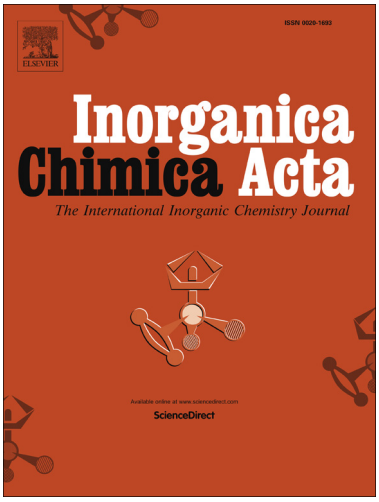

Synthesis, Structural, Continuous shape measure and Bond valence sum characterization of bismuth(III) complexes of substituted dithiocarbamates and their solvothermal decomposition

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Synthesis, Structural, Continuous shape measure and Bond valence sum characterization of bismuth(III) complexes of substituted dithiocarbamates and their solvothermal decomposition

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Bismuth(III) complexes, [Bi(chmdtc)$_3$] (**1**) [Bi(chedtc)$_3$] (**2**) and [Bi(dchdtc)$_3$] (**3**), (where chmdtc = cyclohexylmethyldithiocarbamate, chedtc = cyclohexylethyldithiocarbamate and dchdtc = dicyclohexyldithiocarbamate) have been prepared and characterized by electronic, IR, NMR (^{1}H and ^{13}C) spectra, and single crystal X-ray diffraction. Electronic spectra of the complexes show signature bands in the range: 418-423 nm due to charge transfer transitions. The characteristic thioureide bands occur at 1474, 1467 and 1443 cm^{-1} for (**1**), (**2**) and (**3**) respectively. Single crystal X-ray structures of [Bi(chmdtc)$_3$] (**1**), [Bi(chedtc)$_3$] (**2**) and [Bi(dchdtc)$_3$] (**3**) indicate that the short Bi---S interactions between the molecules lead to dimeric structures. CShM calculations on the chromophores clearly quantify the extent of deviation from the ideal geometry. BiS$_6$ chromophore in (**1**) is a distorted octahedron. The coordination geometry for both [Bi(chedtc)$_3$] (**2**) and [Bi(dchdtc)$_3$] (**3**) should be better described as distorted pentagonal pyramidal. The higher BVS values observed in the present set of compounds support the fact that the Bi-S bonds are more covalent.

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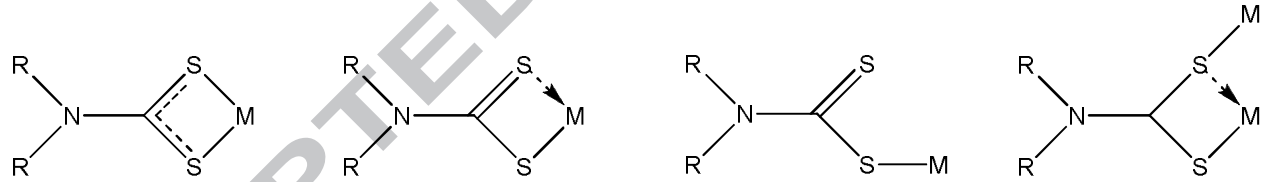
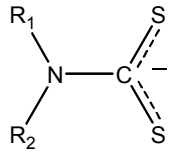
Keywords: Bismuth(III); dithiocarbamate; non-covalent interactions; pentagonal pyramid; crystal structures; nanosulfide.

1. Introduction

Bismuth is a group 15 element with the most common formal oxidation state of +3. Bismuth compounds have long been used as therapeutic agents. The chalcogenides of bismuth(III) find increasing applications in solar cells, photolithography, optical memory devices and as photo- and thermo-electric conductors [1,2]. Trivalent bismuth xanthates, dithiocarbamates and alkyl- as well as alkylenedithiophosphates have been prepared and some of the dithio derivatives show interesting catalytic and biocidal applications [3,4]. The antimicrobial and anti-tumor activity of binary bismuth(III) dithiocarbamates of the general formula, $Bi(S_2CNR_2)_3$ has been reported [5]. Dithiocarbamates are known to show a variety of coordination modes such as isobidentate, anisobidentate, monodentate and triconnective [6]. Bismuth dithiocarbamates serve as useful



precursors for the preparation of Bi_2S_3 and offer a facile transformation at low temperature compared to the traditional high sintering temperature methods [7-11]. In continuation of our efforts to identify new precursors for the preparation of Bi_2S_3, we report the synthesis and characterization of [Bi(chmdtc)$_3$] (**1**), [Bi(chedtc)$_3$] (**2**) and [Bi(dchdtc)$_3$] (**3**) . On heating the trisdithiocarbamates in diethylenetriamine, in a non-conventional solvothermal process, *nano* Bi_2S_3 separated which was characterized by SEM, EDS and HRTEM techniques.



Cyclohexylmethyldithiocarbamate (chmdtc)	Cyclohexylethyldithiocarbamate (chedtc)	Dicyclohexyldithiocarbamate (dchdtc)
R_1: $-CH_3$, R_2: $-C_6H_{11}$	R_1: $-C_2H_5$, R_2: $-C_6H_{11}$	R_1, R_2: $-C_6H_{11}$

2. Experimental

Bismuth nitrate (SD fine chemicals, India), the parent amines (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 points of solid products were determined with digital melting / boiling point apparatus, Jains, India. Elemental analyses were carried out with 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 CCl_4 on a Hitachi U-2001 double beam spectrometer. Thermal analysis was carried out with NETZSCH STA 449F3 instrument under nitrogen atmosphere with a heating rate of 10 K / minute. ^1H and ^{13}C NMR spectra were recorded on a Bruker AMX-400 spectrometer at room temperature using $CDCl_3$ as solvent. NMR spectra were recorded at room temperature with TMS as an internal reference and $CDCl_3$ as the solvent. The powder diffraction data were collected in the 2θ range = 2-80° using Bruker-D8 X-ray diffractometer equipped with Cu-Kα radiation at fixed current and potential. The scan speed and step sizes were 0.05 ^{o} min^{-1} and 0.00657 respectively. Scanning electron micrographs of the samples were recorded with JEOL JSM-5610Lv microscope. HRTEM measurements were carried out on JEOL 2100 (Field emission) with an accelerating voltage of 200kV. Some important infra red spectral bands and the

electronic spectral data are listed in Table 1. NMR spectral data of bismuth complexes are listed in Table 2.

