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Metal dithiocarbamate precursors for the preparation of a binary sulfide and a pyrochlore: Synthesis, structure, continuous shape measure and bond valence sum analysis of antimony(III) dithiocarbamates



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ABSTRACT

The antimony(III) complexes [Sb(chmdtc)₃] (1), [Sb(chedtc)₃] (2) and [Sb(dchdtc)₃] 0.5 C_7H_8 (3) (where chmdtc = cyclohexylmethyldithiocarbamate, chedtc = cyclohexylethyldithiocarbamate and dchdtc = dicyclohexyldithiocarbamate) have been prepared and characterized by electronic, IR and NMR (¹H and ¹³C) spectra and single crystal X-ray diffraction. Electronic spectra of the complexes show charge transfer transitions. The characteristic thioureide bands occur at 1468, 1479 and 1445 cm⁻¹ for (1), (2) and (3) respectively. The single crystal X-ray structures of (1), (2) and (3) reveal anisobidentate binding of the dithiocarbamates. Short C—H···S contacts are observed along the 'a' axis in (2) and (3). CShM calculations on the SbS₆ chromophores support the distorted octahedral geometry in (1) and (2), and the distorted pentagonal pyramidal geometry in (3), clearly quantifying the extent of deviation from the ideal geometries. The nature of the substituents and the lone pair of electrons present in antimony are responsible for the shift of the metal atom position from the geometrical center of the six sulfur atoms. BVS of the compounds show the highly covalent nature of the Sb—S bonds. *Nano* Sb₂S₃ and $(Tl_{2/3-2\delta})[Tl_{1-y}^3Sb^{3+}y]$ Sb₂O₆O'_{1/3-\delta}, a pyrochlore, have been prepared from the precursors and have been characterized by PXRD, FESEM, EDX, HRTEM and SAED.

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1. Introduction

Molecular single source precursors of new materials for various applications have the advantage of containing all the elements necessary for the formation of the final solid material [1]. Most semiconductor devices are prepared from volatile and ultra-pure gaseous derivatives of various organic and inorganic precursors as starting materials. Metal dithiolates, dithiobiurets, diketonates and alkoxides, like many other metallo-organic compounds, have been used as precursors for many new materials which have interesting optical and electronic properties [2–7]. Research interests in



* Corresponding author. Tel.: +91 413 2202834; fax: +91 414 422265. *E-mail address:* krauchem@yahoo.com (K. Ramalingam). metal dithiolates have persisted for over three decades because of their applications and academic diversity. Simple dithiocarbamate salts have shown interesting biological and pharmacological properties [8–11]. Relatively, the chemistry of 1,1-dithiochelates of main group elements is less widely explored than that of the transition metals [12]. Dithiocarbamates show a variety of coordination modes such as isobidentate, anisobidentate, monodentate and triconnective [13]. Metal dithiolates in particular have been used as single source precursors in CVD and other related techniques for the preparation of thin films of semiconductor materials in the recent past [2,14–17].



In particular, Group XV dithiolates continue to attract attention due to their diverse applications in agriculture, industry, medicine and nanotechnology [18,19]. Antimony(III) chalcogenides, Sb₂X₃, where X = S and Se, show excellent photoconductivity, semiconducting properties and are potential candidates for applications in solar energy conversion. Intelligent experimental procedures adopted for the preparation of the chalcogenides result in the desired morphologies [20–22]. Attempts have been made to identify new pyrochlore phases involving Tl—Sb—O oxide because of their potential applications [23,24]. In continuation of our interest in the identification of new materials using metallodithiolates as precursors, in this paper we report the synthesis and characterization of three precursors, viz. [Sb(chmdtc)₃] (1), [Sb(chedtc)₃] (2) and [Sb(dchdtc)₃] 0.5 C_7H_8 (3) (where chmdtc = cyclohexylmethyldithiocarbamate, chedtc = cyclohexylethyldithiocarbamate and dchdtc = dicyclohexyldithiocarbamate anions).



Nano antimony(III) sulfide, and $(T_{1/3-2\delta}^*)[T_{1-y}^{3+}Sb_2O_6O'_{1/3-\delta}$, a pyrochlore, were prepared and characterized by powder XRD, FESEM, EDX, HRTEM and SAED analysis.

