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Preparation of Tin Chalcogenide Nanoparticles Using Tribenzyltin(IV) Semi- and Thiosemicarbazone Precursors

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The reactions of tribenzyltin(IV)chloride with one mole equivalent of sodium salts of semi- and thiosemicarbazone ligands gave complexes of the type Bz_3SnL (L = semicarbazone or thiosemicarbazone moiety). These compounds have been characterized by elemental analysis, IR, ^{1}H, ^{13}C{^{1}H}, and ^{119}Sn (in few cases), NMR spectroscopy, and thermogravimetric analysis. Thermal decomposition of complexes was carried out. The materials obtained were characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), energy dispersive X-ray analysis, absorption, and fluorescence spectroscopy. The XRD showed formation of SnS and SnO from thiosemicarbazone and semicarbazone complexes, respectively. The TEM images showed presence of nearly spherical particles.

Keywords nanocrystallites, single source precursors, semi- and thiosemicarbazones, tin oxide, tin sulfide

INTRODUCTION

Recently, much attention is being paid to the 'nanomaterials' due to their interesting physical and chemical properties, as well as their applications.[1] This has resulted into development of newer preparation methods, such as thermal decomposition,[2] chemical reduction,[3] electrodeposition,[4] solvothermal route,[5] etc. for the preparation of these materials. These methods have been utilized for the preparation of nanocrystallites of metals,[6,7] metal oxides,[8] and metal sulfides.[9,10] Tin sulfides and oxides are important materials. Tin forms many binary sulfides such as SnS, SnS_2, Sn_2S_3, etc.[11] Similarly, tin also forms binary oxides, such as SnO, SnO_2, Sn_2O_3, etc.[12] SnO has litharge structure, SnO_2 has rutile structure, whereas Sn_2O_3 exists in a layered structure. Tin chalcogenides have many applications. For example, tin sulfides are used as semiconductors,[13] holographic recording media,[14] and solar collectors as high conversion efficiency photovoltaic materials.[15] Tin oxide has applications in gas-sensors,[16] catalysis,[17] electrochromic windows,[18] and photodetectors.[19]

Various methods have been used for the preparation of tin chalcogenide nanocrystallites. Tin sulfide nanoparticles can be prepared by dispersing melted tin in a sulfur-dissolved solvent.[20] Also, precursors such as $[Sn(SCH_2 - CF_3)_4]$ and $[Sn(SPh)_4]$ have been used. However, they may require H_2S gas as a source of sulfur.[21,22] This could be due to disulfide elimination, which results from non-covalently bonded S—S interaction in the precursor molecules.[23,24] In the present study, we report preparations of tribenzyltin(IV) semi- and thiosemicarbazone complexes and their further use as single source precursors. It is found that semicarbazone derivatives result in tin oxide (SnO) whereas thiosemicarbazones gave tin sulfide (SnS). The structures of the ligands used and the probable structures of the resulting complexes are given Figure 1 and Figure 2, respectively.

EXPERIMENTAL

Materials and Equipments

All the reactions were carried out in the oxygen free nitrogen atmosphere. The analytical grade solvents were used and they were dried prior to use. Tribenzyltin(IV)chloride,[25] thiosemicarbazones and semicarbazones were prepared by the reported methods.[26] Tin was determined as SnO_2 gravimetrically[27] and chlorine was determined by Volhard's method.[27] Elemental analyses (C, H, N, S) of all the compounds were carried out on Thermo Finnigan, Italy Model FLASH EA 1112 Series elemental analyser. Infrared spectra were recorded as KBr pellets in the region 4000–400 cm^{-1} on Perkin-Elmer Spectrum One FTIR spectrometer. ^{1}H, ^{13}C {^{1}H} and ^{119}Sn NMR spectra were recorded in 5 mm NMR tube in dmso-d_6 on a Brucker-300 spectrometer. The chemical shifts are relative to internal standard tetramethylsilane for ^{1}H and ^{13}C {^{1}H} and tetramethyltin for ^{119}Sn. The electronic spectra were recorded on a UV-2401 PC Shimadzu spectrophotometer. The fluorescence spectra were recorded on a RF-5301PC Shimadzu spectrofluorophotometer.