2.1 X-ray crystallography

Intensity data were collected at ambient temperature (295 K) on a Bruker APEX-II CCD diffractometer with graphite monochromated MoKα radiation (λ = 0.71073 Å) and were corrected for absorptions with a multi-scan technique [12-14]. The structures were solved by direct methods using SIR97 and were refined by SHELX97 [15]. The non-hydrogen atoms were refined anisotropically and all the hydrogen atoms were fixed geometrically. Molecular plots were obtained using the ORTEP-3 program [16]. In (**2**)**,** the CCl_4 solvent molecule and one cyclohexyl group are disordered over two sets of orientations with site occupancy of 0.5. One ethyl group is also disordered over two orientations with site occupancies of 0.65 and 0.35 for the major and minor components of disorder respectively. 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 Figures 1, 2 and 3 respectively.

2.2 Preparation of the complexes

2.2.1 Preparation of tris(cylochexylmethyldithiocarbamato)bismuth(III);[Bi(chmdtc)$_3$](**1**)

N-cyclohexyl-N-methylamine (6 mmol; 0.78 mL) and carbon disulfide (6 mmol; 0.36 mL) in ethanol were mixed under ice-cold condition (5°C) to obtain yellow dithiocarbamic acid solution. To the freshly prepared dithiocarbamic acid solution, acidified solution of $Bi(NO_3)_3$ pentahydrate (2 mmol; 0.96 g) was added with constant stirring. A yellow solid separated from the solution, which was filtered, washed with alcohol and was dried in air. (Yield: 73%, dec., 124°C. Anal. calc. for $C_{24}H_{42}BiN_3S_6$ (774.0): C, 37.24; H, 5.47; N, 5.42.Found: C, 37.19; H, 5.42; N, 5.38 %)

2.2.2 Preparation of tris(cylochexylethyldithiocarbamato)bismuth(III); [Bi(chedtc)$_3$](**2**)

N-cyclohexyl-N-ethylamine (0.03 mol, 4.49 mL), carbon disulfide (0.03 mol, 5 mL) in methanol (20 mL) and a weakly acidified solution of bismuth(III) nitrate pentahydrate (0.01 mol, 4.85g) were used for the preparation. A similar procedure as described in 2.2.1 was used for the preparation. (Yield: 78%, m.p., 188°C. Anal. calc. for $C_{55}H_{96}Bi_2Cl_4N_6S_{12}$ (1785.9): C, 36.99; H, 5.42; N, 4.70. Found: C, 36.95; H, 5.38; N, 4.66 %)

2.2.3 Preparation of tris(dicylochexyldithiocarbamato)bismuth(III); [Bi(dchdtc)$_3$](**3**)

A similar procedure as described in 2.2.1 was employed for the preparation of the dicyclohexylamine analogue. N,N-dicyclohexylamine (0.03 mol, 4.49 mL), carbon disulfide (0.03 mol, 5 mL in 20 mL methanol) and bismuth(III) nitrate pentahydrate (0.01 mol, 4.85g) were used for the preparation. (Yield: 67%, m.p., 145°C. Anal. calc. for $C_{41}H_{69}BiN_4S_6$ (1019.3): C, 48.31; H, 6.82; N, 5.49. Found: C, 48.26; H, 6.78; N, 5.45 %)

2.2.4 Preparation of nano Bi_2S_3 by non-conventional solvothermal decomposition of Tris(disubstituteddithiocarbamato)bismuth(III)

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

3. Results and discussion

3.1 Infrared spectral studies

For complexes (**1**), (**2**) and (**3**) the ν_{C-N} (thioureide) bands are observed at 1474, 1467 and 1443 cm^{-1} respectively. The $\nu_{(C-S)}$ stretching bands are observed around 1000 cm^{-1} supporting [17] the bidentate coordination mode of the dithiocarbamate to the metal center, and the ν_{C-H} bands are observed in the range: 2850-2929 cm^{-1}.

3.2 Electronic spectra

Electronic spectra of the compounds show bands between 364 and 376 nm for the three compounds which are due to intraligand π- π* transitions, mainly associated with the N−C=S and S−C=S groups [18, 19]. The electronic spectra of the complexes show charge transfer transitions in the range: 410-423 nm.

3.3 NMR spectral studies

Chemical shifts reported in Spectral Data Base for Organic compounds (SDBS) for the parent amines are shown in brackets in the Table 2 [20]. ^{1}H NMR of complex (**1**) shows an intense signal at 5.08 ppm (2.303 ppm) corresponding to single proton integration due to α-CH of the cyclohexyl ring. CH_3 protons (α'-CH_3) attached to the nitrogen appear at 3.28(s) ppm (2.421 ppm) with proton integration corresponding to three. The α-CH and α'-CH_3 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 1.69-1.71ppm. ^{13}C NMR spectrum of (**1**) shows a weak signal at 200.7 ppm due to the thiouriede carbon [21]. The α-carbon of cyclohexyl ring appears at 62.8 ppm (58.63 ppm) and α'-CH_3 appears at 35.2 ppm (33.60 ppm). The β,γ- and δ-carbon signals were the least affected and appeared at 25.40, 25.50 and 29.80 ppm respectively.

In complex (**2**), ^{1}H NMR of α-CH proton of the cyclohexyl ring appeared at 5.04 ppm and α'-CH_2 appeared at 3.74-3.80 ppm corresponding to two protons. β´-CH_3 protons of the ethyl group appeared as a well resolved triplet 1.50-1.95 ppm. ^{13}C NMR spectrum of (**2**) showed the characteristic thiouriede signal at 200.6 ppm. β'-CH_3 appeared at 14.40 ppm as a much shielded signal and α'- CH_2 appears to be highly deshielded at 43.60 ppm. α- CH signal of the cyclohexyl

ring appears at 63.20 ppm. The β,γ- and δ- carbon signals which were the least affected on complexation appeared at 30.46 and between 24.60 to 25.70 ppm.

In the case of complex (**3**), α-CH proton of the cyclohexyl ring was observed at 5.31 ppm (2.546 ppm). β, γ- and δ-CH_2 signals appeared in the region of 1.82-2.09(e) ppm (collapsed) (1.606 - 1.856 ppm). The axial proton signals appeared between 1.35-1.53 ppm(1.021 - 1.246 ppm). ^{13}C NMR exhibited a weak characteristic signal due to thiouriede carbon at 200.8 ppm. ^{13}C NMR signal corresponding to the α-C(H) carbon of the cyclohexyl ring was found to be significantly shielded and appeared at 65.21 ppm (53.17 ppm) . β-C(H_2), and γ -C(H_2) carbons appeared in the region of 25.03 - 29.78 ppm (26.32 – 34.51ppm). Signals observed at ~ 7.20 and 2.35 ppm in the ^{1}H NMR spectra of the three compounds are due to the aromatic and methyl protons of toluene which is the solvent used for crystallization. NMR spectra of the complexes clearly indicated that the immediate environment around thiouriede nitrogen was largely affected by complex formation.