2. Experimental

Antimony trioxide (SD fine chemicals, India), the parent amines, carbon disulfide (Fisher Scientific, India) and the solvents (SD fine chemicals, India) were commercially available analytical grade materials and were used as supplied without further purification. Melting/boiling points of the products were determined with a digital apparatus (Jains, India). Elemental analyses were carried out with an Elementar, Vario Micro Cube instrument. IR spectra were recorded on an Avatar Nicolet FT-IR spectrometer (range 4000–400 cm⁻¹) as KBr pellets of the compounds. Electronic spectra were recorded in CH₂Cl₂ on a Hitachi U-2001 double beam spectrometer. Thermal analysis was carried out with a NETZSCH STA 449F3 instrument under a nitrogen atmosphere with a heating rate of 20 K min⁻¹. ¹H and ¹³C NMR spectra were recorded on a Bruker AMX-400 spectrometer at room temperature using CDCl₃ as the solvent. The powder diffraction data were collected in the 2θ range 2°-80° using a Bruker-D8 X-ray diffractometer equipped with Cu Ka radiation at a fixed current and potential. The scan speed and step sizes were 0.05° min⁻¹ and 0.00657 respectively. FE scanning electron micrographs of the samples were recorded with a JEOL JSM-5610Lv microscope. HRTEM measurements were carried out on a JEOL 2100 (Field emission) with an accelerating voltage of 200 kV.

2.1. X-ray crystallography

Intensity data were collected at ambient temperature (295 K) on a Bruker APEX-II CCD diffractometer with graphite monochromated Mo K α radiation (λ = 0.71073 Å) and were corrected for absorptions with a multi-scan technique [25–27]. The structures were solved by direct methods using sir97 and were refined by SHELX97 [28]. The non-hydrogen atoms were refined anisotropically and all the hydrogen atoms were fixed geometrically. Molecular plots were obtained using the ORTEP-3 program [29].

2.2. Preparation of the complexes, nano Sb₂S₃ and pyrochlore

2.2.1. Preparation of tris(cylohexylmethyldithiocarbamato) antimony(III); [Sb(chmdtc)₃] (**1**)

N-cyclohexyl-N-methylamine (0.03 mol, 3.96 mL) and carbon disulfide (0.03 mol, $\sim 5 \text{ mL}$) in methanol (20 mL) were mixed under

ice-cold conditions (5 °C) to obtain a yellow dithiocarbamic acid solution. To the freshly prepared dithiocarbamic acid solution, an acidified solution of Sb₂O₃ (0.01 mol, 2.915 g) was added with constant stirring. A yellow solid separated from the solution, which was filtered, washed with ethanol and dried in air. Yield: 83%, m.p.: 173 °C. *Anal.* Calc. for $C_{24}H_{42}N_3S_6$ Sb (686.8): C, 41.97; H, 6.16; N, 6.11. Found: C, 41.92; H, 6.12; N, 6.07%.

2.2.2. Preparation of tris(cylohexylethyldithiocarbamato)antimony (III); [Sb(chedtc)₃] (**2**)

N-cyclohexyl-N-ethylamine (0.03 mol, 4.49 mL) and carbon disulfide (0.03 mol, ~5 mL) in methanol (20 mL) were mixed under ice-cold conditions (5 °C) to form a yellow solution of dithiocarbamic acid. A weakly acidified solution of Sb₂O₃ (0.01 mol; 2.915 g) was then added with continuous stirring. A similar procedure as described in Section 2.2.1 was used for the preparation. A pale yellow precipitate was obtained, which was washed with methanol and then dried in air. Yield: 78%, m.p.: 153 °C. *Anal.* Calc. for C₂₇H₄₈N₃S₆Sb (728.8): C, 44.49; H, 6.64; N, 5.77. Found: C, 44.45; H, 6.61; N, 5.72%.

2.2.3. Preparation of tris(dicylohexyldithiocarbamato)antimony(III); $[Sb(dchdtc)_3] 0.5 C_7H_8$ (**3**)

A similar procedure as described in Section 2.2.1 was employed for the preparation of the dicyclohexylamine analogue. N,N-dicyclohexylamine (0.03 mol, 3.66 mL), carbon disulfide (0.03 mol, ~5 mL) in methanol (20 mL) and Sb₂O₃ (0.01 mol, 2.915 g) were used for the preparation. Yield: 82%, m.p. 265 °C. *Anal.* Calc. for C_{42.50}H₇₀N₃S₆Sb (937.2): C, 54.47; H, 7.53; N, 4.48. Found: C, 54.43; H, 7.49; N, 4.44%.

All three compounds were recrystallized from toluene and only compound (**3**) showed the presence of stoichiometric toluene of crystallization.

2.2.4. Preparation of tris(cylohexylmethyldithiocarbamato) thallium(III); [Tl(chmdtc)₃]

Tris(cylohexylmethyldithiocarbamato)thallium(III), [Tl(chmdtc)₃], was prepared as per the procedure reported earlier from this laboratory [30].

