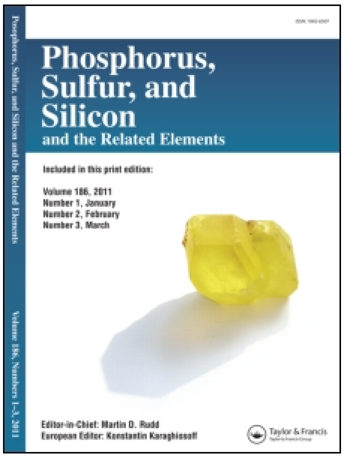

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TELLURIUM(II)-THIOSEMICARBAZONE COMPLEXES—A PARALLEL TO THE LIGATION OF THIOUREAS

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The tellurium(II)-complexes of the type $Te(XTSC)_2Cl_2$ (**I**) and $Te(XTSC)_4Cl_2$ (**II**), where XTSC = benzaldehyde, acetophenone, salicylaldehyde or 2-hydroxyacetophenone thiosemicarbazone have been isolated. The IR, PMR and CMR spectra of the complexes in conjunction with their elemental analyses and conductance measurements, indicate the formation of a three centre-four electron bond between tellurium and two sulphur atoms of the thiosemicarbazones, *trans* to each other. These results exhibit for the first time that thiosemicarbazones may ligate with tellurium(II) in a manner parallel to that of thioureas. The square planar and octahedral arrangement of the ligands around tellurium are proposed for **I** and **II** type complexes respectively.

Key words: Tellurium(II); benzaldehydethiosemicarbazone; salicylaldehydethiosemicarbazone; acetophenonethiosemicarbazone; 2-hydroxyacetophenonethiosemicarbazone; thiosemicarbazone.

INTRODUCTION

The tellurium(II and IV)-sulphur donor complexes are interesting on two accounts. First, some of them, such as tellurium(IV)-dithiocarbamates find applications[1–4] in rubber and polymer strengthening. Second, some such species have novel structural features e.g. in tellurium(II)-thiourea complexes[5–6] the Te—S bond lengths are such that the concept of three centre-four electron bond is required to explain them and therefore have got the attention of crystallographers[6] too. The sulphur donors whose complexation with tellurium(II and IV) has been studied so far, are thioureas, xanthates, dithiocarbamates and thiocyanate. In case of thioureas[5] it is observed that the variation in experimental conditions easily results in a change in the composition of tellurium(II or IV)-complex. However, no attempt has been made to study the complexation of tellurium with thiosemicarbazones which constitute an important class of sulphur donors. The complexes may be suitable for rubber and polymer strengthening. Therefore, we are carrying out systematic investigations on Te(II and IV)-thiosemicarbazone complexes and have already reported[7] the reactions of $TeCl_4$ with some of these ligands.

The TeO_2 dissolved in concentrated hydrochloric acid reacts with methanolic solution of benzaldehyde, salicylaldehyde, acetophenone and 2-hydroxyacetophenone thiosemicarbazone (abbreviated in general as XTSC and individually as BTSC, STSC, ATSC and HTSC respectively) to give tellurium(II)

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complexes of the type $Te(XTSC)_2Cl_2$ (**I**) and $Te(XTSC)_4Cl_2$ (**II**) as reported for thioureas. The preparation and spectral properties of these derivatives are described in the present paper.