3.4 Thermogravimetric analysis

Thermal analyses of the compounds were carried out under nitrogen atmosphere. A toluene recrystallized sample of (**1**) was used for the thermal analysis and hence a loss of solvent was observed. [Bi(chmdtc)$_3$](**1**) showed initial loss of the solvent of crystallization, toluene around 198°C. A large mass loss (63.9%) was observed in the range of 260-320 ^{o}C. At temperatures above 500 ^{o}C, the mass loss was insignificant and the residue agreed well for Bi_2S_3 as the residue (Exptl.: 30.3%; Calcd.: 29.7%). [Bi(chedtc)$_3$](**2**) showed a minor loss due to the solvent of crystallization, CCl_4 at160^{o}C. A large chunk of mass (60.1%) was lost in the temperature range: 220-280 ^{o}C. Above 500 ^{o}C, the mass remained constant and the final residue confirmed the formation of Bi_2S_3 (Exptl.: 28.5%; Calcd.: 28.8%). [Bi(dchdtc)$_3$] (**3**) followed a similar pattern of decomposition. Loss of solvent of crystallization, CH_3CN was observed at 240 ^{o}C. Largest mass loss (62.0%) was observed in the temperature range: 250-290 ^{o}C. The final residue formed above 500 ^{o}C was Bi_2S_3 (Exptl.: 26.2%; Calcd.: 25.2%). Thermal analysis confirmed the proposed formulae of the compounds. The

most important observation is that in all the three compounds the final residue was found to be Bi_2S_3. Among the three compounds the dicyclo- analogue, [Bi(dchdtc)$_3$] (**3**) showed the highest thermal stability.

3.5 Structural analysis

[Bi(chmdtc)$_3$](**1**) crystallizes in monoclinic lattice with four molecules per unit cell. The asymmetric unit of (**2**) contains two crystallographically independent [Bi(chedtc)$_3$] complex molecules of similar conformation and one disordered CCl_4 solvent molecule of crystallization. Complex (3) crystallizes with acetonitrile solvent molecules in a stoichiometric complex/solvent molar ratio of 1:1. The dithiocarbamate group in all complexes acts in the usual asymmetric bidentate mode, each ligand chelating Bi through a shorter (mean value 2.72(3) Å) and a longer (mean value 2.88(2) Å) Bi–S bond. It is noticeable that in the ligands the C–S bonds associated with the shorter Bi–S bonds are significantly longer (mean value 1.734(4) Å) than those associated with the longer Bi–S bonds (mean value 1.717(4) Å). The thioureide C–N distances (mean value 1.332(3) Å for all complexes) indicate a delocalization of the electron density over the S_2CN fragment and suggest a partial double bond character of these bonds. The observed values of the Bi–S, C–S and C–N bonds are in good agreement with those calculated for 13 related bismuth dithiocarbamate complexes reported in the literature recently [22, 23], where the mean shorter and longer Bi–S distances are 2.719(14) and 2.889(6) Å, respectively, the corresponding mean longer and shorter C–S distances are 1.728(3) and 1.709(3) Å, respectively, and the mean value of the C–N bonds is 1.330(3) Å. The BiS_6 chromophore in [Bi(mchdtc)$_3$] (**1**) assumes a remarkably distorted octahedral geometry, similar to that observed in tris(N-(n-hexyl)-N-methyldithiocarbamato-S,S')bismuth(iii) [24]. The best equatorial plane is defined by the S1/S3/S4/S6 set of donor atoms (r.m.s. 0.0501; maximum deviation 0.0767(10) Å

for atom S4) and the apical positions occupied by atoms S2 and S5. The bismuth cation is displaced from the equatorial plane by 0.58752(10) Å toward S5. The S–Bi–S bond angles fall in the range 61.55(3)–153.34(3)°. The coordination geometry for both [Bi(chedtc)$_3$] (**2**) and [Bi(dchdtc)$_3$] (**3**) should be better described as distorted pentagonal pyramidal instead, as usually observed in most related bismuth dithiocarbamate complexes. The basal plane is defined by atoms S1/S2/S3/S5/S6 (r.m.s 0.4141; maximum displacement 0.605(2) Å for atom S2) and S7/S8/S9/S10/S11 (r.m.s. 0.2883; maximum displacement 0.466(3) Å for atom S9) in (**2**), and by atoms S1/S2/S3/S4/S6 (r.m.s. 0.1891; maximum displacement 0.3072(9) Å for atom S4) in (**3**). Atoms S4 and S12 in (**2**) and S5 in (**3**) occupy the vertices and are displaced by 2.2479(1), 2.2610(16) and 2.0983(7) Å, respectively, from the least square mean basal plane. The bismuth centres protrude from the respective mean basal plane in opposite direction to the apical position by 0.3024(2) and 0.2789(2) Å in (**2**) and 0.43876(11) Å in (**3**). The S–Bi–S bond angles are not dissimilar to those found in (**1**) ranging from 62.25(5) to 158.22(5)° in (**2**) and from 61.89(6) to 159.97(6)° in (**3**). The different coordination geometry observed in [Bi(chmdtc)$_3$] (**1**) may be attributed to the steric demand of the methyl substituent of the carbamate groups which is comparatively less demanding than that of the ethyl and cyclohexyl analogues and hence the six coordinated bismuth distorts to a lesser extent from the preferred octahedral geometry.

All complexes form dimeric units through non-covalent Bi···S interactions involving symmetry related molecules as depicted in Figure 4, with Bi···S distances (3.2375(10) Å in (**1**); 3.3587(17) and 3.1449(15) Å in (**2**); 3.3260(6) Å in (**3**) notably shorter than the sum of the van der Waals radii (1.80 for S [25] and 2.07 for Bi [26]). The Bi···Bi separations within the dimers are 4.9110(5), 4.4655(4)-4.8894(4) and 4.5058(3) Å in (**1**), (**2**) and (**3**), respectively. The molecular conformation of the complexes is stabilized by intramolecular C–H···S hydrogen

bonds involving methine and methylene hydrogen atoms of the ligands with H···S distances varying in the range 2.44–2.46 Å in (**1**), 2.44–2.46 Å in (**2**) and 2.39–2.76 Å in (**3**).