2.2.5. Preparation of nano Sb_2S_3 by the non-conventional solvothermal decomposition of tris(disubstituted dithiocarbamato)antimony(III)

1 mM of the tris(disubstituted dithiocarbamato)antimony(III) complexes (1), (2) and (3) as clear solutions in chloroform (100 mL) were heated with diethylenetriamine (2 mL) at 60 °C for 45 min. Solid yellow antimony sulfide was separated from chloroform, washed with ether and dried in air.

2.2.6. Preparation of $(Tl_{2/3-2\delta}^{1})[Tl_{1-y}^{3+}Sb_{y}^{3+}]Sb_{2}O_{6}O'_{1/3-\delta}$ pyrochlore

 $(Tl_{2/3-2\delta}^{1}][Tl_{1-y}^{3+}Sb_{y}^{2}]Sb_{2}O_{6}O'_{1/3-\delta}$ pyrochlore was prepared by mixing finely ground recrystallized samples of $[Sb(chmdtc)_{3}]$ (1 mmol, 0.69 g) and $[Tl(chmdtc)_{3}]$ (1 mmol, 0.77 g) in a pestle and mortar which were then ground again thoroughly to obtain an intimate fine powder of a 1:1 mixture of the dithiocarbamates. The mixture was then loaded into a platinum crucible and heated in a furnace in air. Three samples of the above were heated at 295, 350 and 750 °C and subsequently characterized.

3. Results and discussion

3.1. Infrared spectral studies

Some important infrared spectral bands are presented in Table 1. For complexes (1), (2) and (3), the v_{C-N} (thioureide) bands are observed at 1468, 1479 and 1445 cm⁻¹, respectively. The v_{C-S}

Table 1Electronic and IR spectral data.

Compound	UV–Vis (nm)		$IR (cm^{-1})$		
	СТ	Intraligand	V _{C-N}	v _{C-S}	v _{C—H}
$[Sb(chmdtc)_3](1)$	442	340	1468	1001	2849-2928
[Sb(chedtc) ₃] (2)	443	342	1479	1009	2851-2928
$[Sb(dchdtc)_3](3)$	439	358	1445	1006	2851-2924

stretching bands are observed around 1000 cm⁻¹, supporting [31] the bidentate coordination mode of the dithiocarbamate ligand to the metal center. However, the single crystal X-ray structures of the compounds show the anisobidentate nature of bonding of the dithiocarbamates. The v_{C-H} bands are observed in the range 2849–2928 cm⁻¹.

3.2. Electronic spectra

Electronic spectra of the compounds (Table 1.) show bands between 340 and 358 nm due to intraligand π – π * transitions, mainly associated with the N–C=S and S–C=S groups [32,33]. The charge transfer transitions, which impart the characteristic color to the compounds, are observed in the range 439–443 nm.

3.3. NMR spectral studies

The NMR spectral data of the antimony complexes are listed in Table 2. The chemical shifts reported in the spectral database for organic compounds (SDBS) for the parent amines are shown in brackets [34]. The ¹H NMR spectrum of complex (1) shows an intense signal at 4.92 ppm, corresponding to single proton integration, due to the α -CH proton of the cyclohexyl ring. The CH₃ protons (α' -CH₃) attached to the nitrogen appear at 3.28(s) ppm with a proton integration corresponding to three. The α -CH and α' -CH₃ protons are affected to a maximum extent on complexation. In the cyclohexyl ring all the equatorial protons are deshielded to a large extent compared to the axial protons. The equatorial protons appear in the range 1.80-1.88 ppm. The axial protons appear between 1.66 and 1.69 ppm. The ¹³C NMR spectrum of (1) shows a weak signal at 199.41 ppm due to the thioureide carbon [35]. The α -carbon atom of the cyclohexyl ring appears at 62.60 ppm and the α' -C(H₃) carbon atom appears at 35.43 ppm. The β -, γ - and δ - carbon signals are the least affected and appear at 25.35, 25.45 and 29.93 ppm respectively.

In complex (**2**), the ¹H NMR signal for the α -CH proton of the cyclohexyl ring appears at 4.95 ppm and α' -CH₂ appears at 3.80–3.81 ppm, corresponding to two protons. The β' -CH₃ protons of the ethyl group appears as a well resolved triplet at 1.29–1.38 ppm. The ¹³C NMR spectrum of (**2**) shows a characteristic thioureide signal at 199.38 ppm. The β' -CH₃ signal appears at

Table 2
NMR spectral data (ppm).
Complex

14.32 ppm as a much shielded signal and α' -C(H₂) appears to be highly deshielded at 43.66 ppm. The α -C(H) signal of the cyclohexyl ring appears at 63.13 ppm. The β -, γ - and δ - carbon signals, which are the least affected by complexation, appear at 30.60 and between 25.40 and 25.64 ppm respectively.