RESULTS AND DISCUSSION

The results of elemental analyses recorded in Table I agree well with the proposed stoichiometries of the complexes. In $Te(BTSC)_4Cl_2.2H_2O$ the presence of two water molecules has been supported by a 5% weight loss step between temperature 90 and 100°C in its TGA curve. The thiosemicarbazones seem to react according to equations (1) and (2) to give the tellurium(II) complexes, because on reacting TeO_2 dissolved in concentrated HCl with them in 1:2 ratio, species of the type **I** do not result and $Te(XTSC)_4Cl_2$ is not obtained in reaction (1).

$$Te^{4+} + 4(XTSC) \rightarrow Te(XTSC)_2Cl_2 + (XTSC)_2^{2+} \qquad (1)$$

$$Te^{4+} + 6(XTSC) \rightarrow Te(XTSC)_4Cl_2 + (XTSC)_2^{2+} \qquad (2)$$

Contrary to thiosemicarbazones, the thiosemicarbazide precipitates elemental tellurium when reacted with TeO_2 dissolved in concentrated HCl. This difference is probably due to the greater reducing power of thiosemicarbazide.

The complexes **I** and **II** are more soluble in polar solvents. However their stability in solution is poor, for example, in their DMSO solutions deposition of elemental tellurium can be noticed after 1 h of dissolution. The decomposition is very slow in DMF (no tellurium deposition for 5–6 h), except for $Te(BTSC)_4Cl_2$ and $Te(BTSC)_2Cl_2$ whose solutions in acetonitrile and acetone respectively have stability of the same order. The light was found to accelerate the decomposition. However, the solid complexes can be stored without any noticeable decomposi-

TABLE I

Elemental analyses and physical properties of the complexes

Compound	M.P. °C	Colour	% Found (Cald) Te	Cl	C	H
$Te(BTSC)_2Cl_2$	99–101	Orange	20.60	10.95	34.40	2.77
		yellow	(21.92)	(11.25)	(34.43)	(3.23)
$Te(BTSC)_4Cl_2$	97–99	Orange	14.00	8.40	38.86	5.01
$2H_2O$		yellow	(13.40)	(7.46)	(40.38)	(4.24)
$Te(ATSC)_2Cl_2$	155–158	Lemon	22.80	11.58	35.13	3.30
		yellow	(21.82)	(12.15)	(36.95)	(3.76)
$Te(ATSC)_4Cl_2$	135–137	Lemon	13.19	7.78	43.66	5.35
		yellow	(13.13)	(7.30)	(44.48)	(4.53)
$Te(STSC)_2Cl_2$	135–138	Brownish	22.14	11.03	33.69	3.15
		yellow	(21.00)	(12.00)	(32.42)	(3.00)
$Te(STSC)_4Cl_2$	143–144	Brownish	12.20	8.64	38.53	3.48
		yellow	(12.90)	(7.20)	(39.00)	(3.60)
$Te(HTSC)_2Cl_2$	180–183	Lemon	19.56	11.79	35.72	3.50
		yellow	(20.64)	(11.51)	(35.03)	(3.56)
$Te(HTSC)_4Cl_2$	170–171	Lemon	11.80	7.80	41.26	4.09
		yellow	(12.33)	(6.86)	(41.75)	(4.25)

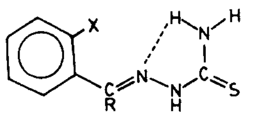
TABLE II

Chemical shifts (δ, ppm) in ^{1}H NMR spectra in DMSO-d_6 at 25°C

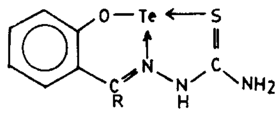
Compound	—CH_3	Phenyl	—NH_2	—CH	—NH	—OH
BTSC	—	7.41–8.09	8.24	8.04	11.40	—
$Te(BTSC)_2Cl_2$	—	7.37–8.05	8.23	8.05	11.47	—
$Te(BTSC)_4Cl_2$	—	7.41–7.82	8.24	8.09	11.54	—
ATSC	2.31	7.30–7.90	8.26	—	10.22	—
$Te(ATSC)_2Cl_2$	2.30	7.30–7.91	8.35	—	10.26	—
$Te(ATSC)_4Cl_2$	2.34	7.37–8.00	8.48	—	10.38	—
STSC	—	6.75–7.96	8.05	8.39	9.93	11.37
$Te(STSC)_2Cl_2$	—	6.75–7.78	8.07	8.39	9.12	11.21
$Te(STSC)_4Cl_2$	—	6.74–7.95	8.05	8.39	9.85	11.44
HTSC	2.31	6.77–7.55	7.83	—	10.59	12.59
$Te(HTSC)_2Cl_2$	2.32	6.84–7.42	7.61	—	9.37	12.50
$Te(HTSC)_4Cl_2$	2.33	6.78–7.56	7.81	—	10.84	12.50