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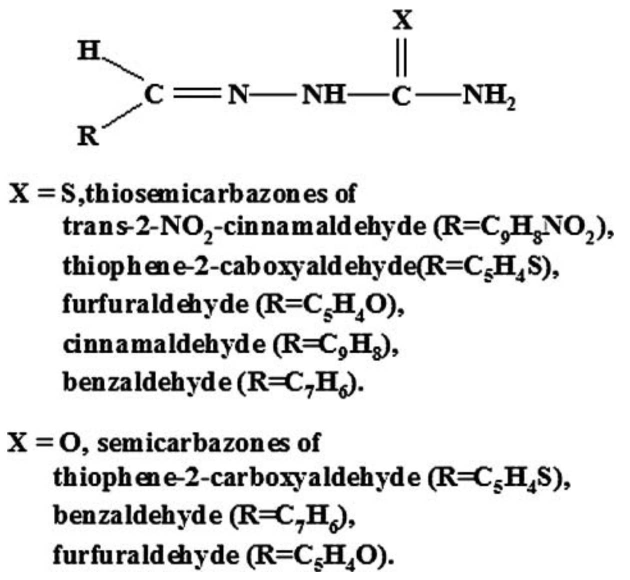


FIG. 1. General structure of the ligands used.

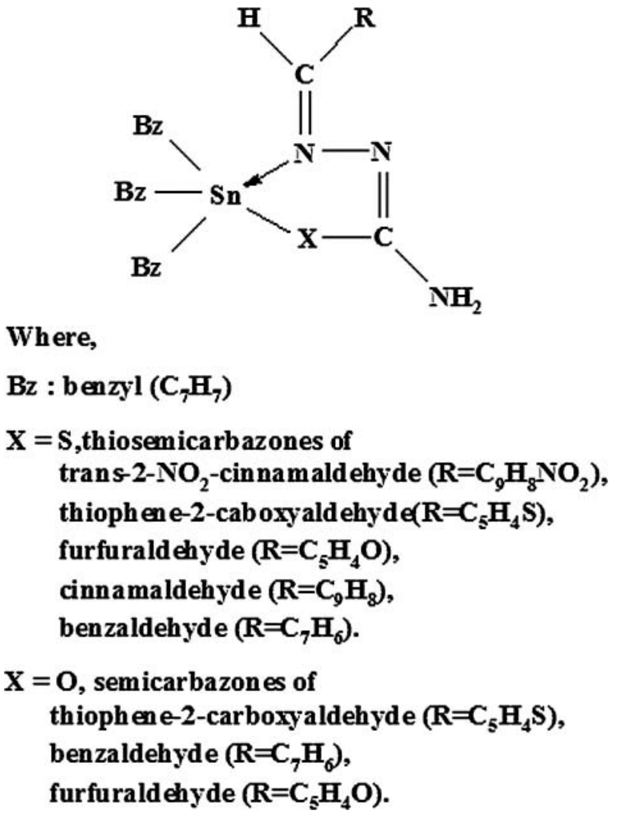


FIG. 2. Probable structure of the tribenzyltin(IV) semi- and thiosemicarbazone complexes.

The thermogravimetric analysis (TGA) was carried out using a Perkin Elmer instrument, Pyris Diamond TG/DTA model with heating rate of 10°C/min under nitrogen atmosphere. X-ray diffraction (XRD) studies were carried out using Cu Kα radiation on X'pert PRO PANalytical X-ray diffractometer (Philips). Transmission electron microscopy (TEM), selected area electron diffraction (SAED) and energy dispersive X-ray analysis (EDAX) were performed on a PHILIPS, CM 200 with operating voltages 20–200 kV.

Preparation of Complexes

Various semi- and thiosemicarbazone complexes of tin (IV) of the type Bz_3SnL [LH = thiosemicarbazones of trans-2-nitro-cinnamaldehyde (trans-2-nitrocinnamtscz), thiophene-2-carboxyaldehyde (thioptscz), furfuraldehyde (furtscz), cinnamaldehyde (cinnamtscz), benzaldehyde (benztscz) and semicarbazones of thiophene-2-carboxyaldehyde (thiopscz), benzaldehyde (benzscz), furfuraldehyde (furscz)] were prepared. A representative preparation is given below.