In the case of complex (**3**), the α -CH proton of the cyclohexyl ring is observed at 5.16 ppm. The β -, γ - and δ -CH₂ signals appear in the region 1.79–1.82(e) ppm (collapsed). The ¹³C NMR spectrum exhibits a weak characteristic signal due to the thioureide carbon at 199.95 ppm. The ¹³C NMR signal corresponding to the α -C(H) carbon of the cyclohexyl ring is found to be significantly shielded and appears at 65.71 ppm. The β -C(H₂) and γ -C(H₂) carbons appear in the regions 25.03–29.78 and 26.32–34.51 ppm. The NMR spectra of the complexes clearly indicate that the immediate environment around the thioureide nitrogen is largely affected upon complex formation. The alkyl groups are non-equivalent in the complexes as the α . β and γ -methylene protons and terminal methyl protons result in broad signals, indicating a substantial barrier to C-N < bond rotation. The prominent deshielding of the -CH₂ protons in the compounds is attributed to the shift of electron density on the sulfur atom (or the metal) through the thioureide π system. In a similar manner, the α -methylene protons adjacent to the nitrogen atom undergo strong deshielding and are observed in the region 3.80–3.81 ppm. The β -CH₂ signals are observed in the range 1.48–1.95 ppm and assignments are made on the basis of proton integral values obtained for the corresponding signals. The thioureide signals observed in the compounds are mostly similar, except in the case of [Sb(dchdtc)₃] (**3**), which has a signal slightly higher than the other two compounds, indicating an increased contribution of the thioureide form in $[Sb(dchdtc)_3]$ (3).

3.4. Thermogravimetric analysis

Thermal analyses of the compounds were carried out under a nitrogen atmosphere. $[Sb(chmdtc)_3](1)$ showed a large single step mass loss, observed in the range 280-310 °C. The residue stabilized at 540 °C corresponds to Sb₂S₃ (Exptl.: 26.0%; Calcd.: 26.7%). [Sb(chedtc)₃] (2) showed a similar pattern of mass loss, with a single step thermal decay at temperatures <500 °C. The final residue confirmed the formation of Sb₂S₃ (Exptl.: 23.0%; Calcd.: 23.2%). $[Sb(dchdtc)_3]$ 0.5 C₇H₈ (**3**) showed loss toluene, the solvent of crystallization, (Exptl.: 5.0%; Calcd.: 5.0%) up to 240 °C. The bulk of the mass was lost on continued heating to a temperature of 510 °C and the residue perfectly agreed with the mass expected for Sb₂S₃ (Exptl.: 18.0%; Calcd.: 18.1%). The thermal analysis confirmed the proposed formulae of the compounds perfectly. The most important observation is that in all three compounds the final residue was found to be Sb₂S₃. Among the three compounds, the dicycloanalogue [Sb(dchdtc)₃] 0.5 C₇H₈ (3) showed a relatively higher thermal stability.

Complex	NMR	α-CH	γ -CH ₂ & δ -CH ₂	CH ₃ /CH ₂ (alkyl)	$N^{13}CS_2$
$[Sb(chmdtc)_3](1)$	¹ H	4.92 (2.30)	1.80-1.88(e)	3.28 (2.42)	-
			1.66-1.69		
	¹³ C	62.60 (58.63)	29.93 25.35,	35.43	199.41
			25.45		
	^{1}H	4.95	1.80-1.95(e)	3.80-3.81	-
			1.58-1.69	1.29-1.38	
$[Sb(chedtc)_3]$ (2)	¹³ C	63.13	30.60	43.66	199.38
			25.40-25.64	14.32	
	^{1}H	5.16 (2.55)	1.78-1.81(e)	-	-
			1.25-1.60 (collapsed)		
$[Sb(dchdtc)_3]$ (3)	¹³ C	65.71 (53.17)	29.70	-	199.95
			25.33-26.68		

Table 3

 $Crystal \ data \ collection \ and \ refinement \ parameters \ for \ [Sb(chmdtc)_3], \ [Sb(chedtc)_3] \ and \ [Sb(dchdtc)_3] \ 0.5 \ C_7 H_8.$

