2-hydroxyacetophenone thiosemicarbazone, have been synthesized. The molecular weight measurements on millimolal solutions of I and II in acetonitrile reveal them to be ionic but due to ion association their conductances have been found to be lower than that of a 1/1 electrolyte. IR, PMR and CMR spectra indicate that XTSC ligates only through sulfur in I as well as II and therefore Te is five coordinated. A square pyramidal geometry around tellurium is proposed based on infrared data and reported crystal structures of $PhTeCl_3$ and Ph_2TeCl_2.

Key words: Benzaldehydethiosemicarbazone; acetophenonethiosemicarbazone; salicyladehydethiosemicarbazone; 2-hydroxyacetophenonethiosemicarbazone; aryltellurium(IV) chloride; diaryltellurium(IV) chloride; molecular complexes; thiosemicarbazone; pentacoordinated tellurium(IV) complex.

INTRODUCTION

The molecular addition complexes of $TeCl_4$ with a variety of neutral molecules containing N, O and S donor atoms are well known[1–4] but probably none of them has pentacoordinated tellurium. The $ArTeCl_3$ does not form many such compounds due to its lower Lewis acidity than $TeCl_4$. The known molecular complexes of $ArTeCl_3$ also have six coordinated tellurium[5] except $MeTeX_3$.tmtu (tmtu = tetramethyl-thiourea; X = Cl or Br) in which it is five coordinated.[6] The Ar_2TeCl_2 has even lower Lewis acidity and consequently its pentacoordinated molecular complexes are rare.[7] However, some other types of compounds having five coordinated Te(IV) are known[2–3] e.g. $[TeBr(Me_2NCS_2)_2]$[8] and $[(Ph_2Te(NCS))_2O]$.[9–10] In the course of investigations on the reactions of organotellurium(IV) and diorganotellurium(IV) halides with thiosemicarbazones, it has been observed that $ArTeCl_3$ and Ar_2TeCl_2 form 1:1 molecular addition complexes with benzaldehyde, salicylaldehyde, acetophenone and 2-hydroxyacetophenone thiosemicarbazones (abbreviated as BTSC, STSC, ATSC and HTSC respectively). Thiosemicarbazones in these complexes seem to behave as monodentate (coordinating through sulfur only) ligands resulting in pentacoordinated tellurium(IV). Such a behaviour of the ligands of this class is found in their complexes with metals too.[11]

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RESULTS AND DISCUSSION

The molecular addition complexes $ArTeCl_3 \cdot XTSC$ (I) and $Ar_2TeCl_2 \cdot XTSC$ (II) (where XTSC = thiosemicarbazone; Ar = C_6H_5, p-MeC_6H_4 or p-$MeOC_6H_4$) have been found to give satisfactory elemental analyses. The molar conductances (Λ_M, ohm^{-1} cm^2 mol^{-1}) of their acetonitrile solutions (0.5 to 1 mM) were found in the ranges 50–70 and 20–50 respectively for I and II. These values are lower than of a 1/1 electrolyte. However, the molecular weights in acetonitrile (10 to 50 millimolal solutions) have been osmometrically found to be nearly half of the formula weight. On considering these two opposite observations together, it appears that I and II ionize to a heavy tellurium containing cation and a Cl^- ion but due to dissimilar mobilities the two ions remain strongly associated, resulting in lower Λ_M values.

The complexes II have been found to be more stable than I in solution as well as in the solid state. In polar organic solvents I and II both were found to be more soluble than in nonpolar ones. However, the complexes of $(p\text{-}MeC_6H_4)_2TeCl_2$ and $(p\text{-}MeOC_6H_4)_2TeCl_2$ have fairly good solubility in hot chloroform, benzene and toluene. The solutions of these molecular complexes, unlike tellurium(II) thiosemicarbazone complexes,[12–13] can be stored for two weeks without any noticeable change.