TABLE 1
Physical and analytical data for Bz_3SnL (L = semi- and thiosemicarbazone) complexes

		Analysis found (calculated)					
Compound	Nature (% Yield)	%Sn	%Cl	%C	%H	%N	%S
Bz_3Sn(trans-2-nitrocinnamtscz)	Brown solid (60.20)	18.72 (18.52)	Nil	57.83 (58.09)	4.39 (4.68)	8.68 (8.73)	4.79 (5.00)
Bz_3Sn(thioptscz)	Yellow solid (55.40)	20.64 (20.61)	Nil	56.75 (56.30)	4.60 (4.69)	7.12 (7.30)	10.91 (11.11)
Bz_3Sn(furtscz)	Brown solid (52.10)	21.21 (21.20)	Nil	58.02 (57.86)	4.96 (4.86)	7.21 (7.50)	5.80 (5.72)
Bz_3Sn (cinnamtscz)	Yellow solid (47.21)	20.05 (19.92)	Nil	62.82 (62.47)	5.50 (5.23)	6.89 (7.04)	5.12 (5.37)
Bz_3Sn(benztscz)	Yellow solid (46.49)	20.68 (20.81)	Nil	61.25 (61.06)	5.06 (5.29)	7.42 (7.36)	5.49 (5.61)
Bz_3Sn(thiopscz)	Yellow solid (57.59)	21.32 (21.19)	Nil	57.96 (57.90)	4.74 (4.85)	7.39 (7.50)	5.87 (5.71)
Bz_3Sn(benzscz)	Yellowish brown solid (54.72)	21.02 (21.45)	Nil	63.11 (62.94)	5.32 (5.24)	7.69 (7.59)	—
Bz_3Sn(furscz)	Yellow solid (46.13)	21.81 (21.82)	Nil	59.52 (59.61)	5.12 (4.96)	7.61 (7.72)	—

Preparation of Bz_3Sn(trans-2-nitro-cinnamtscz) complex

0.037 g (1.56 mmol) of NaH in 20 mL of dry isopropanol was taken in a 100 mL two necked round bottom flask and the mixture was stirred for about half an hour till a clear solution of sodium isopropoxide was obtained. To this solution, 0.395 g (1.58 mmol) trans-2-nitrocinnamldehyde thiosemicarbazone in 25 mL of dry THF was added drop wise and the mixture was refluxed for 2 h. The color changed from colorless to reddish brown. The contents were allowed to cool to room temperature. Then 0.666 g (1.56 mmol) of tribenzyltinchloride dissolved in 20 mL dry THF was added drop wise. The contents were refluxed for 24 h in order to complete the reaction. The reaction mixture was then cooled to room temperature and filtered through G-3 disc to remove the NaCl formed as byproduct. Solvent was evaporated under vacuo. The product was repeatedly washed with dry hexane and dry cyclohexane, dried in vacuum over a period of 1 h, and weighed (yield, 0.602 g, 60.20%).

Similarly, all other complexes were prepared. The physical and analytical data for these complexes is given in Table 1.

Thermal Decomposition in Furnace

Thermal decomposition of complexes was carried out in a horizontal wall furnace. In a typical run, about 0.200 g of complex was taken in quartz boat. It was then heated to 480°C in a furnace under flowing nitrogen atmosphere. The temperature

TABLE 2
^{1}H, ^{13}C {^{1}H} and ^{119}Sn NMR data for Bz_3SnL (L = thiosemicarbazones) complexes