Complex	[Sb(mchdtc) ₃]	[Sb(chedtc) ₃]	$[Sb(dchdtc)_3] 0.5 C_7 H_8$
Empirical formula	$C_{24}H_{42}N_3S_6Sb$	C ₂₇ H ₄₈ N ₃ S ₆ Sb	C _{42.50} H ₇₀ N ₃ S ₆ Sb
Formula weight	686.72	728.79	1874.39
Color	yellow	yellow	yellow
Habit	block	block	block
Crystal system	hexagonal	triclinic	monoclinic
Space group	P 63	ΡĪ	P 2 ₁ /c
Crystal dimension (mm ³)	$0.25\times0.18\times0.14$	$0.35 \times 0.20 \times 0.19$	$0.33 \times 0.26 \times 0.21$
a (Å)	13.8776(6)	10.1061(3)	12.1780(8)
b (Å)	13.8776(6)	12.2458(3)	14.0520(10)
<i>c</i> (Å)	9.4649(4)	14.5676(4)	28.7180(19)
α (°)	90.00	78.5810(10)	90.00
β (°)	90.00	84.8840(10)	100.6135(11)
γ (°)	120.00	81.5590(10)	90.00
$U(Å^3)$	1578.61(18)	1744.66(8)	4830.3(6)
Z	2	2	2
D_{calc} (g cm ⁻³)	1.445	1.387	1.289
F (000)	708	756	1972
λ (Å)	Μο Κα (0.71073)	Μο Κα (0.71073)	Μο Κα (0.71073)
θ range (°)	1.69–30.66	1.71-25.00	1.44–25.25
Scan type	multi	multi	multi
Index range	$-19 \leqslant h \leqslant 19; -19 \leqslant k \leqslant 19; -13 \leqslant l \leqslant 13$	$-12 \leqslant h \leqslant 11; -14 \leqslant k \leqslant 14; -15 \leqslant l \leqslant 17$	$-14 \leq h \leq 14$; $-16 \leq k \leq 16$; $-34 \leq l \leq 34$
Reflections collected	3252	5975	8757
Reflections $[F_o > 2\sigma(F_o)]$	3133	5308	7504
Weighting scheme	$w = 1/[s^2(F_0^2) + (0.0265P)^2]$	$w = 1/[s^2(F_0^2) + (0.0212P)^2 + 1.100P]$	$w = 1/[s^2(F_0^2) + (0.0373P)^2 + 2.7376P]$
	where $P = (F_0^2 + 2F_c^2)/3$	where $P = (F_0^2 + 2F_c^2)/3$	where $P = (F_{o}^{2} + 2F_{c}^{2})/3$
Number of parameters refined	104	334	459
Final R, Rw (obs, data)	0.0167, 0.0421	0.0238, 0.0537	0.0282, 0.0726
Goodness-of-fit (GOF)	1.043	1.007	1.036

Table 4

Selected bond distances (Å) and bond angles (°).

[Sb(chmdtc) ₃]		[Sb(chedtc) ₃]		[Sb(dchdtc) ₃] 0.5 C ₇ H ₈	
Bond distances					
Sb—S(1)	2.5251(4)	Sb—S(1)	2.5411(6)	Sb(1)—S(1)	2.6683(7)
Sb—S(2)	2.9732 (4)	Sb—S(2)	2.8483(8)	Sb(1)—S(2)	2.7856(7)
S(1)-C(1)	1.6988(13)	Sb—S(3)	2.5331(5)	Sb(1)—S(3)	2.4557(7)
S(2)-C(1)	1.7493(13)	Sb—S(4)	2.9513(6)	Sb(1)—S(4)	2.8853(7)
C(1)-N(1)	1.3297(17)	Sb—S(5)	2.5511(7)	Sb(1)—S(5)	2.6228(7)
C(2)—N(1)	1.462(2)	Sb—S(6)	2.9962(6)	Sb(1)—S(6)	2.8571(7)
C(3)—N(1)	1.4833(18)	S(1)-C(1)	1.697(2)	S(1)-C(1)	1.745(3)
		S(2)-C(1)	1.750(2)	S(2)-C(1)	1.708(3)
		N(1)-C(1)	1.327(3)	N(1)-C(1)	1.331(3)
Bond angles					
S(1)— Sb — $S(2)$	64.71(3)	S(1)— Sb — $S(2)$	66.46(2)	S(1)-Sb(1)-S(2)	64.76(2)
S(1)-C(1)-S(2)	118.67(10)	S(3)—Sb—S(4)	64.85(2)	S(3) - Sb(1) - S(4)	66.09(2)
N(1)-C(1)-S(1)	122.99(10)	S(5)—Sb—S(6)	64.16(2)	S(5)-Sb(1)-S(6)	64.55(2)
N(1)-C(1)-S(2)	118.34(10)	S(1)-C(1)-S(2)	118.63(14)	S(1)-C(1)-S(2)	115.66(14)
C(1)-N(1)-C(2)	121.60(10)	S(3)-C(10)-S(4)	118.74(14)	S(3)-C(14)-S(4)	116.19(15)
C(1)-N(1)-C(3)	120.91(12)	S(5)—C(19)—S(6)	118.78(14)	S(5)—C(27)—S(6)	116.52(16)