3.6 Continuous shape measure

Continuous Shape measure (CShM) effectively quantifies the distance of a given structure from the desired ideal symmetry or from a reference shape [27-30]. In practice, idealizations of molecular structures is achieved by associating the position of a set of atoms with the vertices of a reference polyhedron and qualitative descriptions such as 'slightly distorted' or 'severely distorted' relative to the reference polyhedron are often required. To quantify the degree of distortion of a particular molecular structure from an ideal polyhedron one can use symmetry measures. Continuous shape measure (CShM) methodology has been successfully applied to 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 bismuth in (**2**) and (**3**) is distorted pentagonal pyramid whereas in (**1**) it's a distorted octahedron. It is natural to consider the transformation of ppy to iOh or itp. In the present case, the Continuous Shape measure calculations on the three complexes for the BiS_6 core yielded 10.237607, 27.662944 and 29. 921790 for (**1**), (**2**) and (**3**) respectively. The observed CShM values follow the order for (**3**) > (**2**) > (**1**). Complex (**3**) deviates to the largest extent from the octahedral geometry than the other two because of the largest steric demand of the two cyclohexyl rings. Between the two, the methyl analogue (**1**) is closer to the octahedral geometry than its ethyl analogue (**2**). The observed CShM value clearly indicate the closeness of (**1**) to octahedral geometry. The other two BiS_6 cores associated with (**2**) and (**3**) are not close to octahedral geometry but to pentagonal pyramid (ppy) geometry as evident from S-Bi-S angles. Between the two, compound (**2**), shows four of the five S-Bi-S angles in the range of 87.34(5) to 93.63(6)^o indicating a distorted pentagonal pyramid. The axial Bi-S bonds are

shorter than the equatorial bonds in compounds (**2**) and (**3**). All the three complexes show little tendency to distort towards trigonal prismatic geometry. Distortion from the octahedral geometry to pentagonal pyramid is minimal in the methyl analogue and is a maximum in the dicyclohexyl analogue due to steric demands which is quantified by the reported values.

3.7 BVS calculations

Bond valence sum (BVS) calculations offer a reliable method of assigning formal oxidation states of an atom in a compound from the bond parameters. The method depends on the Rij value for an i-j bond in a compound which is predominantly ionic [31]. 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, $\Sigma S_{ij} = \exp[(Ro - Rij)/b]$ and *R*o is used as reported[32,33] and *Rij* is the experimentally determined bond distance. The constant *b* can be assumed to be 0.37[34, 35]. Bond valence sums calculated for the complexes from the structural data reported for the compounds in this study are 3.2618, 3.2811 and 3.3833 for (**1**), (**2**) and (**3**) respectively. The calculated values have been 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 Bi-S bonds are more covalent.

3.8 Characterization of Bi_2S_3

3.8.1 Powder XRD

Powder XRD of the solvothermally prepared bismuth sulfide is shown in Figure 5 along with SEM and EDX. The broadened PXRD indicates the *nano* sized nature of the sample and matched well with the JCPDS pattern reported for Bi_2S_3, PDF # 75-1306 and two strong signals corresponding to 26.76^o (130), 29.93^o (211) are observed[36,37]. On heating the three compounds under identical conditions in diethylenetriamine at 60°C, Bi_2S_3 appeared as a precipitate very early

in the case of (**3**) compared to other two compounds within the shortest period compared to the other two. Hence qualitatively, the ease of formation of the nanosulfide from the dithiocarbamates based on its first appearance from (**3**) was slightly better than from the compounds (**1**) and (**2**). Based on the observation, the ease of formation of nanosulfide from the bismuth dthiocarbamates follows the order: (**3**) > (**1**) > (**2**). However, the mean Bi-S bond distances for the three compounds are almost similar (2.8125(10), 2.8129(17) 2.7977(9) Å in (**1**), (**2**) and (**3**) respectively).

3.8.2 SEM-EDX

SE micrographs of the prepared bismuth sulfide are shown in Figures 5. The morphology of surface shows crystalline grains with large size distribution. The energy dispersive spectrum confirmed the presence of bismuth and sulfur in 2:3 ratio.

3.8.3 HRTEM and SAED

HRTEM and SAED (inset) are shown in Figure 6. HRTEM showed the Bi_2S_3 to be *nano* wires < 10 nm size. SAED pattern confirmed the crystalline nature of the sample. Fringe spacing of the Bi_2S_3 wires is ~ 0.5nm. The SAED pattern showed strong diffractions due to (001) and (120) oriented single crystals.

4. Conclusions

[Bi(chmdtc)$_3$] (**1**), [Bi(chedtc)$_3$] (**2**) and [Bi(dchdtc)$_3$] (**3**) show interesting variations in the geometry around bismuth. The single crystal X-ray structures showed the Bi-S bonds to vary largely due to variations in the steric effects. NMR spectra of the complexes clearly indicated that the immediate environment around thiouriede nitrogen was largely affected by complex formation. CShM calculations on the chromophores clearly quantify the extent of deviation from the ideal octahedral geometry. BiS_6 chromophore in (**1**) is a distorted octahedron whereas in the other two,

distorted pentagonal pyramidal geometry prevails. Stabilization of the dimer in (**2**) is favoured to a large extent than the other two because of the pentagonal pyramid geometry assumed by the BiS_6 core. In the three compounds, the steric effect is active in controlling the geometry around bismuth. The bond valence sums indicate the highly covalent nature of the Bi-S bonds. Non conventional solvothermal decomposition of the compounds yield *nano* Bi_2S_3. The ease of formation of the nanosulfide followed the order: (**3**) > (**1**) > (**2**). The *nano* wires of Bi_2S_3 have been characterized by a host of techniques.