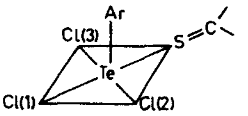
The comparison of PMR spectra of the present molecular complexes and the corresponding thiosemicarbazones[12] reveals that NH_2, NH and OH (if present) signals of the ligands remain unaffected on the formation of these complexes. This observation suggests that these potential coordinating sites of thiosemicarbazones do not ligate with tellurium in I or II. Probably XTSC coordinates through sulfur only. This has been further supported by infrared spectra of I and II. The $\nu(NH)$, $\nu(NH_2)$ and $\nu(OH)$ (if present) of XTSC appearing in the region 3100–3500 cm^{-1} were negligibly shifted on the formation of these complexes. Similarly $\nu(C{=}N)$ band observed in the spectra of XTSC around 1600 cm^{-1} remains unchanged on the formation of molecular complexes of either type. The $\nu(C{=}S)$ band occurs in the spectra of these complexes between 798 and 845 cm^{-1}. The red shifts in this band are of the order 20–55 and 10–40 cm^{-1} respectively for I and II, indicating that XTSC in these complexes is coordinated with tellurium through sulfur only and that its coordination is somewhat stronger in I. The bands in the region 275 to 300 cm^{-1} seem to be due to Te–Cl stretching.[14–16] In comparison with the parent organotellurium chlorides[14,16] the Te–Cl stretching undergoes a red shift (~20 cm^{-1}) for I and a blue shift (~10 cm^{-1}) for II. The $\nu(Te{-}C)$ bands have been observed around 250 cm^{-1} for both the complexes. Their positions may be considered as almost unchanged for I but are red shifted (~10 cm^{-1}) for II. The band in the region 225 cm^{-1} seems to have some contribution from Te–S bond.

The methyl signals in the PMR spectra of $(p\text{-}MeOC_6H_4)_2TeCl_2 \cdot BTSC$, $(p\text{-}MeC_6H_4)_2TeCl_2 \cdot BTSC$ and $(p\text{-}MeC_6H_4)_2TeCl_2 \cdot HTSC$ were carefully examined and compared with the signals of the parent diaryltellurium dichloride to ascertain whether the two aryl groups of Ar_2TeCl_2 on formation of molecular complexes remain equivalent or not. Nearly unshifted methyl singlets in spectra of all these three complexes suggest the equivalence of the two aryl groups.

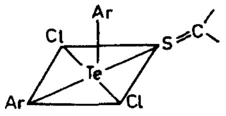
The CMR spectra of I and II show no methyl (if present) and azomethine carbon shifts compared to the corresponding signals of thiosemicarbazones. The CMR spectra of I have $>$C=S carbon signals deshielded by 20–30 ppm with respect to XTSC. However, $>$C=S signals of II do not differ from the similar signals of thiosemicarbazones, indicating weak coordination[12–13] of tellurium with sulfur in these complexes, as inferred from the infrared spectra. The CMR spectra of II also suggest the virtual equivalence of the two Ar groups as inferred from PMR spectra.

CONCLUSION

Based on the spectral data given above, tellurium in I and II may be assumed to be five coordinated. $PhTeCl_3$ has a polymeric chain structure.[17] Each tellurium atom in it is surrounded by two terminal and two bridging Cl, constituting with a carbon of the phenyl group an almost square pyramidal geometry. The two terminal as well as bridging Cl are *cis* to each other. On the formation of I with $PhTeCl_3$ it seems that these bridges are broken and one bridging Cl at the base of pyramid is replaced by sulfur of XTSC (structure **A**). The outcome of noninvolvement of Cl(2) in bridging and strong *trans* effect of XTSC is that Te–Cl bonds become a little longer, as reflected by a red shift in (Te–Cl). The (Te–C) virtually does not change, supporting the structure **A** for I. The Ph_2TeCl_2 also has a distorted square pyramidal geometry[18] around tellurium. The distorted base of the pyramid is constituted by its two Cl atoms, a carbon atom of one phenyl group and a Cl of neighbouring molecule, *trans* to phenyl and involved in a secondary interaction. On the formation of II this secondary interaction seems to be replaced by a coordination of XTSC through sulfur (structure B). Thus ν(Te–Cl) undergoes a blue shift, and due to a strong *trans* effect of XTSC ν(Te–C) appears at lower wave numbers. The structure B also seems to be reasonable for $(p\text{-MeOC}_6H_4)_2TeCl_2\cdot$BTSC, $(p\text{-MeC}_6H_4)_2\cdot$BTSC and $(p\text{-MeC}_6H_4)_2TeCl_2$. HTSC. The ionic nature of I is easily explainable, as due to strong *trans* effect of XTSC, Cl(1) would be labile. The ionic nature of II is surprising. The only explanation which can be offered for this intricate behaviour at the moment, of course speculative, is that the XTSC makes either of the two *cis* Cl mobile in solution by its steric effects. Probably Te in I and II adopts a sp^3d^2 hydridization, with a corner trans to Ar group occupied by a lone pair. The coordination of Te with XTSC seems to be weaker in II than that of I. This seems to arise as a combined effect of lower Lewis acidity of Ar_2TeCl_2 in comparison to $ArTeCl_3$ and the strong *trans* effect of aryl group exerted on XTSC in II (see structure **B**).