3.5. Structural analysis

Crystal data, data collection and refinement parameters are given in Table 3. Selected bond parameters are given in Table 4. ORTEP diagrams of (1), (2) and (3) are shown in Figs. 1–3 respectively. In [Sb(chmdtc)₃] (1), two formula units are present in the unit cell. The molecule shows C3 point group symmetry and hence all three ligands are equivalent. The SbS₆ chromophore of [Sb(mchdtc)₃] is of a distorted octahedral (dOh) geometry. The asymmetric unit shows two Sb—S bonds, 2.5251(4) and 2.9732(4) Å, indicating anisobidentate binding. The short thioure-ide C—N distance, 1.3297(17) Å, is due to electron delocalization over the S₂CN moiety. The bite angle associated with the dithiocarbamate ligand is $64.71(3)^{\circ}$. In [Sb(chedtc)₃] (2), the antimony center is in a distorted octahedral coordination environment of six sulfur atoms. The Sb—S bonds show the anisobidentate binding of the dithiocarbamate ligand (Sb—S: 2.5331(5)-2.9962(6) Å). The mean thioureide C—N distance was found to be 1.330(1) Å, which indicates it has partial double bond character. The sulfur atom is involved in a supramolecular interaction with the hydrogen atom of the next molecule at a distance of 2.706 Å (S(1)···H(7A); the sum of the van der Waals radii is 3.0 Å). In (**2**), antimony lies below the plane of the sulfur atoms (S1/S3/S5/S6: r.m.s. 0.3171; maximum deviation 0.2162 Å for S5). The coordination geometry in [Sb(dchdtc)₃] (**3**) is a distorted pentagonal pyramid. In (**3**), the Sb—S distances are in the range 2.4557(7)-2.8853(7) Å, indicating anisobidentate binding of the dithiocarbamate ligand. The mean thioureide distance in the compound is 1.331(3) Å. A number of short contacts, such as H(9B)···Sb: 2.964 Å (the sum of the van der Waals radii is 3.46 Å), S(3)···H(32A): 2.844 Å, H(7A)···C(30):



Fig. 1. ORTEP of $[Sb(chmdtc)_3]$ (1) S1', S2' = -x + y, -x, *z*; S1", S2" = -y, x - y, *z* (hydrogens are excluded).



Fig. 2. ORTEP of [Sb(chedtc)₃] (2) (hydrogens are excluded).

2.867 Å and $H(30A)\cdots C(30)$: 2.369 Å, are observed. The nature of the substituents to a large extent is responsible for the structural variations, in addition to the lone pair of electrons on the antimony atom. The shift of the metal atom position relative to the geometrical center of the ligating sulfur atoms (0.511; 0.421 and 0.612 Å in (1), (2) and (3) respectively) is due to the lone pair effect. An analogous shift was observed in other transition metal compounds [36]. In compound (1), supramolecular interactions are absent whereas in compounds (2) and (3), they are observed, which clearly indicates the influence of the substituents in the crystal packing in these types of compounds [37].

3.6. Continuous shape measure

The continuous shape measure (CShM) quantifies the distance of a given structure from the desired ideal symmetry or from a reference shape [36,38-40]. Descriptions of geometries, such as 'slightly distorted' or 'severely distorted', relative to the reference polyhedron is a common practice. The degree of distortion of a particular molecular structure from an ideal polyhedron can be quantified by symmetry measures. CShM methodology has been successful in such quantification in dealing with transition metal complexes and metal oxides. For 'six coordination' the ideal geometries are ideal octahedron (iOh) or ideal trigonal prism (itp). In the present investigation, the coordination around antimony has been found to be distorted octahedron (dOh) in (1) and (2). In the case of compound (3), it has been found to be distorted pentagonal pyramid (dPpy). It is natural to consider the transformation of dPpy to iOh or itp. In the present case, the CShM values of the SbS₆ cores in the three complexes are 8.995, 8.063 and 26.895 for (1), (2) and (3) respectively. The observed CShM values follow the order (3) > (1) > (2). Complex (3) deviates to the largest extent from the octahedral geometry compared to (1) and (2) because of the largest steric demand of the two cyclohexyl rings. The observed CShM values clearly indicate the closeness of (1) and (2) to an octahedral geometry. The other SbS_6 core associated with compound (3) is not clearly octahedral. Distortion from the octahedral geometry is minimal in the ethyl and methyl analogues and is a maximum in the dicyclohexyl analogue due to steric demands, which is quantified by the reported CShM values.