Appendix A

Supplementary material

CCDC **967477**, **954122** and **954123** contain the supplementary crystallographic data for (**1**), (**2**) and (**3**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Captions for figures

Figure 1. ORTEP of [Bi(chmdtc)$_3$] (**1**). Hydrogen atoms are omitted for clarity

Figure 2. ORTEP of one complex molecule in [Bi(chedtc)$_3$] (**2**). Only the major component of the disordered ethyl chain is shown. Hydrogen atoms are omitted for clarity

Figure 3. ORTEP of [Bi(dchdtc)$_3$] (**3**). Hydrogens atoms are omitted for clarity

Figure 4. ORTEP plot of the dimers

Figure 5 PXRD, SEM and EDX of *nano* Bi_2S_3

Figure 6 HRTEM and SAED of *nano* Bi_2S_3

Table 1 Electronic and IR spectral data

Compound	Uv-Vis (nm)		IR (cm^{-1})		
	CT	Intraligand	ν_{C-N}	†ν_{C-S}	ν_{C-H}
[Bi(chmdtc)$_3$] (**1**)	418	364	1474	1004 (1010)	2850-2925*
[Bi(chedtc)$_3$] (**2**)	420	367	1467	1009 (1017)	2852-2929*
[Bi(dchdtc)$_3$] (**3**)	423	376	1443	1010 (1018)	2851-2927*

† Free dithiocarbamate ν_{C-S} wave numbers are given in parentheses

* ν_{C-H} wave numbers for the free dithiocarbamates are in the range of 2850-2930 cm^{-1}

430

431 Table 2 NMR spectral data (ppm) †

Complex	NMR	α-CH	β-CH_2/ γ- CH_2 & δ- CH_2	α'-CH_3/ CH_2	$N^{13}CS_2$
[Bi(chmdtc)$_3$] (**1**)	^{1}H	5.08 (2.303)	1.80-1.88(e) 1.69-1.71	3.28 (2.421)	-
	^{13}C	62.8 (58.63)	29.80 25.40,25.50	35.2 (33.60)	200.7
[Bi(chedtc)$_3$] (**2**)	^{1}H	5.04	1.83-1.93(e) 1.56-1.69	3.74-3.80 1.31-1.37	-
	^{13}C	63.2	30.46 24.60-25.70	43.60 14.40	200.6
[Bi(dchdtc)$_3$] (**3**)	^{1}H	5.31 (2.546)	1.82-2.09(e) (1.606 - 1.856) 1.35-1.53 (1.021 - 1.246) (Collapsed)	-	-
	^{13}C	65.21 (53.17)	29.66 25.03 - 29.78 (26.32 – 34.51)	-	200.8

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433 † Chemical shifts reported in Spectral Data Base for Organic compounds (SDBS) for the parent amines are

434 shown in brackets

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436

437 Table 3. Crystal data, data collection and refinement parameters for

438 [Bi(chmdtc)$_3$], [Bi(chedtc)$_3$] and [Bi(dchdtc)$_3$]

Complex	[Bi(chmdtc)$_3$]	[Bi(chedtc)$_3$]	[Bi(dchdtc)$_3$]
Empirical formula	$C_{24}H_{42}BiN_3S_6$	$2(C_{27}H_{48}BiN_3S_6)\cdot CCl_4$	$C_{39}H_{66}BiN_3S_6\cdot C_2H_3N$
Formula weight	774.0	3571.96	1019.34
Colour	Yellow	Yellow	Yellow
Habit	Block	Block	Prism
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P 2_1/c	C 2/c	P 2_1/c
Crystal dimension(mm^3)	0.32 × 0.24 × 0.18	0.28 x 0.27 x 0.24	0.27 x 0.23x 0.18
a (Å)	12.6224(17)	30.3139(17)	10.5705(8)
b(Å)	20.526(3)	14.9828(8)	16.1324(12)
Å)	13.1879(17)	34.549(3)	27.975(2)
α (°)	90.00	90.00	90.00
β (°)	109.137(2)	108.3958(12)	97.9920(12)
γ(°)	90.00	90.00	90.00
U (A3)	3228.0(8)	14889.8(17)	4724.2(6)
Z	4	4	4
Dc(g cm^{-3})	1.593	1.593	1.433
F(000)	3228.0(8)	7152	2088
λ(Å)	MoKα (0.71073)	MoKα (0.71073)	MoKα (0.71073)
θ range (°)	1.42-25.25	1.42-25.25	1.46-25.50
Scan type	ω scan	ω scan	ω scan
Index range	$-15 \le h \le 15$; $-25 \le k \le 25$; $-16 \le l \le 16$	$-36 \le h \le 36$; $-17 \le k \le 17$; $-41 \le l \le 41$	$-12 \le h \le 12$; $-19 \le k \le 19$; $-33 \le l \le 33$
Reflections collected	6350	13477	8789
Reflections [Fo> 2 σ (Fo)]	4885	9374	7644
Weighting scheme	w = 1/[\S^2(Fo^2) + (0.0212p)^2] where P = (Fo^2 + 2Fc^2)/3	w=1/[s^2(Fo^2)+(0.0405P)^2+46.8561P] where P=(Fo^2+2Fc^2)/3	w=1/[s^2(Fo^2)+(0.0218P)^2 +2.2017P] where P=(Fo^2+2Fc^2)/3
Number of parameters refined	307	743	470
Final R, Rw (obs, data)	0.0206, 0.0432	0.0391, 0.0872	0.0210, 0.0485
GOOF	0.995	1.011	1.029