(A)



(B)

EXPERIMENTAL

The carbon and hydrogen analyses were carried out on a Perkin–Elmer elemental analyzer 240C. The tellurium and chlorine contents were estimated volumetrically.[19–20] The conductance measurements were made on a Pye conductivity bridge and molecular weights were determined on a Knauer vapour pressure osmometer. The IR spectra in the range 200–4000 cm^{-1} were recorded in KBr pellets or in Nujol as a mull on a CsI disc on a Nicolet 5DX–FTIR spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded on a JEOL FX 100 FT-NMR spectrometer.

Published methods were used for the synthesis of $PhTeCl_3$,[21] Ph_2TeCl_2,[21] $(p\text{-}MeC_6H_4)_2TeCl_2$[22] and $(p\text{-}MeOC_6H_4)_2TeCl_2$.[23]

Synthesis of $PhTeCl_3$*·BTSC.* The $PhTeCl_3$ (0.5 g, 1.61 m mol) and BTSC (0.29 g, 1.61 m mol) were stirred in 50 ml dry benzene under nitrogen atmosphere at room temperature for 3 h. The yellow compound formed was filtered, washed with benzene and recrystallized from 1:1 benzene-acetonitrile mixture. Yield, 72%; m.p. 75–77°C. Analyses: Found: C, 35.08; H, 2.95; N, 9.28; Te, 27.33; Cl, 21.60. Calc.: C, 34.28; H, 2.86; N, 8.57; Te, 26.04; Cl, 21.73%. NMR (^{1}H, DMSO-d$_6$, 25°C): δ, 7.24–8.42 (m, 13H, phenyl + NH_2 + CH), 11.61 (s, 1H, NH); (^{13}C{H}, DMSO-d$_6$, 25°C): δ, 127.5–139.3 (phenyl), 142.5 (C=N), 206.5 (C=S).

Synthesis of $PhTeCl_3$*·ATSC,* $PhTeCl_3$*·STSC and* $PhTeCl_3$*·HTSC.* They were prepared by reacting equimolar amounts of $PhTeCl_3$ and the appropriate thiosemicarbazone in the manner described for $PhTeCl_3$·BTSC. Yield, m.p., results of elemental analyses and their NMR spectral data are given below.

$PhTeCl_3$*·ATSC.* Yield, 68%; m.p. 77–79°C. Analyses: Found: C, 33.95; H, 3.01; N, 8.52; Te, 26.50; Cl, 20.54. Calc.: C, 35.71; H, 3.17; N, 8.33; Te, 25.30; Cl, 21.13%. NMR (^{1}H, DMSO-d$_6$, 25°C): δ, 2.32 (s, 3H, CH_3), 7.22–8.52 (m, 12H, phenyl + NH_2), 10.44 (s, 1H, NH); (^{13}C{H}, DMSO-d$_6$, 25°C): δ, 14.6 (CH_3), 127–138 (phenyl), 152 (C=N), 206.5 (C=S).

$PhTeCl_3$*·STSC.* Yield, 73%; m.p. 66–68°C. Analyses: Found: C, 33.35; H, 2.97; N, 9.20; Te, 24.65; Cl, 20.50. Calc.: C, 33.19; H, 2.77; N, 8.29; Te, 24.21; Cl, 21.04%. NMR (^{1}H, DMSO-d$_6$, 25°C): δ, 6.75–8.39 (m, 12H, phenyl + NH_2 + CH); 10.26 (s, 1H, NH); 11.46 (s, 1H, OH); (^{13}C{H}, DMSO-d$_6$, 25°C): δ, 116.5–140.3 (phenyl); 156.9 (C=N); 198.1 (C=S).