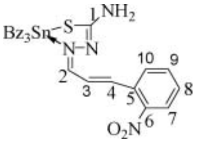
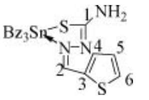
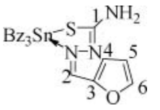
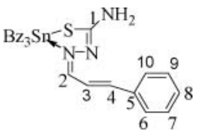
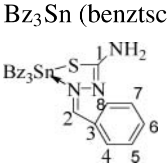
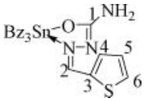
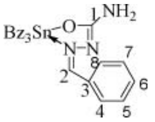
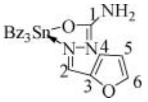
Compound	NMR data (δ in ppm)		
	^{1}H	^{13}C ^{1}H	^{119}Sn
Bz_3Sn (trans-2-nitrocinnamtscz) 	2.50 (s, $C_6H_5\underline{CH_2}$); 6.30–8.49 (m, C_6H_5+ $NO_2C_6H_4CH$ = CH-CH = N + NH_2)	Benzyl group: 31.1 {$C_6H_5\underline{CH_2}$}, 124.3 (m-C), 128.6 (p-C), 129.6 (o-C), 140.7 (i-C); ligand moiety: 125.1, 128.2, 128.5, 130.2, 130.9, 132.9 (C-5 to 10), 134.1 (C-4), 144.1 (C-3), 148.1 (C-2), 178.5 (C-1);	−284.5
Bz_3Sn (thioptscz) 	2.43 (s, $C_6H_5\underline{CH_2}$); 6.79–8.03 (m, C_6H_5+ C_4H_3SCH = N + NH_2)	Benzyl group: 31.1 {$C_6H_5\underline{CH_2}$}, 124.4 (m-C), 128.5 (p-C), 128.7 (o-C), 139.1 (i-C); ligand moiety: 128.4, 129.3, 131.0, 138.1 (C-3 to 6), 140.7 (C-2), 178.1 (C-1);	———-
Bz_3Sn (furtscz) 	2.49 (s, $C_6H_5\underline{CH_2}$); 6.69–7.79 (m, C_6H_5+ C_4H_3OCH = N + NH_2);	Benzyl group: 30.6 {$C_6H_5\underline{CH_2}$}, 124.4 (m-C), 128.6 (p-C), 128.7 (o-C), 140.7 (i-C); ligand moiety: 112.3, 112.8, 132.5, 149.3 (C-3 to 6), 144.9 (C-2), 178.2 (C-1);	———-
Bz_3Sn (cinnamtscz) 	2.49 (s, $C_6H_5\underline{CH_2}$); 6.34–7.85 (m, C_6H_5+ C_6H_5CH = CH-CH = N + NH_2)	Benzyl group: 31.0 {$C_6H_5\underline{CH_2}$}, 124.3 (m-C), 128.6 (p-C), 128.7 (o-C), 140.7 (i-C); ligand moiety: 128.2, 128.5, 129.4, 129.3 (C-5 to 10), 136.3 (C-4), 139.3 (C-3), 145.2 (C-2), 178.2 (C-1);	———-
Bz_3Sn (benztscz) 	2.48 (s, $C_6H_5\underline{CH_2}$); 6.30–7.79 (m, C_6H_5+ C_6H_5CH = N + NH_2)	Benzyl group: 31.0 {$C_6H_5\underline{CH_2}$}, 124.3 (m-C), 128.4 (p-C), 128.5 (o-C), 139.3 (i-C); ligand moiety: 125.5, 127.3, 129.3, 136.3 (C-3 to 8), 140.2 (C-2), 178.2 (C-1);	−294.0

TABLE 3
^{1}H, ^{13}C ^{1}H and ^{119}Sn NMR data for Bz_3SnL (L = semicarbazones) complexes

	NMR data (δ in ppm)		
Compound	^{1}H	^{13}C ^{1}H	^{119}Sn
Bz_3Sn (thiopscz) 	2.49 (s, $C_6H_5\underline{CH_2}$); 6.79–8.03 (m, C_6H_5+ $C_4H_3SCH = N + NH_2$)	benzyl group: 31.1 {$C_6H_5\underline{CH_2}$}, 124.4 (m-C), 128.4 (p-C), 128.7 (o-C), 139.9 (i-C); ligand moiety: 128.4, 128.5, 139.2, 135.4 (C-3 to 6), 140.7 (C-2), 156.8 (C-1);	———
Bz_3Sn (benzscz) 	2.50 (s, $C_6H_5\underline{CH_2}$); 6.45–8.42 (m, C_6H_5+ $C_6H_5CH = N + NH_2$)	benzyl group: 31.1 {$C_6H_5\underline{CH_2}$}, 124.4 (m-C), 128.6 (p-C), 129.0 (o-C), 139.7 (i-C); ligand moiety: 127.0, 128.5, 129.5, 135.2 (C-3 to 8), 140.7 (C-2), 157.2 (C-1);	−287.8
Bz_3Sn (furscz) 	2.50 (s, $C_6H_5\underline{CH_2}$); 6.69–8.40 (m, C_6H_5+ $C_4H_3OCH = N + NH_2$)	benzyl group: 31.2 {$C_6H_5\underline{CH_2}$}, 124.3 (m-C), 128.5 (p-C), 128.7 (o-C), 140.8 (i-C); ligand moiety: 111.3, 112.4, 130.4, 150.4 (C-3 to 6), 144.8 (C-2), 156.9 (C-1);	−288.3

was maintained for 3 h. Then the contents were cooled and the decomposition product was taken out.

RESULTS AND DISCUSSION

The tribenzyltin(IV) semi- and thiosemicarbazone complexes were prepared by the reactions of tribenzyltin(IV)chloride with sodium salts of semi- and thiosemicarbazone ligands in 1:1 stoichiometry in dry THF under refluxing conditions (eqn. 1).

$$Bz_3SnCl + LNa \xrightarrow[-NaCl]{THF,\ Reflux} Bz_3SnL \qquad [1]$$

Where, LNa = Sodium salts of semi- and thiosemicarbazone ligands

The resulting complexes are coloured solids. They were characterized by elemental analysis, IR, NMR spectra and TGA.

