Journal of Organometallic Chemistry, 346 (1988) 349–353
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Arylbis(thiosemicarbazone)tellurium(II) chlorides; three coordinate tellurium(II) complexes

A.K. Singh* **and J.K. Basumatary**

Department of Chemistry, Indian Institute of Technology, New Delhi 110 016 (India)

(Received September 21st, 1987)

Abstract

Three coordinate tellurium(II) complexes of the type $[ArTe(XTSC)_2]Cl$, where $Ar = C_6H_5$, $4\text{-}HOC_6H_4$ or $4\text{-}CH_3OC_6H_4$ and XTSC = thiosemicarbazone of benzaldehyde, acetophenone, salicylaldehyde or 2-hydroxyacetophenone, have been synthesized by treating $ArTeCl_3$ with the thiosemicarbazones in aqueous methanol. Molecular weight and conductivity measurements suggest that the chlorine in these complexes is ionic. The IR, ^1H and ^{13}C NMR data suggest that coordination of the XTSC is through sulphur alone, probably giving three coordinate tellurium in $[ArTe(XTSC)_2]^+$. The nature of Te–S bonding and the stability of the complexes is discussed.

Introduction

Three coordinate complexes of tellurium(II) are somewhat rare. The known examples [1–2] of such compounds are: $[PhTe(L)_2]X$ (where L = thiourea or substituted thiourea; X = halide or pseudo halide), $Me_3N[PhTe(XCN)_2]$ (where X = S or Se) and $Ph_4As[PhTeX_2]$ (where X = halide). The X-ray analysis [3–5] of single crystals of the thiourea complexes has revealed their structures to be 'T'-shaped, with two thiourea ligands *trans* to each other and the chloride (*trans* to phenyl) roughly at 3.578(2) Å from the tellurium (Van der Waals' contact 3.81 Å). It has been suggested for these thiourea complexes that the phenyl group, through its strong *trans*-effect, virtually expels the fourth ligand chloride [6] from the normal square planar arrangement, resulting in three coordinated tellurium(II). In view of the recently observed close parallel [7] between the ligation of thiosemicarbazones and thioureas with tellurium(II), we thought it of interest to attempt to use the *trans* effect of the phenyl group to enable synthesis of three coordinate tellurium(II)-thiosemicarbazone complexes. This approach was successful, treatment of $ArTeCl_3$ ($Ar = C_6H_5$, $4\text{-}HOC_6H_4$ or $4\text{-}CH_3OC_6H_4$) with the thiosemicarbazones (XTSC) of benzaldehyde, salicylaldehyde, acetophenone and 2-hydroxyacetophenone giving new $[ArTe(XTSC)_2]Cl$ species that probably contain three-coordinate tellurium.

0022-328X/88/$03.50

Experimental

Published methods were used to synthesize phenyltellurium trichloride [8], (4-hydroxyphenyl)tellurium trichloride [9] and (4-methoxyphenyl)tellurium trichloride [10]. The thiosemicarbazones of benzaldehyde, salicylaldehyde, acetophenone and 2-hydroxyacetophenone were obtained by refluxing the aldehyde or ketone with equimolar amounts of thiosemicarbazide in ethanol and recrystallising the product from ethanol/acetone/acetonitrile.

The chloride and tellurium were determined by standard methods [11,12]. The C, H and N analyses were carried out with a Perkin–Elmer elemental analyser 240C. The ^{1}H and ^{13}C NMR spectra were recorded on a JEOL FX 100 FT-NMR spectrometer, at 99.55 and 25 MHz, respectively. The IR spectra (of Nujol mulls or KBr/CsI discs) in the range 4000–200 cm^{-1} were recorded on a Nicolet 5DX FT-IR spectrophotometer. The conductivities of 0.3 to 1 mM solutions in acetonitrile and nitrobenzene were measured with a Pye conductivity bridge. The molecular weights were determined in acetonitrile for 1–9 mM solutions with a Knauer vapour pressure osmometer.

(a) Phenylbis(benzaldehydethiosemicarbazone)tellurium(II) chloride

A solution of $PhTeCl_3$ (1 g, 3.2 mmol) in methanol (30 cm^3) added to a solution of benzaldehydethiosemicarbazone (2.3 g, 12.84 mmol) in warm water (30 cm^3). The mixture was stirred for 0.5 h then set aside overnight. The yellow crystals were filtered off and recrystallized from methanol. Yield 79%; m.p. 70–72° C. Analysis: Found: C, 45.79; H, 4.08; N, 14.22; Te, 20.50; Cl, 5.98. $C_{22}H_{23}N_6S_2TeCl$ calc.: C, 44.14; H, 3.86; N, 14.02; Te, 21.33; Cl, 5.94%.