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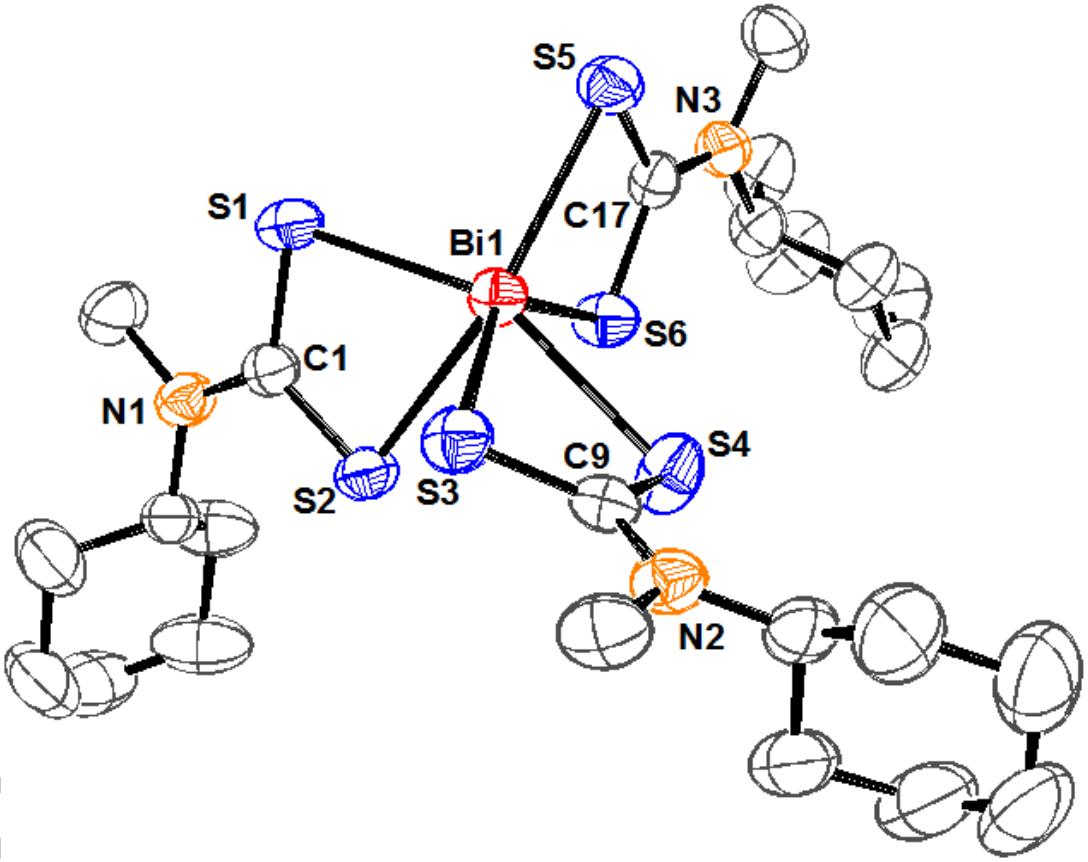
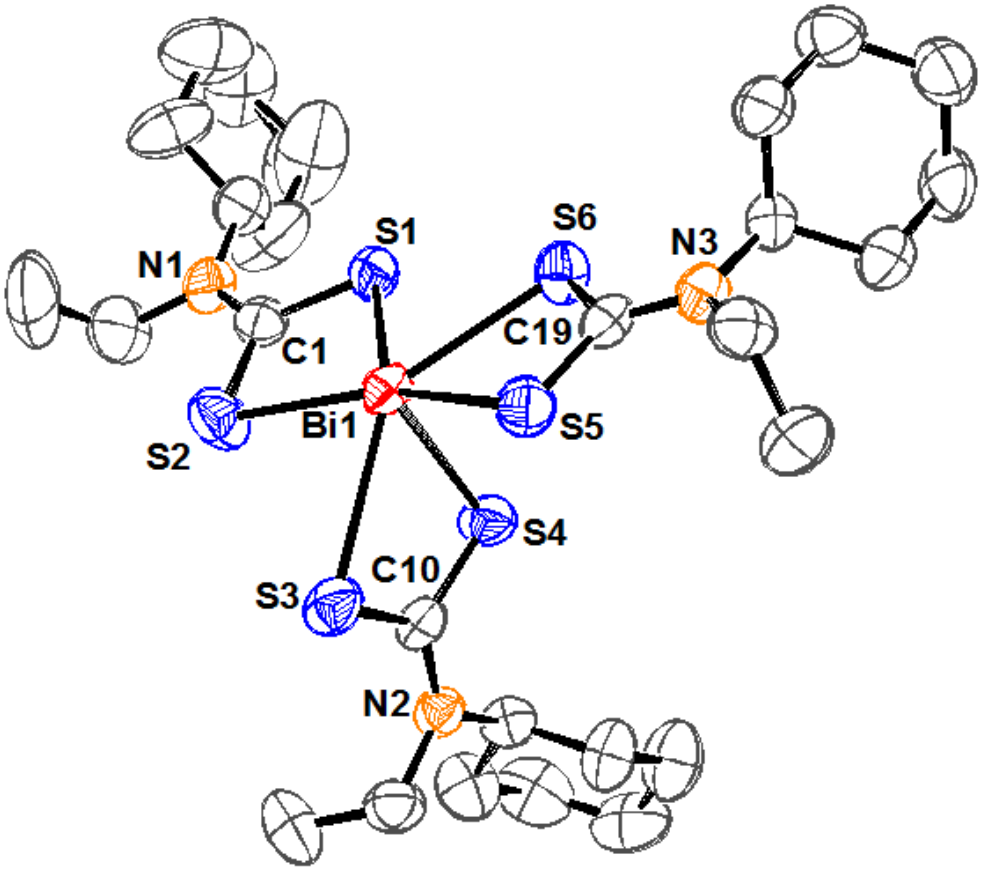
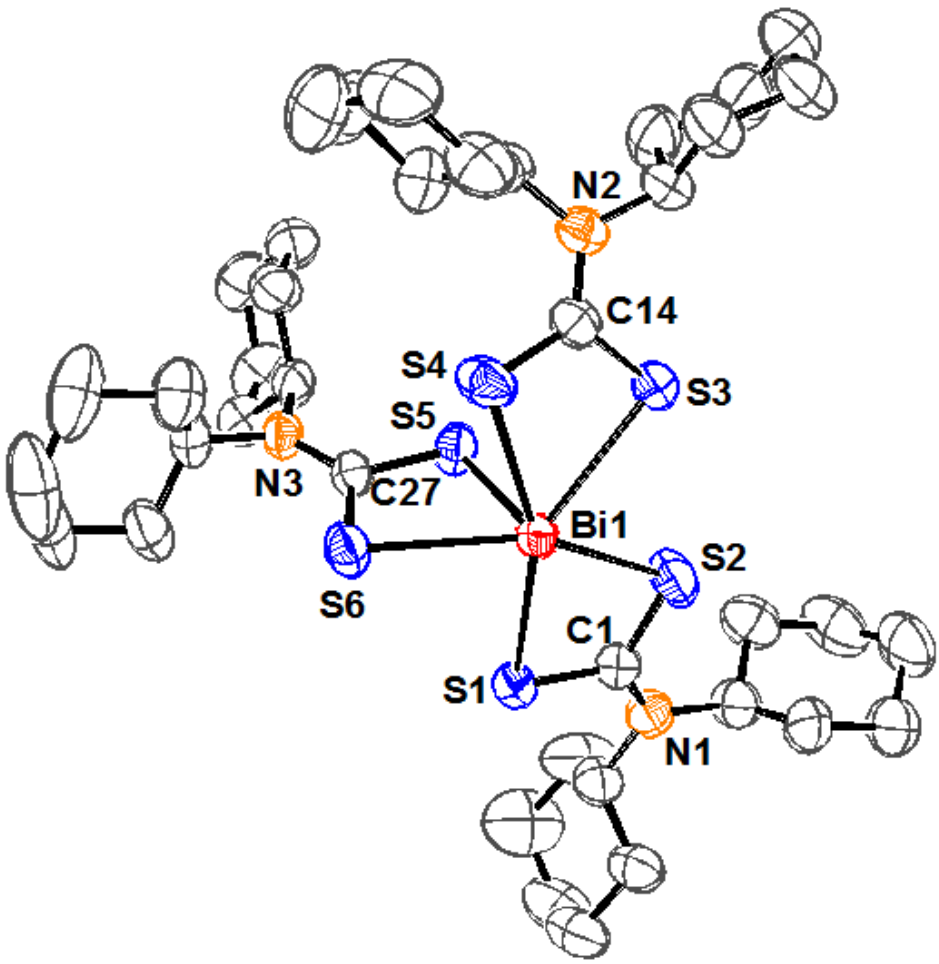
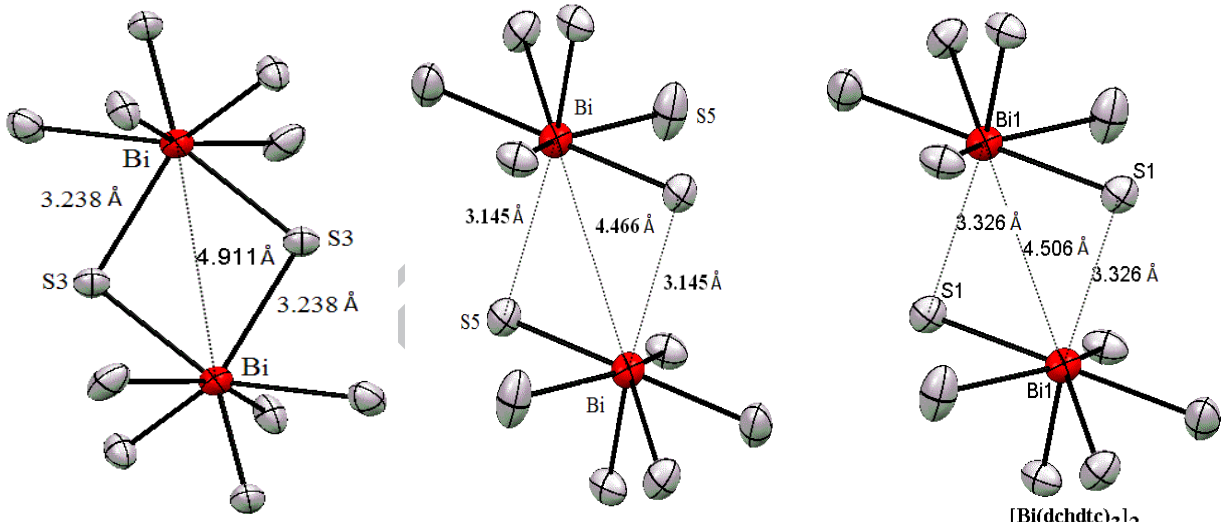
Table 4 Selected bond distances (Å) and bond angles (°)