IR Spectra

The infrared spectra of the complexes have been compared with the spectra of ligands and from the shifts in peak positions and/or from the intensity lowering, coordination sites have been ascertained. In the IR spectra of the ligands, bands in the region 3442–3244 cm^{-1} are assigned to ν_{NH2} which remain unaltered in the spectra of complexes. This ruled out coordination of NH_2 group to metal. The other bands in the spectra of ligands at 3150, 1620, 1024, and 1660–1720 cm^{-1} are assigned to ν_{NH}, $\nu_{C=N}$, $\nu_{C=S}$ and $\nu_{C=O}$, respectively.[28] The bands at 3150 cm^{-1} are absent in the spectra of complexes, indicating deprotonation of NH group. The band due to $\nu_{C=N}$ is observed at ∼1600 cm^{-1} in complexes, which is shifted to lower wavenumber compared to band positions in the spectra of ligands. New bands observed at ∼750 cm^{-1} in thiosemicarbazone complexes and at 568–585 cm^{-1} in semicarbazone complexes are assigned to $\nu_{(C-S)}$[29] and $\nu_{(Sn-O)}$,[28] respectively.

NMR Spectra

In the ^{1}H NMR spectra of the ligands, the signals due to NH proton are observed at ∼ 10.5 ppm in semicarbazones and at ∼ 11.5 ppm in thiosemicarbazones. These signals are absent in the spectra of complexes indicating deprotonation of NH group (Tables 2, 3). These observations are consistent with the ligand coordination through azomethine nitrogen and sulfur (in thiosemicarbazone complexes) or oxygen (in semicarbazone complexes).[30,31] ^{119}Sn chemical shifts have been used extensively for predicting coordination number and geometry around tin atom.[32] Penta coordinated tin have been suggested in the tin compounds for which ^{119}Sn chemical shift is observed between -90 to -330 ppm.[32] ^{119}Sn chemical shifts of the present tin complexes lie in this range confirming penta coordinated geometry around tin.

Thermal Decomposition Studies

Thermogravimetric analyses of complexes were carried out before the thermal decomposition studies in order to evaluate their use as single source precursors. It is found that the weights

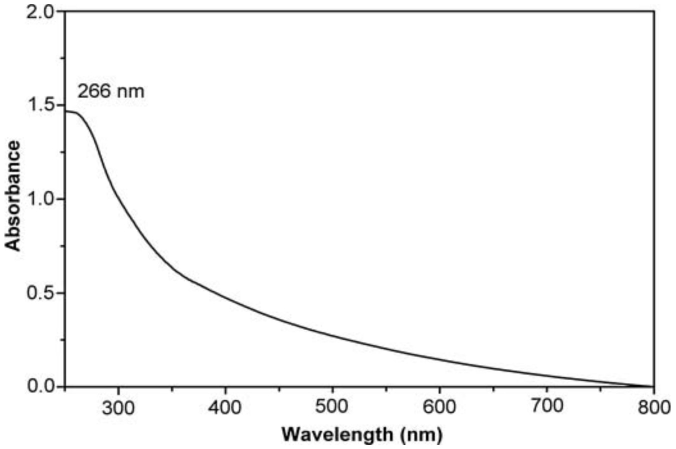


FIG. 3. Absorption spectrum of SnS nanocrystallites dispersed in methanol obtained from Bz_3Sn(trans-2-NO_2-cinnamtscz).

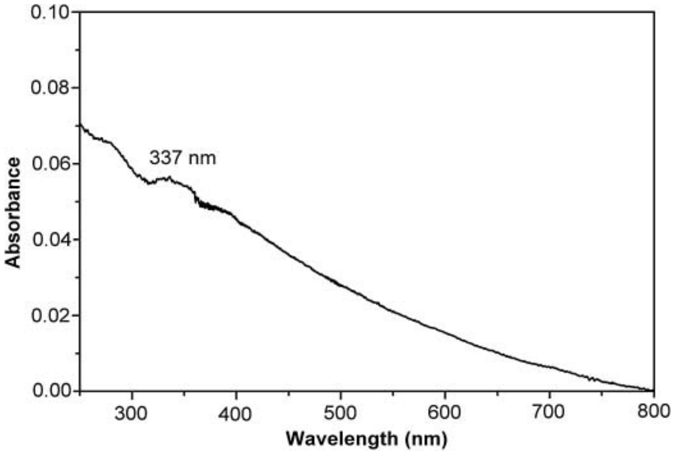


FIG. 4. Absorption spectrum of SnO nanocrystallites dispersed in methanol obtained from Bz_3Sn(furscz).