(b) Phenylbis(salicylaldehydethiosemicarbazone)tellurium(II) chloride

The orange-yellow complex was isolated by treating $PhTeCl_3$ with salicylaldehydethiosemicarbazone in the way described under (a). Yield 72%; m.p. 81–83° C. Analysis: Found: C, 39.85; H, 3.55; N, 13.26; Te, 21.32; Cl, 5.49. $C_{22}H_{23}N_6S_2O_2TeCl$ calc.: C, 41.89, H, 3.65; N, 13.33; Te, 20.25; Cl, 5.63%.

(c) Phenylbis(acetophenonethiosemicarbazone)tellurium(II) chloride

Similar reaction of $PhTeCl_3$ with acetophenonethiosemicarbazone gave the yellow-orange complex. Yield 76%; m.p. 73–75° C. Analysis: Found: C, 47.01; H, 4.40; N, 13.26; Te, 19.65; Cl, 4.98. $C_{24}H_{27}N_6S_2TeCl$ calc.: C, 46.0; H, 4.31; N, 13.42; Te, 20.38; Cl, 5.67%.

(d) Phenylbis(2-hydroxyacetophenonethiosemicarbazone)tellurium(II) chloride

Similar reaction of $PhTeCl_3$ with 2-hydroxyacetophenonethiosemicarbazone gave the brown complex. Yield 73%; m.p. 89–91° C. Analysis: Found: C, 45.79; H, 4.77; N, 13.52; Te, 20.15; Cl, 4.98. $C_{24}H_{27}N_6O_2S_2TeCl$ calc.: C, 43.76; H, 4.10; N, 12.76; Te, 19.39; Cl, 5.39%.

(e) (4-Hydroxyphenyl)bis(benzaldehydethiosemicarbazone)tellurium(II) chloride

A solution of (4-hydroxyphenyl)tellurium trichloride (0.5 g, 1.53 mmol) in methanol (20 cm^3) added to a solution of benzaldehydethiosemicarbazone (1.09 g, 6.12 mmol) in warm water (20 cm^3) and the mixture was stirred for 0.5 h, then set aside overnight. The yellow precipitate was filtered off and recrystallized from methanol. Yield 81%; m.p. 78–80 °C. Analysis: Found: C, 44.63; H, 4.16; N, 14.50; Te, 19.83; Cl, 5.42. $C_{22}H_{23}N_6OS_2TeCl$ calc.: C, 42.92; H, 3.76; N, 13.66; Te, 20.74; Cl, 5.77%.

(f) (4-Hydroxyphenyl)bis(salicylaldehydethiosemicarbazone)tellurium(II) chloride

A similar procedure to that described under (c), but involving reaction of $(4\text{-}HOC_6H_4)TeCl_3$ with salicylaldehydethiosemicarbazone gave the brownish yellow complex. Yield 75%; m.p. 98–100 °C. Analysis: Found: C, 41.28; H, 3.96; N, 14.15; Te, 20.54; Cl, 5.98. $C_{22}H_{23}N_6S_2TeO_3Cl$ calc.: C, 40.79; H, 3.55; N, 12.98; Te, 19.75; Cl, 5.49%.

(g) (4-Methoxyphenyl)bis(benzaldehydethiosemicarbazone)tellurium(II) chloride

A solution of $(4\text{-}CH_3OC_6H_4)TeCl_3$ (0.5 g, 1.46 m mol) in methanol (20 cm^3) was mixed with a warm aqueous solution (20 cm^3) of benzaldehyde thiosemicarbazone (1.05 g, 5.84 mmol) and the mixture was stirred for 0.5 h then set aside overnight. The yellow precipitate was filtered off and recrystallized from methanol. Yield 72%; m.p. 87–89 °C. Analysis: Found: C, 45.79; H, 4.23; N, 14.70; Te, 19.51; Cl, 6.15. $C_{23}H_{25}N_6S_2OTeCl$ calc.: C, 43.87; H, 3.97; N, 13.35, Te, 20.28; Cl. 5.64%.