3.7. BVS calculations

Bond valence sum (BVS) calculations offer a reliable method of assigning formal oxidation states to an atom in a compound from the bond parameters. The method depends on the R_{ii} value for an *i*–*j* bond in a compound which is predominantly ionic [41–43]. In a compound, the oxidation state of a central atom 'i' bonded to 'j' corresponds to the bond valence, S_{ij}, and the total valence of the central atom, which is its oxidation state, $\Sigma S_{ij} = \exp[(R_o - R_{ij})/b]$ where R_0 is used as reported [41] and R_{ij} is the experimentally determined bond distance. The constant *b* can be assumed to be 0.37 [44,45]. Bond valence sums calculated for the complexes from the structural data reported in this study are 3.3957, 3.3528 and 3.4256 for (1), (2) and (3) respectively. The calculated values are found to be higher than the expected formal oxidation state of +3. The higher values observed in the present set of compounds support the fact that the Sb—S bonds are more covalent and the back bonding effect is very highly pronounced in the compounds.

3.8. Characterization of Sb₂S₃

3.8.1. Powder XRD

A powder XRD of the solvothermally prepared antimony sulfide is shown in Fig. 4. The broad pattern indicates *nano* sized particles and it matches well with the JCPDS pattern reported for Sb₂S₃, PDF# 42:1393. The pattern was indexed to an orthorhombic unit cell with the following constants: a = 11.22, b = 11.28 and c = 3.84 Å. Three important signals, namely (130), (310) and (211), are observed as indicated in the Fig. 4 [46]. The ease of formation of Sb₂S₃ (<20 nm) from the parent dithiocarbamate precursors followed the order: (**3**) > (**1**) > (**2**).

3.8.2. FESEM and EDX

An SE micrograph of the prepared antimony sulfide is shown in Fig. 5. The morphology of the surface shows oval shaped crystalline grains with a large size distribution. The energy dispersive spectrum confirmed the presence of antimony and sulfur in a 2:3 ratio.



Fig. 3. ORTEP of [Sb(dchdtc)₃] (3) (hydrogens and solvent of crystallization are excluded).



Fig. 4. Powder XRD of nano Sb₂S₃.

3.8.3. HRTEM and SAED

HRTEM and SAED (2 insets) are shown in Fig. 6. HRTEM shows the Sb_2S_3 to be *nano* fibers which are <20 nm size. The crystal lattice fringes are clearly visible in the HRTEM pattern,

indicated by markers in the figure. The average distance between the fringes is less than 1 nm. The two SAED patterns confirm the crystalline nature of the sample along the fringe planes.



Fig. 5. FESEM and EDX of nano Sb₂S₃.



Fig. 6. HRTEM and SAED of nano Sb₂S₃.

3.9. Characterization of the $(Tl^+_{2/3}\ _{2\delta})[Tl^{3+}_{1\ _y}Sb^{3+}_{y}]Sb_2O_6O'_{1/3\ _\delta}$ pyrochlore

3.9.1. Powder XRD

The powder XRD of the $(Tl_{2/3-2\delta}^{1})[Tl_{-y}^{3+}Sb^{3+}_{y}]Sb_{2}O_{6}O'_{1/3-\delta}$ (where $\delta \sim 0.05$) pyrochlore prepared from an equimolar mixture of $[Sb(chmdtc)_{3}]$ and $[Tl(chmdtc)_{3}]$ precursors is shown in Fig. 7. The powder XRD pattern of the sample obtained by heating the reactants at 295 °C showed no resemblance to the precursors or the reported sulfides of antimony and thallium. The pattern also does not bear any resemblance to the patterns reported for the corresponding oxides. EDX analysis also showed non-specific ratios of elements such as Tl, Sb, S and O, indicating the formation of an intermediate. The PXRD pattern of the sample obtained at 350 °C matches the pattern reported for the $(Tl_{2/3-2\delta})[Tl_{1-y}^{3+}Sb^{3+}y]Sb_2O_{6}O'_{1/3-\delta}$ pyrochlore [24]. The PXRD pattern of the sample obtained at 350 °C showed signals at (311), (222), (400) and (440). The sample obtained at 750 °C showed an increase in the (311)/(222) intensity ratio, which is a characteristic occurrence in this class of pyrochlores [24].

3.9.2. FESEM and EDX

EDX of the two samples obtained at two different temperatures are shown in Fig. 8. The SE micrograph of $(TI_{2/3-2,\delta}^{+})[TI_{1-\nu}^{3+}]$



Fig. 7. Powder XRD patterns of precursor mixtures at three temperatures.