[Bi(chmdtc)$_3$]		[Bi(chedtc)$_3$]				[Bi(dchdtc)$_3$]	
Bi1–S1	2.7770(9)	Bi1–S1	2.7554(17)	Bi2–S7	2.951(2)	Bi1–S1	2.9201(6)
Bi1–S2	2.6884(8)	Bi1–S2	2.8545(18)	Bi2–S8	2.8167(19)	Bi1–S2	2.8288(10)
Bi1–S3	2.9974(10)	Bi1–S3	2.9428(18)	Bi2–S9	2.776(2)	Bi1–S3	2.8359(8)
Bi1–S4	2.7876(10)	Bi1–S4	2.6060(18)	Bi2–S10	2.816(2)	Bi1–S4	2.8057(9)
Bi1–S5	2.9326(9)	Bi1–S5	2.9560(18)	Bi2–S11	2.8396(19)	Bi1–S5	2.5841(8)
Bi1–S6	2.6921(11)	Bi1–S6	2.7669(17)	Bi2–S12	2.6400(16)	Bi1–S6	2.8121(8)
C1–S1	1.721(3)	C1–S1	1.733(6)	C28–S7	1.731(6)	C1–S1	1.736(3)
C1–S2	1.729(3)	C1–S2	1.709(6)	C28–S8	1.714(7)	C1–S2	1.717(3)
C9–S3	1.706(3)	C10–S3	1.705(6)	C37–S9	1.719(9)	C14–S3	1.730(3)
C9–S4	1.739(4)	C10–S4	1.743(6)	C37–S10	1.719(8)	C14–S4	1.711(3)
C17–S5	1.702(3)	C19–S5	1.717(6)	C46–S11	1.703(6)	C27–S5	1.751(2)
C17–S6	1.742(3)	C19–S6	1.728(6)	C46–S12	1.743(6)	C27–S6	1.709(3)
N1–C1	1.329(3)	N1–C1	1.329(8)	N4–C28	1.330(9)	N1–C1	1.333(4)
N2–C9	1.337(4)	N2–C10	1.323(8)	N5–C37	1.334(11)	N2–C15	1.484(4)
N3–C17	1.331(4)	N3–C19	1.335(8)	N6–C46	1.327(8)	N3–C27	1.330(3)
S1–Bi1–S3	112.39(3)	S1–Bi1–S2	63.45(6)	S7–Bi2–S8	61.89(6)	S1–Bi1–S2	61.46(2)
S1–Bi1–S4	153.34(3)	S1–Bi1–S4	90.52(5)	S7–Bi2–S11	78.20(5)	S1–Bi1–S5	84.99(2)
S1–Bi1–S6	94.00(3)	S1–Bi1–S6	75.84(5)	S7–Bi2–S12	82.49(5)	S1–Bi1–S6	82.11(2)
S3–Bi1–S4	61.55(3)	S2–Bi1–S3	77.28(5)	S8–Bi2–S9	75.35(6)	S2–Bi1–S3	73.62(2)
S3–Bi1–S6	140.36(3)	S2–Bi1–S4	91.31(7)	S8–Bi2–S12	97.79(5)	S2–Bi1–S5	91.49(2)
S4–Bi1–S6	81.44(3)	S3–Bi1–S4	64.24(5)	S9–Bi2–S10	63.94(7)	S3–Bi1–S4	62.71(2)
S2–Bi1–S5	136.50(3)	S3–Bi1–S5	85.82(5)	S9–Bi2–S12	87.56(7)	S3–Bi1–S5	83.53(2)
		S4–Bi1–S5	93.63(6)	S10–Bi2–S11	81.83(6)	S4–Bi1–S5	81.95(2)
		S4–Bi1–S6	87.35(5)	S10–Bi2–S12	90.66(6)	S4–Bi1–S6	76.42(3)
		S5–Bi1–S6	62.25(5)	S11–Bi2–S12	65.56(5)	S5–Bi1–S6	66.09(2)