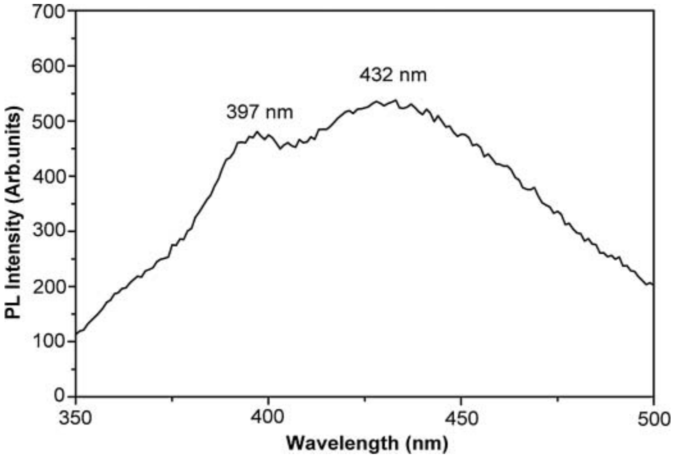


FIG. 5. PL spectrum of SnS nanocrystallites dispersed in methanol obtained from Bz_3Sn(trans-2-nitro-cinnamtscz).

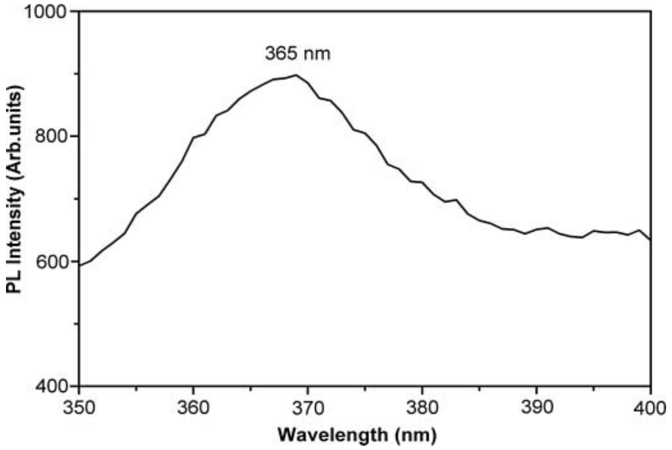


FIG. 6. PL spectrum of SnO nanocrystallites dispersed in methanol obtained from Bz_3Sn(furscz).

of residues obtained in TGA of thiosemi- and semicarabzone complexes are higher than those calculated for tin sulfide (expected 26.5%, observed 39.6%) and tin oxide (expected 24.3%, observed 28.1%), respectively, which may be due to carbon contamination.[33] From TGA, it is evident that the decomposition of complexes takes place in the temperature range 450–600°C. Therefore, thermal decomposition of the complexes was carried out at 480°C. The resulting materials were characterized by UV-VIS spectroscopy, XRD and TEM and EDAX techniques.

Optical Studies

In the absorption spectrum of SnS nanocrystallites obtained from Bz_3Sn(trans-2-nitro-cinnamtscz), a peak is observed at 266 nm (Figure 3). Figure 4 shows absorption spectrum of SnO obtained from Bz_3Sn(furscz). The absorption peak is observed at 337 nm. Figure 5 and Figure 6 show photoluminescence (PL) spectra of the SnS and SnO nanocrystallites, respectively, dispersed in methanol. The PL feature of SnS nanoparticles shows two strong emission bands at 432 nm (blue emission)

TABLE 4
Decomposition products obtained from Bz_3SnL (L = thiosemicarbazone or semicarbazone) complexes

Precursor	Final product
Bz_3Sn (trans-2-nitrocinnamtscz)	Orthorhombic SnS
Bz_3Sn (thioptscz)	Orthorhombic SnS
Bz_3Sn (furtscz)	Orthorhombic SnS
Bz_3Sn (cinnamtscz)	Orthorhombic SnS
Bz_3Sn (benztscz)	Orthorhombic SnS
Bz_3Sn (thiopscz)	Tetragonal SnO
Bz_3Sn (benzscz)	Tetragonal SnO
Bz_3Sn (furscz)	Tetragonal SnO