$PhTeCl_3$*·HTSC.* Yield, 69%; m.p. 70–72°C. Analyses: Found: C, 35.13; H. 3.28; N, 8.98; Te, 25.25, Cl, 19.75. Calc.: C, 34.61; H, 3.04; N, 8.08; Te 24.53; Cl, 20.48%. NMR (^{1}H, DMSO-d$_6$, 25°C): δ, 2.31 (s, 3H, CH_3); 6.86–8.51 (m, 11H, phenyl + NH_2); 10.66 (s, 1H, NH); 12.45 (s, 1H, OH); (^{13}C{H}, DMSO-d$_6$, 25°C): δ, 15.35 (CH_3); 117.4–136.9 (phenyl); 156.9 (C=N); 206.9 (C=S).

Synthesis of Ph_2TeCl_2*·BTSC.* The Ph_2TeCl_2 (0.5 g, 1.42 m mol) and BTSC (0.25 g, 1.42 m mol) were refluxed in 40 ml dry benzene under N_2 atmosphere for 2 h. The pale yellow compound was filtered and recrystallized from dry acetonitrile to give crystals with m.p. 115–117°C. Yield, 71%. Analyses: Found: C, 46.44; H, 3.79; N, 8.48; Te, 23.51; Cl, 12.65. Calc.: C, 45.15; H, 3.57; N, 7.90; Te, 24.00; Cl, 13.36%. NMR (^{1}H, DMSO-d$_6$, 25°C): δ, 7.39–8.41 (m, 18H, phenyl + CH + NH_2); 11.44 (s, 1H, NH); (^{13}C{H}, DMSO-d$_6$, 25°C): δ, 127.6–138.8 (phenyl), 142.7 (C=N); 178.4 (C=S).

Synthesis of Ph_2TeCl_2*·ATSC,* Ph_2TeCl_2*·STSC and* Ph_2TeCl_2*·HTSC.* All of them were prepared by refluxing equimolar amounts of Ph_2TeCl_2 and appropriate thiosemicarbazone in the manner described for Ph_2TeCl_2. BTSC. The yield, m.p., results of elemental analyses and their NMR spectral data are given below.

Ph_2TeCl_2*·ATSC.* Yield, 73%; m.p. 68–70°C. Analyses: Found: 47.53; H, 3.91; N, 7.28; Te, 24.18; Cl. 13.92. Calc.: C, 46.19; H, 3.85; N, 7.70; Te, 23.39; Cl, 13.01%. NMR (^{1}H, DMSO-d$_6$, 25°C): δ, 2.31 (s, 3H, CH_3); 7.26–7.98 (m, 15H, phenyl); 8.28 (s, 2H, NH_2); 10.32 (s, 1H, NH); (^{13}C{H}, DMSO-d$_6$, 25°C: δ, 14.5 (CH_3); 127.1–138.8 (phenyl); 148.5 (C=N); 179.3 (C=S).

Ph_2TeCl_2*·STSC.* Yield 75%, m.p. 136–138°C. Analysis: Found: C, 42.93; H, 3.91; N, 8.48; Te, 24.50; Cl, 14.15. Calc.: C, 43.83; H, 3.47; N, 7.67; Te, 23.30; Cl, 13.00%. NMR (^{1}H, DMSO-d$_6$, 25°C): δ, 6.74–8.04 (m, 16H, phenyl + NH_2); 8.38 (s, 1H, CH); 9.88 (s, 1H, NH); 11.30 (s, 1H, OH); (^{13}C{H}, DMSO-d$_6$, 25°C): δ, 116.5–140.3 (phenyl); 156.8 (C=N); 178.1 (C=S).