(h) (4-Methoxyphenyl)bis(salicylaldehydethiosemicarbazone)tellurium(II) chloride

This complex was obtained by treatment of $(4\text{-}CH_3OC_6H_4)TeCl_3$ with salicylaldehydethiosemicarbazone in a procedure similar to that used for complex (g). Yield 79%; m.p. 92–94 °C. Analysis: Found: C, 43.38; H, 4.15; N, 13.53; Te, 18.28; Cl, 6.25. $C_{23}H_{25}N_6O_3S_2TeCl$ calc.: C, 41.81; H, 3.79; N, 12.73; Te, 19.33; Cl, 5.38%.

Results and discussion

The trichloride $ArTeCl_3$ reacts with thiosemicarbazones (XTSC) according to eq. 1, no complex being obtained if the reagents are used in 1/2 molar ratio. The molecular weights measured in acetonitrile are half of the formula weight, indicating

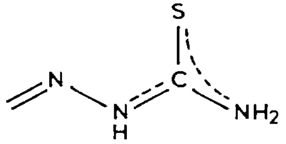
$$ArTeCl_3 + 4XTSC \xrightarrow{CH_3OH} (XTSC)_2{}^{2+} + 2Cl^- + [ArTe(XTSC)_2]Cl \qquad (1)$$

an ionic character for the complexes, and this is supported by lability of chloride which is readily exchangeable with bromide, iodide and $TeCl_6{}^{2-}$. The molar conductance (Λ_M 30–40 ohm^{-1} cm^2 mol^{-1} in CH_3CN and 8–12 ohm^{-1} cm^2 mol^{-1} in nitrobenzene) is lower than expected for a 1/1 electrolyte. This may be due to the dissimilarities in the mobility of the cation and chloride ion, which leads to an increase in ion association. Such behaviour is common when one of the ion is much larger than the other, and the low molar conductance values have been reported for some other tellurium compounds, viz. Ph_3TeCl [13] and 1-organo-1-halo-1-telluracyclopentane [14] that are known to ionize into a heavy tellurium containing cation and Cl^-, and expected to behave as 1/1 electrolytes.

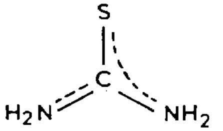
IR and NMR spectra

Comparison of the IR spectra of tellurium complexes (a) to (h) with those of the corresponding thiosemicarbazones reveals that the band near 1600 cm^{-1} in the spectrum of the free ligand remains unchanged or undergoes a small blue shift on complexation with tellurium. This suggests that $\rangle$C=N group is not involved in the coordination. Similarly N–H and O–H (if present) vibrations appear in the spectra of thiosemicarbazones and their Te^{II} complexes at almost identical positions in the range 2800–3500 cm^{-1}, ruling out involvement of the nitrogen or oxygen in coordination. The ν(C=S) band observed in the spectra of thiosemicarbazones near 860 cm^{-1} is shifted by 25 to 35 cm^{-1} towards lower wave numbers in the spectra of Te complexes, suggesting that the coordination of the ligands is through sulphur only. The ν(Te–C) and ν(Te–S) bands appear in all the complexes at 245–260 and 218–237 cm^{-1}, respectively. These observations, taken along with the molecular weight and conductance data, suggest that the complexes can best be represented as $[ArTe(XTSC)_2]^+ Cl^-$, with the tellurium three-coordinate. However, a band in the region of 300 cm^{-1}, usually associated with Te–Cl stretching, is observed in the IR spectra of the complexes, though with reduced intensity, and probably arises from a Te–C bond. Unfortunately an X-ray diffraction study, which would reveal the structures unambiguously, was ruled out because no suitable crystals could be grown.

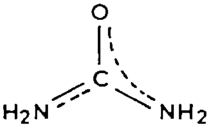
The ^1H and $^{13}C\{^1H\}$ NMR spectra in DMSO-d_6 were as expected for all the complexes. The signals due to aryl protons and carbons appeared at positions characteristic of Ar–Te groups [15]. The positions of signals due to NH_2, NH and OH (if present) protons in the ^1H NMR spectra of thiosemicarbazones, at δ 7.9–8.4, 9.9–11.6, and 11.4–11.9, respectively, almost unchanged in the spectra of their Te^{II} complexes (a) to (h), this supports the view that the N and O atoms are not involved in complexation with tellurium(II), as inferred from the infrared data. The ^{13}C NMR spectra of the thiosemicarbazones and their Te^{II} complexes (a)–(h) were also examined. The azomethine carbon signal (δ 144.2–159.8) remains almost unchanged on complexation but the $\rangle$C=S signal in the spectra of complexes (δ 176–180 ppm) is shifted upfield by δ 1–4 ppm. If structure **A** is assumed for thiosemicarbazones by analogy with those of thiourea and urea [16] (structures **B** and **C**), the increased localization of electron density around carbon of thiocarbonyl group when S ligates with tellurium may be responsible for this shielding. The small shift confirms that there is weak coordination of sulphur with tellurium. Similar observations were made for $[PhTe(tu)_2]Cl$ (tu = thiourea) too; the signal from the $\rangle$C=S group observed in the ^{13}C NMR spectrum of thiourea at δ 184.05 ppm is shifted upfield to δ 179.80 ppm in the spectrum of the complex $[PhTe(tu)_2]Cl$, probably owing to increased localization of electron density around carbon (structure **B**).