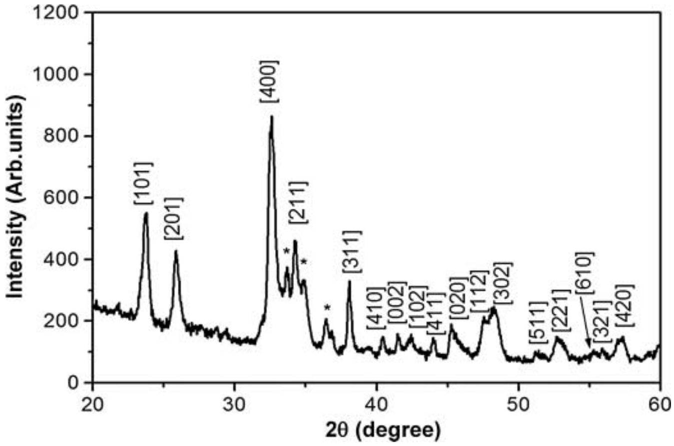


FIG. 7. XRD pattern of orthorhombic SnS (JCPDS: 73-1859) obtained from Bz_3Sn(trans-2-nitro-cinnamtscz) (*these peaks match with elemental tin, JCPDS: 01–0926).

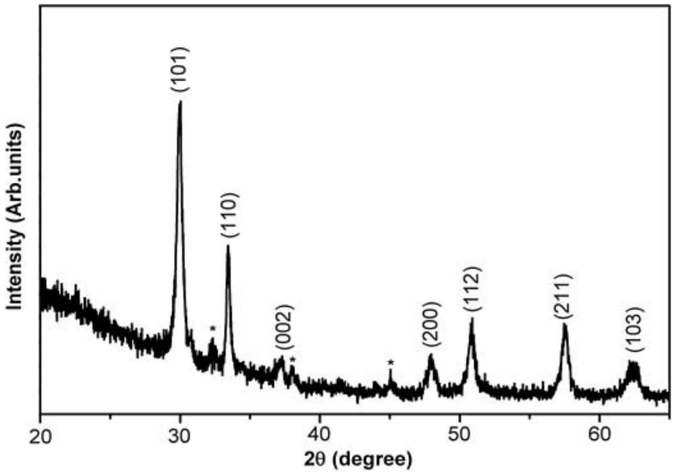


FIG. 8. XRD pattern of tetragonal SnO (JCPDS: 85-0712) obtained from Bz_3Sn(furscz) (* these peaks match with elemental tin, JCPDS: 01-0926).

and at 397 nm (UV emission), respectively. The PL feature of SnO is observed at 365 nm. These values are consistent with the values reported in the literature.[20]

XRD Patterns

XRD patterns of the particles obtained reveal that the thermal decomposition of thiosemicarbazone complexes results in SnS and that of semicarbazone complexes gave SnO (Table 4). The XRD of the product obtained by decomposition of Bz_3Sn(trans-2-nitrocinnamtscz) is shown in Figure 7. It matches well with orthorhombic SnS (JCPDS: 73–1859). Peak broadening due to nanocrystalline nature of particles can be seen. The preferred orientation along (400) direction is observed. All other thiosemicarbazone complexes also gave orthorhombic SnS. Figure 8 shows XRD pattern of the product obtained from Bz_3Sn(furscz). It matches with tetragonal SnO (JCPDS: 85–0712). The preferred orientation is along (101) direction. Similarly, decomposition of other semicarbazone precursors gave tetragonal SnO. Some minor impurity peaks due to tetragonal tin (JCPDS:01-0926) are seen in the XRD patterns of both SnS and SnO nanocrystallites.

TEM Images

The morphologies of the decomposed products were further examined by TEM images. Figure 9a shows a typical TEM image of as-prepared SnS obtained from Bz_3Sn(trans-2- nitrocinnamtscz). Figure 10a shows a TEM image of as-prepared SnO obtained from Bz_3Sn(furscz). Spherical particles with average particle size of ∼ 40 nm (for SnS) and ∼ 30 nm (for SnO) were observed. The corresponding SAED patterns (Figure 9b and Figure 10b) of SnS and SnO particles reveal the well crystalline nature of the samples. EDAX of SnS gave atomic percentage of Sn and S as 50.91% and 49.09%, respectively. Whereas, for SnO atomic percentage of Sn and O are found to be 52.11%