Ph_2TeCl_2*·HTSC.* Yield 78%; m.p. 110–112°C. Analyses: Found: C, 43.98; H, 3.81; N, 8.17; Te, 21.85; Cl, 12.13. Calc.: C, 44.87; H, 3.92; N, 7.48; Te, 22.72; Cl, 12.64%. NMR (^{1}H, DMSO-d$_6$, 25°C): δ, 2.31 (s, 3H, CH_3); 6.83–7.94 (m, 16H, phenyl + NH_2); 10.66 (s, 1H, NH); 12.45 (s, 1H, OH); (^{13}C{H}, DMSO-d$_6$, 25°C): δ, 15.4 (CH_3); 117.4–138.8 (phenyl); 157.7 (C=N); 180.8 (C=S).

Synthesis of $(p\text{-}MeC_6H_4)_2TeCl_2 \cdot BTSC$. The $(p\text{-}MeC_6H_4)_2TeCl_2$ (0.5 g, 1.31 m mol) and BTSC (0.24 g, 1.31 m mol) were refluxed in 50 ml dry benzene in nitrogen atmosphere until all the reactants dissolved (3 h). The solution was filtered while hot and half of the solvent was removed under reduced pressure. To the concentrated solution petroleum ether (30 ml) was added. The resulting pinkish yellow compound was filtered and recrystallized with benzene to give crystals with m.p. 115–117°C. Yield, 75%. Analyses: Found: C, 48.08; H, 4.78; N, 8.08; Te, 23.50; Cl, 11.73. Calc.: C, 47.18; H, 4.11; N, 7.51; Te, 22.80; Cl, 12.69. NMR (^{1}H, DMSO-d$_6$, 25°C): δ, 2.37 (s, 3H, CH_3); 7.31–8.22 (m, 16H, phenyl + NH_2 + CH); 11.46 (s, 1H, NH); (^{13}C{H}, DMSO-d$_6$, 25°C): δ, 21.3 (CH_3 linked to phenyl); 127.0–141.3 (phenyl); 142.7 (C=N); 178.3 (C=S).

Syntheses of $(p\text{-}MeC_6H_4)_2TeCl_2 \cdot HTSC$ *and* $(p\text{-}MeOC_6H_4)_2TeCl_2 \cdot BTSC$. They were prepared by reacting equimolar amounts of appropriate Ar_2TeCl_2 and thiosemicarbazone in the manner described for $(p\text{-}MeC_6H_4)_2TeCl_2 \cdot BTSC$. Their yield, m.p., results of elemental analyses and NMR spectral data are as follows.

$(p\text{-}MeC_6H_4)_2TeCl_2 \cdot HTSC$. Yield, 68%; m.p. 125–127°C. Analyses: Found: C, 47.92; H, 4.78; N, 7.84; Te, 20.56; Cl, 11.34. Calc.: C, 46.81; H, 4.24; N, 7.12; Te, 21.64; Cl, 12.04%. NMR (^{1}H, DMSO-d$_6$, 25°C): δ, 2.33 (s, 3H, CH_3 of HTSC); 2.37 (s, 3H, CH_3 linked to phenyl); 6.78–7.89 (m, 14H, phenyl + NH_2); 10.71 (s, 1H, NH); 12.45 (s, 1H, OH); (^{13}C{H}, DMSO-d$_6$, 25°C: δ, 15.2 (CH_3 of HTSC); 21.4 (CH_3 linked to phenyl); 117.4–141.4 (phenyl); 157.7 (C=N); 180.8 (C=S).

$(p\text{-}MeOC_6H_4)_2TeCl_2 \cdot BTSC$. Yield, 70%; m.p. 125–127°C. Analyses: Found: C, 45.62; H, 4.21; N, 7.30; Te, 22.18; Cl, 10.85. Calc.: C, 44.62; H, 3.89; N, 7.10; Te, 21.54; Cl, 12.00%. NMR (^{1}H, DMSO-d$_6$, 25°C): δ, 3.82 (s, 3H, CH_3O); 6.84–7.94 (m, 15H, phenyl + NH_2); 8.07 (s, 1H, CH); 11.47 (s, 1H, NH); (^{13}C{H}, DMSO-d$_6$, 25°C): δ, 56 (OCH_3); 115.3–136.6 (phenyl); 161.6 (phenyl C linked to 0), 142.9 (C=N); 178.3 (C=S).

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