(A)



(B)



(C)

Bonding and stability of $[ArTe(XTSC)_2]Cl$

The weakness of the coordination between tellurium(II) and the Sulphur atoms of thiosemicarbazones suggested by the foregoing discussion can be associated for in terms of a model based on three centre-four electron bonds, as suggested by Foss [17] for Te^{II}–thiourea complexes. The two lone pairs in the T-shaped 3-coordinate complexes would presumably tend to take up equatorial positions together with the carbon atom, to give a distorted trigonal bipyramidal arrangement of electron pairs involving bonding through *sp*-hybrid orbitals [18].

In general the stability of the Te^{II}-thiosemicarbazone complexes, particularly in solution (no decomposition of solids is evident after months), is poorer than that of thiourea analogues. This suggests that the 3-centre overlap between the orbital of one Te and 2 S atoms decreases when the sulphur is part of a thiosemicarbazone molecule. However, the solutions of the complexes (a) to (h) in polar solvents such as DMSO and acetonitrile are more stable (at least 2–3 days) than the solutions of $Te(XTSC)_2Cl_2$ and $Te(XTSC)_4Cl_2$ in similar solvents [6]. The presence of a C–Te bond usually stabilizes the Te complex. Probably the virtual expulsion of Cl^-, due to the strong trans effect of phenyl, from the coordination sphere of Te makes the overlap between the orbitals of sulphur and tellurium more effective, and thus enhances the Te–S bond strength and in turn the solution stability of complexes (a) to (h) relative to $Te(XTSC)_2Cl_2$ and $Te(XTSC)_4Cl_2$.

References

1 S. Husebye, in F.J. Berry and W.R. McWhinnie (Eds.), Proc. 4th Conf. Org. Chem. of Selenium and Tellurium' Univ., Birmingham, 1983, p. 297.
2 S. Hauge and O. Vikane, Acta Chem. Scand., A, 37 (1983) 723.
3 S. Hauge, Ø. Johannessen and O. Vikane, Acta Chem. Scand. A, 32 (1978) 901.
4 O. Foss and S. Husebye, Acta Chem. Scand., 20 (1966) 132.
5 O. Vikane, Acta Chem. Scand. A, 29 (1975) 738, 763, 787.
6 O. Foss, S. Husebye and K. Maroy, Acta Chem. Scand., 17 (1963) 1806.
7 A.K. Singh, J.K. Basumatary and N. Mann, Phosphorus Sulfur, in press.
8 R.C. Paul, K.K. Bhasin and R.K. Chadha, J. Inorg. Nucl. Chem., 37 (1975) 2337.
9 B.L. Khandelwal, K. Kumar and F.J. Berry, Inorg. Chim. Acta, 47 (1981) 135.
10 G.T. Morgan and R.E. Kellet, J. Chem. Soc., (1926) 1080.
11 A.I. Vogel, A Textbook of Quantitative Inorganic Analysis, 3rd edit., Longmans, London, 1961, p. 324.
12 F.H. Kruse, R.E. Sanftner and J.F. Suttle, Anal. Chem., 25 (1953) 500.
13 D.A. Couch, P.S. Elmas, J.E. Fergusson, M.L. Greenfield and C.J. Wilkins, J. Chem. Soc. A, (1967) 1813.
14 A.Z. Al-Rubaie, H.A.Y. Alshirayada, P. Granger and S. Chapella, J. Organomet. Chem., 287 (1985) 321.
15 R.K. Chadha and J.M. Miller, J. Chem. Soc. Dalton Trans., (1982) 117.
16 T. Theophanides and P.D. Harvey, Coord. Chem. Rev., 76 (1987) 237.
17 O. Foss, Pure Appl. Chem., 24 (1970) 31.
18 P.W.C. Barnard, J.D. Donaldson, R.M.A. Grimsey, G. Dennes, U. Rosso and S. Calogero, Inorg. Chim. Acta, 51 (1981) 217.