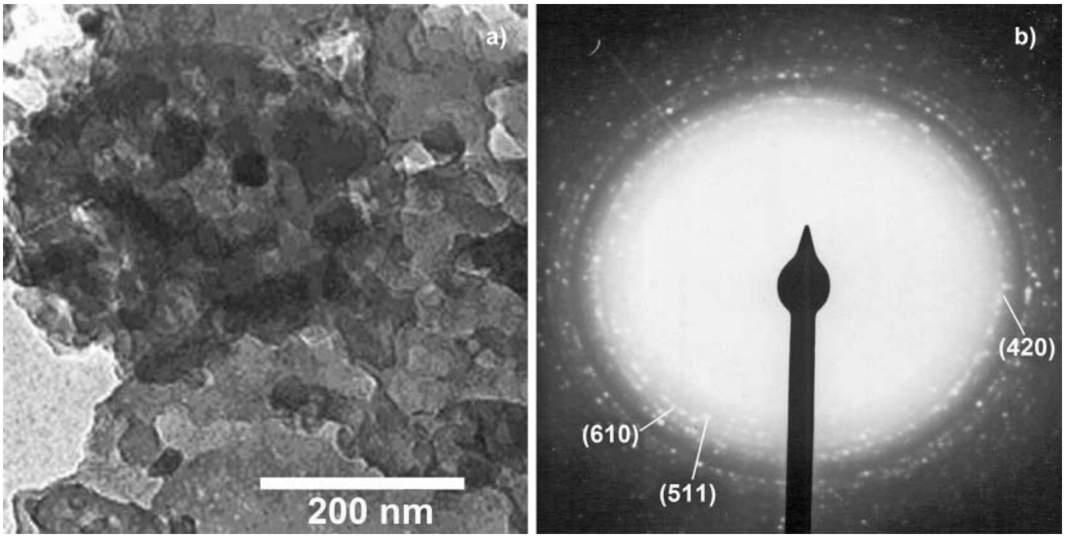


FIG. 9. a) TEM image and b) SAED pattern of SnS nanocrystallites obtained from Bz_3Sn(trans-2-nitro-cinnamtscz).

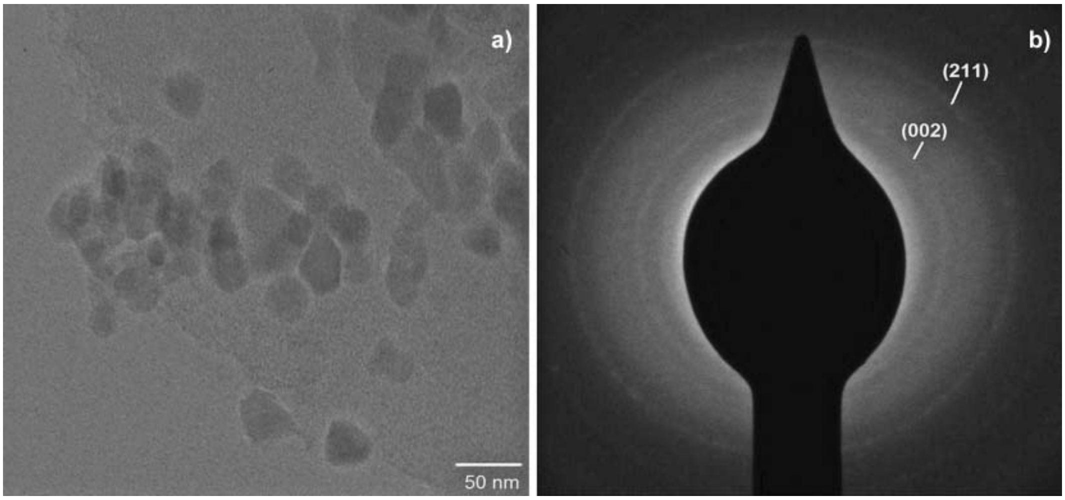


FIG. 10. a) TEM image and b) SAED pattern of SnO nanocrystallites obtained from Bz_3Sn(furscz).

and 47.89%, respectively. Thus, the materials have slight deficiency of sulfur and oxygen.

Reductive recombination mechanisms have been reported in the literature.[34] These involve reduction of metal center followed by recombination with a chalcogen to give metal chalcogenides. Similarly, mechanism can be proposed in the present case where reduction of tin center might be taking place followed by recombination with chalcogen to form SnS or SnO. This is also supported by the presence of peaks due to elemental tin in the XRD patterns of both types of materials.

CONCLUSIONS

It is found that the thiosemicarbazone and semicarbazone complexes are useful single-source precursors for the preparation of tin chalcogenides. Thiosemicarbazone complexes results in the formation of SnS whereas semicarbazone complexes gave SnO nanocrystallites. The method used here is very convenient for the preparation of tin chalcogenides.

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