tion for several months. The molar conductance values of complexes of both the types in DMF (27–49 ohm^{-1} cm^2 mol^{-1}) have been found lower than that of a 1 : 1 electrolyte.

The chemical shifts observed in the PMR spectra of thiosemicarbazones and their tellurium(II)-complexes of type **I** and **II** are recorded in Table II. The NH_2 signal in the spectra of thiosemicarbazones could not be observed around δ 2.5 ppm as reported by Saxena and Tandon.[8] Their assignment is incorrect because the amino protons of a thioamide group are expected at lower field in comparison to similar protons of a primary amine which appear around δ 5–6 ppm. In our view the assignment of the signal between 7.6 and 8.5 ppm to NH_2 group of thiosemicarbazones (Table II) seems to be very logical. The NH_2 signals in the PMR spectra of analogous compounds, 1-phenylthiosemicarbazide and thiourea have been found at 7.3 to 9.4[9] and 7.8 ppm respectively, supporting strongly our interpretation. The NH_2 protons also seem to be locked in an intramolecular hydrogen bonding (structure A) because on formation of the complex of type B the shielding of NH_2 protons by 3.5 to 4.0 ppm with respect to the parent ligand has been observed.[7] The crystal structure of pyridoxalthiosemicarbazone[10] reported recently also supports the conformation of NH_2 group as shown in structure A and the thesis of intramolecular hydrogen bonding between nitrogen of azomethine and NH_2 group. The assignments[7] of OH protons given in Table II have been made by comparing the PMR spectra of STSC and HTSC with the spectra of their type B complexes. The NH, NH_2 and OH signals in the PMR spectra of thiosemicarbazones and their tellurium(II)-complexes **I** and **II** were found almost identical, indicating that these groups do not ligate with tellurium. The CMR spectra (Table III) have been analysed to look further into the Tellurium(II)-thiosemicarbazone complexation. Unfortun-



(A)



(B)

TABLE III

Chemical shifts (δ, ppm) in ^{13}C NMR spectra in DMSO-d_6 at 25°C

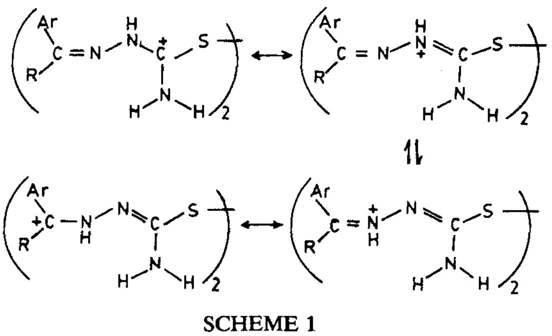
Compound	—CH_3	Phenyl	$>C{=}N$	$>C{=}S$
BTSC	—	127.59–134.52	142.62	178.37
$Te(BTSC)_2Cl_2$	—	129.39–134.08	142.62, 151.2	178.25, 193.64
$Te(BTSC)_4Cl_2$	—	127.77–134.66	142.60, 149.61	178.20, 192.63
ATSC	14.50	126.98–138.04	148.27	179.36
$Te(ATSC)_2Cl_2$	14, 28, 60.00	125.56–134.08	148.30, 153.27	179.30, 197.00
$Te(ATSC)_4Cl_2$	15, 28, 60.00	126.46–138.03	148.32, 153.42	179.26, 198.48
STSC	—	110.64–140.52	150.86	178.11
$Te(STSC)_2Cl_2$	—	116.71–146.16	150.86, 157.38	178.20, 192.76
$Te(STSC)_4Cl_2$	—	116.64–140.74	150.85, 157.01	178.15, 192.69
HTSC	16.25	117.40–131.14	157.84	180.82
$Te(HTSC)_2Cl_2$	16, 28, 62.27	117.30–186.78	154.74, 156.71	181.81, 205.30
$Te(HTSC)_4Cl_2$	16, 28, 62.27	117.44–136.93	158.62, 161.63	180.85, 205.37