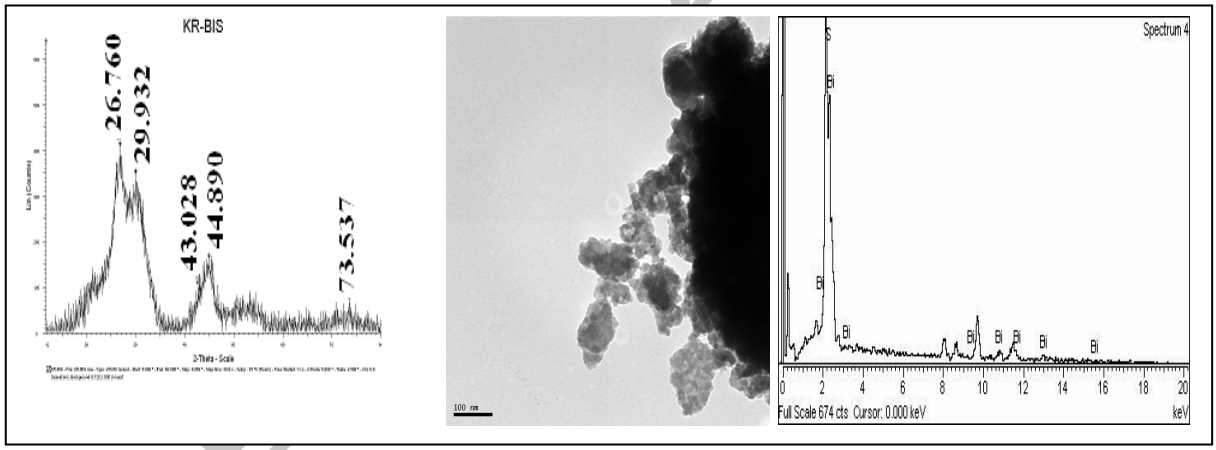


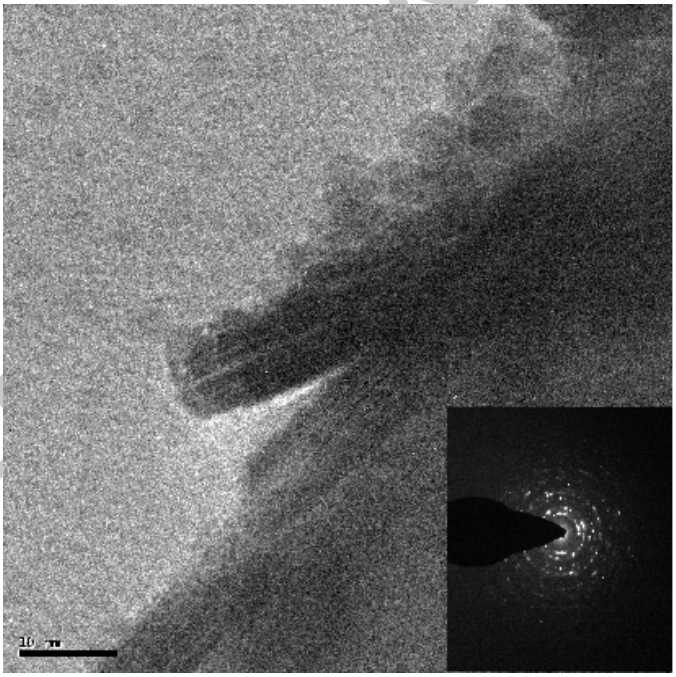






$[Bi(chmdtc)_3]_2$ $[Bi(chedtc)_3]_2$ $[Bi(dchdtc)_3]_2$





Synthesis, Structural, Continuous shape measure and Bond valence sum characterization of bismuth(III) complexes of substituted dithiocarbamates and their solvothermal decomposition

Subbarayan Sivasekar, Kuppukkannu Ramalingam,* Corrado Rizzoli and Nagarajan Alexander

Geometrical distortions from iOh in tris(dithiocarbamato)bismuth(III) have been quantified by Continuous Shape Measure (CShM) analysis. BiS_6 chromophore in $[Bi(chmdtc)_3]$ (**1**) is a distorted octahedron. The coordination geometry in $[Bi(chedtc)_3]$ (**2**) and $[Bi(dchdtc)_3]$ (**3**) should be described as distorted pentagonal pyramid. The higher BVS values observed in the present set of compounds support the fact that the Bi-S bonds are more covalent.

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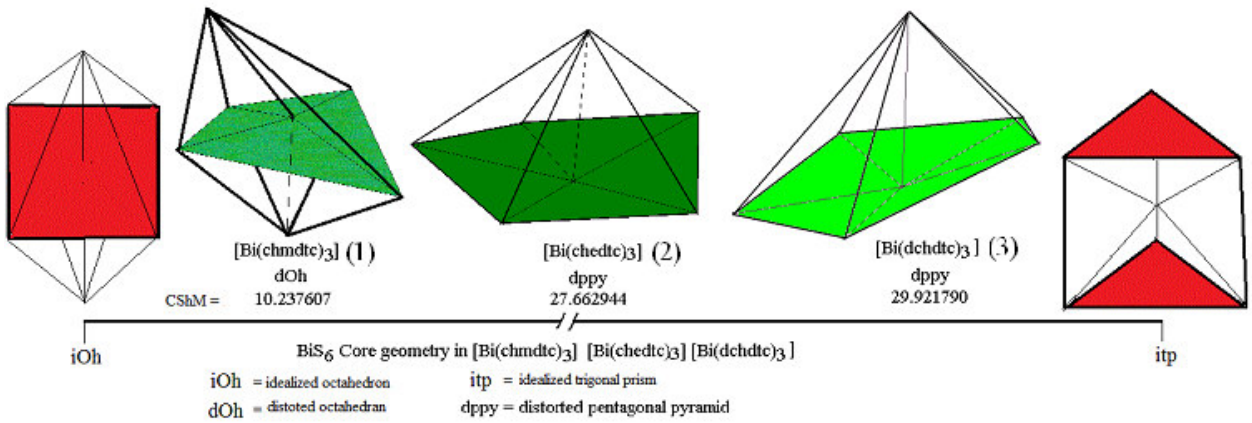
540 Synthesis, structural, Continuous shape measure and Bond valence sum characterization of
541 bismuth(III) complexes of substituted dithiocarbamates and their solvothermal decomposition

542 **Subbarayan Sivasekar, Kuppukkannu Ramalingam,* Corrado Rizzoli and Nagarajan Alexander**



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Highlights

- Complete characterization of three bismuth - dithio complexes
- Three well refined single crystal X-ray structures
- The CShM evaluation correlated to distortion in geometry
- Bond Valence Sums confirm the trivalent nature of bismuth
- Nano bismuth sulfide characterized by PXRD, SEM, EDX and HRTEM