Sb³⁺_y]Sb₂O₆O'_{1/3- δ} pyrochlore obtained at 750 °C is shown in Fig. 9. The experimental ratio of Sb/Tl in the sample heated at 350 °C was found to be 1.88 and the ratio for the sample heated at 750 °C was found to be 5.37. It has been observed that the powder XRD patterns for all the allowed variations of ' δ ', will be similar. The sample obtained at 350 °C corresponds to (Tl_{0.57}) [Tl₃³-₂Sb₃³-₄₄]Sb₂O₆O'_{0.29}, with a Sb/Tl ratio of 1.90, matching the EDX value. Thallium within () brackets refers to its presence in the +1 oxidation state and within [] brackets refers to Tl and Sb being in the +3 state, conventionally. The decreased thallium content of the pyrochlore obtained at 750 °C indicates the volatilization of thallium, leading to enhanced defects and still retaining the pyrochlore phase. The pyrochlore appears as *nano* crystals (<100 nm), as observed in the FESEM micrograph.



Fig. 8. EDX of Tl—Sb—O pyrochlore at 350 and 750 °C.



Fig. 9. FESEM micrograph of $(Tl_{2/3-2\delta}^+)[Tl_{1-y}^{3+}Sb_y^{3+}]Sb_2O_6O'_{1/3-\delta}$.

4. Conclusions

The compounds $[Sb(chmdtc)_3]$ (1), $[Sb(chedtc)_3]$ (2) and $[Sb(dchdtc)_3]$ (3) reported in this study showed only charge transfer transitions, apart from intraligand transitions, in their electronic spectra. The IR spectra of the compounds showed the contribution of thioureide bonds to the structures. The ¹H and ¹³C NMR spectra of the complexes clearly indicated that the immediate environment around the thioureide nitrogen was largely affected by complex formation. TG analysis confirmed the stoichiometry of the compounds perfectly and the formation of Sb₂S₃ as the final residue was unequivocally proven. Single crystal X-ray structures of the compounds showed the Sb-S bonds to be clearly anisobidentate in nature. The thioureide bond distances were between 1.327 and 1.331 Å, clearly indicating the resonant flow of electron density from the nitrogen atom to the metal. The bite angles of the dithiocarbamate ligands, observed in the range 64.16-66.46° in the complexes, organize the geometry around the antimony center. Short contacts involving S.-. H interactions are absent in $[Sb(chmdtc)_3]$ (1), in contrast to those observed in the other two compounds in spite of the fact that its density (g/cm³) was relatively maximal (1.475 for (1), 1.387 for (2), 1.289 for (**3**)). In [Sb(chmdtc)₃] (**1**) and [Sb(chedtc)₃] (**2**), the coordination geometries around antimony were found to be distorted octahedral (dOh). In $[Sb(dchdtc)_3]$ (**3**), the coordination polyhedron was found to be a distorted pentagonal pyramid (dPpy) and the geometry is forced on it by the steric influence of the cyclohexyl substituents in addition to the rigid bite angle of the dithiocarbamate ligands. CShM calculations on the chromophores clearly quantify the extent of deviation from the ideal octahedral geometry. Compounds (1) and (2) showed relatively small deviations from an octahedral geometry compared to the SbS₆ core associated with compound (3), in line with the CShM values. The higher bond valence sums (BVS) observed in the present set of compounds support the fact that the Sb–S bonds are more covalent and the back bonding effect is very highly pronounced. The three dithiocarbamates yielded nano Sb₂S₃ (<20 nm) in a non-conventional solvothermal process. The ease of formation of the nanosulfide followed the order: (3) > (1) > (2). The *nano* wires of Sb₂S₃ have been characterized by FESEM, EDX, HRTEM and SAED. $(Tl_{2/3-2\delta}^{+})[Tl_{1-y}^{3+}Sb_{y}^{3+}]$ $Sb_2O_6O'_{1/3-\delta}$ (where $\delta \sim 0.05$) pyrochlore has been prepared from an equimolar mixture of [Sb(chmdtc)₃] and [Tl(chmdtc)₃] as precursors. The pyrochlore, $(Tl_{0.57}^+)[Tl_{0.22}^{3+}Sb_{0.44}^{3+}]Sb_2O_6O'_{0.29}$ was found to consist of cuboids with sizes less than 100 nm and it was characterized by PXRD, EDX and FESEM techniques.

Appendix A. Supplementary data

CCDC 954049, 954050 and 954051 contains the supplementary crystallographic data for (**1**), (**2**) and (**3**), respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2014.09.028.

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