ately due to decomposition of these complexes (Equations (3) and (4)) while recording the CMR spectra in DMSO,

$$Te(XTSC)_2Cl_2 \rightarrow Te + (XTSC)_2^{2+} + 2Cl^- \tag{3}$$

$$Te(XTSC)_4Cl_2 \rightarrow Te + 2(XTSC) + (XTSC)_2^{2+} + 2Cl^- \tag{4}$$

weak signals attributable to free and oxidized ligand ($(XTSC)_2^{2+}$) also appear making the interpretation difficult. The two additional methyl signal around δ 28 and 60 ppm appear in the CMR spectra of ATSC/HTSC-complex, suggesting a tautomeric equilibrium (Scheme I) for the oxidized ligand in solution. Of the two azomethine signals observed in the spectrum of each of these complexes, the weak and deshielded one seems to arise from $>C{=}N$ group of $(XTSC)_2^{2+}$. The two signals attributable to carbon of $>C{=}S$ group have been observed in the CMR spectra of **I** as well as **II**. The low field one (δ 195–205 ppm) and weaker in intensity than the other, seems to arise from $(XTSC)_2^{2+}$. Its deshielding by δ 20–25 ppm with respect to $>C{=}S$ signal of thiosemicarbazones supports the delocalization of positive charge as depicted in Scheme I, otherwise it would appear further down field.[11] The other $>C{=}S$ signal seems to arise from the complexes. Almost no change in the position of $>C{=}S$ signal on complexation of thiosemicarbazone with tellurium(II) suggests that the coordination of these ligands with Te is weak. The $>C{=}S$ signal has been found unaffected or shielded



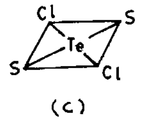
SCHEME 1

by few ppm on comparing the CMR spectra of Te(II)-thiourea complexes and $TeCl_4 \cdot BTSC$ type adducts[7] with the spectra of corresponding sulphur donors, too. In analogy with Te(II)-thiourea complexes the Te—S bond in the complexes **I** and **II** can also be regarded as three centre-four electron bond. However, the poor stability of solutions of **I** and **II** suggests that Te—S bond in these complexes may be weaker in comparison to similar bond of their thiourea analogues.

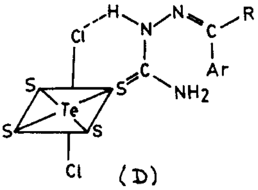
The bands at 1056–1065 and 850–880 cm^{-1} in the IR spectra of thiosemicarbazones have contribution from $>C{=}S$ group. In the spectra of complexes **I** and **II** these occur with a red shift of 15–20 cm^{-1}, suggesting the coordination through $>C{=}S$ group. The ν_{OH} observed in the IR of STSC and HTSC as a broad band between 3000–3500 cm^{-1} has been found at similar position in the spectra of **I** and **II**. This observation in conjunction with the occurrence of $\nu_{C=N}$ around 1610 cm^{-1} in the IR spectra of complexes **I** and **II** as well as the ligands suggest that in these complexes thiosemicarbazones are bonded to tellurium(II) through sulphur only. The bands from 270 to 300, 240 to 260 and 215 to 230 cm^{-1} observed in the spectra of complexes seem to have contribution[12] from Te–Cl vibrations and the last one from Te–S vibrations.

CONCLUSION

The structures C and D can be tentatively assigned to $Te(XTSC)_2Cl_2$ and $Te(XTSC)_4Cl_2$ type species keeping in view the foregoing discussion on the spectral data and the analogy with tellurium(II)-thiourea complexes. The surprisingly lower values of the molar conductances observed for the complexes of type **II** may be the result of either an intra-molecular hydrogen bonding (structure D) or stronger association between tellurium containing cation and chloride due to incompatibility of their mobilities and weak coordination of Te(II) with sulphur of thiosemicarbazones. However, it is not unlikely that the axial Te–Cl bonds (structure D) are somewhat elongated mainly because of steric reasons.



(C)



(D)

The results of present investigations unequivocally reveal that thiosemicarbazones and thioureas ligate with tellurium(II) in a very similar manner.

EXPERIMENTAL

The carbon and hydrogen analyses were carried out on a Perkin–Elmer elemental analyzer 240 C. The tellurium and chlorine contents were estimated volumetrically.[13–14] The conductance was measured on a WG Pye conductivity bridge. The IR spectra in the range 200–4000 cm^{-1} were recorded in KBr/CsI on a Nicolet 5DX FTIR spectrometer. The PMR and CMR were recorded on a Jeol FX-100 FT-NMR spectrometer. The Du Pont thermal analyzer was used for recording TGA.

Synthesis of dichlorobis(benzaldehydethiosemicarbazone)tellurium(II)(Te(BTSC)$_2$Cl$_2$). The solution of TeO_2 (1.01 g, 6.32 mmole) in a minimum volume of concentrated hydrochloric acid was added to thin slurry of BTSC (4.5 g, 25.4 mmole) in a minimum volume of methanol. The reaction mixture was stirred for 2 h at room temperature. The yellowish orange complex thus formed was filtered, washed thoroughly with chloroform to remove the excess of ligand and dried *in vacuo*. Yield 80%.

Synthesis of Te(STSC)$_2$Cl$_2$, Te(ATSC)$_2$Cl$_2$ and Te(HTSC)$_2$Cl$_2$. These complexes were prepared by reacting TeO_2 (6 mole) dissolved in concentrated HCl with the slurry/solution of appropriate thiosemicarbazone in a minimum volume of methanol in a manner described for Te(BTSC)$_2$Cl$_2$. The unreacted ligands were, however, washed with acetonitrile. Yield 80–90%.

Synthesis of tetrakis(benzaldehydethiosemicarbazone)tellurium(II)(Te(BTSC)$_4$Cl$_2$). The warm solution of TeO_2 (1.217 g, 7.6 mmole) in a minimum volume of concentrated hydrochloric acid was added to a hot solution of BTSC (8.4 g, 46 mmole) in a minimum volume of methanol. The reaction mixture (orange in colour) was refluxed for 2h. The yellowish orange crystals precipitated on cooling were separated, washed with methanol, recrystallized with acetonitrile (quickly) and dried *in vacuo*. Yield 80%.

Synthesis of Te(STSC)$_4$Cl$_2$ and Te(ATSC)$_4$Cl$_2$. These complexes were prepared by the method described for Te(BTSC)$_4$Cl$_2$ except that the reaction mixture was stirred at room temperature for 2 h instead of refluxing and the unreacted ligands and other impurities associated with the complexes were removed by thoroughly washing them with acetonitrile rather than recrystallization. Yield 76 and 90% respectively.

Synthesis of Te(HTSC)$_4$Cl$_2$. The ice cooled solution of TeO_2 (0.5 g, 3.13 mmole) in a minimum volume of concentrated HCl was added to ice cooled thin slurry of HTSC (4 g, 19 mmole) in a minimum volume of methanol. The reaction mixture was stirred for 1 h on an ice bath. The yellow complex formed was filtered, washed thoroughly with acetone to remove the excess of HTSC and impurities and dried *in vacuo*. Yield 85%.

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