

Synthesis and Structural Characterization of Bismuth (III) Complexes with Dithiocarbamate

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ABSTRACT. Six new bismuth (III) complexes with dithiocarbamate {[NH (CH₂CH₂)₂ NCS₂]₂BiI}₂ (1), [(ⁿBu₂ NCS₂)₂ BiI]₂ (2), {[O (CH₂CH₂)₂ NCS₂]₂BiI}₂ (3), {[(CH₂)₅ NCS₂]₂ BiI}₂ (4), {(Bz₂NCS₂)₂BiI}₂ (5), {(Et₂NCS₂)₂BiI}₂ (6) were synthesized by the reaction of bismuth triiodide and dithiocarbamate in 1:2 stoichiometry and characterized by elemental analysis, UV, IR and ¹H NMR. The crystal structure of complex 1 was determined by X-ray single crystal diffraction. The structure shows that the bismuth atom is rendered six-coordinated in a distorted octahedron bipyramidal coordination geometries.

KEYWORDS: Iodobismuth (III), Crystal structure, Dithiocarbamate

1. Introduction

The chemistry of 1, 1'-dithiochelates of the main group elements is less widely explored than that of the transition metals [1]. This is particularly so for the heavy metal complexes and their structural characterization. A variety of coordination modes have been noted in metal complexes involving dithiocarbamate ligands. In many transition metal complexes involving the dithiocarbamate anion the anion acts as a bidentate ligand forming equidistant M-S bonds [2]. Dialkyl-substituted dithiocarbamate anions have proved to be highly versatile chelating agents for the separation of metals as metal chelates using gas chromatography [3]. Their good performance in liquid-liquid extraction and other analytical procedures [4] makes them more attractive for the determination of metals using gas chromatography [5]. Some of dialkyl-substituted dithiocarbamate salts have also shown interesting biological effects which include anti-alkylation [6, 7] or anti-HIV properties [8, 9]. They are also used as effective antidotes for cadmium intoxication [10, 11]. The ability of dtc to bind to metal has been known for many years. It forms a chelate

with virtually all transition elements [12]. Water-soluble dialkyldithiocarbamate complexes are known to have been tested in various medical applications [13]. Bismuth complexes are used for the treatment of gastrointestinal disorders and may also be useful for the treatment of other disease. Bi (III) exhibits a highly variable coordination number [14-21] and often an irregular coordination geometry. The coordination chemistry of Bi (III) with carboxylates and aminocarboxylates is dominated by intermolecular interactions which leads to polymeric structure. Bi (III) binds strongly to the thiolate sulfur of the tripeptide glutathione, however these adducts are also kinetically labile which allows rapid translocation of Bi (III) inside cells. However, the chemistry of main-group metal complexes with dithiocarbamate has been scarcely studied, and few reports have appeared on the syntheses and structures of the bismuth (III) complexes with dithiocarbamate.

As an extension of studies of bismuth complex and sulfur-containing ligands, we synthesized six new bismuth (III) complexes with dithiocarbamate {[NH(CH₂CH₂)₂NCS₂]₂Bi} (1), [(tBu₂NCS₂)₂Bi] (2), {[O(CH₂CH₂)₂NCS₂]₂Bi} (3), {[C(CH₂)₅NCS₂]₂Bi} (4), {(Bz₂NCS₂)₂Bi} (5), {(Et₂NCS₂)₂Bi} (6) were synthesized by the reaction of bismuth triiodide and dithiocarbamate in 1:2 stoichiometry and characterized by elemental analysis, UV, IR and ¹H NMR. The details of the synthesis, structure and spectra characterizations of the complexes 1-6 are reported herein. The crystal structure of complex 1 was determined by X-ray single crystal diffraction. The structure shows the bismuth (III) atom is rendered six-coordinated in distorted octahedron bipyramidal coordination geometries.

2. Experimental

2.1 General Procedures

Bismuth triiodide was commercially available and used without further purification. The melting points were obtained with Kolfer micro melting point apparatus and were uncorrected. The elemental analyses were performed on a PE-2400- II elemental analyzer. IR spectra were recorded on a Nicolet-460 spectrophotometer, as KBr discs. UV spectra were obtained on a UV 210A spectrometer. ¹H NMR spectra were recorded on a Mercury Plus-400 NMR spectrometer; chemical shifts were given in ppm relative to Me₄Si in CDCl₃ solvent. X-ray measurements were made on a Bruker Smart-1000 CCD diffractometer with graphite monochromated Mo-Kα (0.071073 nm) radiation.

2.2 Preparation of the N, N'-dialkyldithiocarbamate sodium [Na(R₂dtc)]

To a stirred solution of dialkyl-secondary amine (0.05 mol) in ethanol or methanol (5 ml) was added, at less than 4°C, carbon disulfide (3.1 ml, 0.052 mol) and sodium hydroxide (50% aqueous solution, 4 ml). After stirring for 4-5 h, evaporation of the volatile was performed without heating. The pure [Na(R₂dtc)]

was obtained by recrystallization of ethanol (or methanol). The molecular structures, melting points, abbreviation and yield of the six dithiocarbamate are shown as follows (TABLE 1).

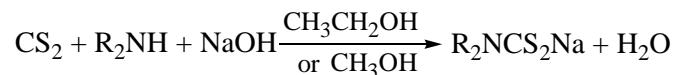
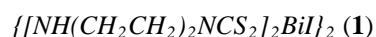


Table 1 Structures, abbreviations and melting points of the dithiocarbamate

Structure	Abbreviation	Yield	Melting point
	NH (CH ₂ CH ₂) ₂ NCS ₂ Na	91%	173°C
	Bu ₂ NCS ₂ Na	89%	decomposed (≅ 200°C)
	O (CH ₂ CH ₂) ₂ NCS ₂ Na	91%	182°C
	(CH ₂) ₅ NCS ₂ Na	87.3%	179°C
	Bz ₂ NCS ₂ Na	84%	decomposed (≅ 200°C)
	Et ₂ NCS ₂ Na	88%	163°C

2.3 Synthesis of bismuth complexes with dithiocarbamate



To a stirred acetonitrile (20 ml) solution of BiI₃ (0.1179 g, 0.2 mmol) was added NH (CH₂CH₂)₂NCS₂Na (0.0737 g, 0.4 mmol). The reaction mixture was stirred for 5 h at 45 °C. An yellow solution was obtained and then filtered. The solvent is

gradually removed by evaporation under vacuum until a solid product is obtained. The solid is recrystallized from ethanol and the orange-red crystal is formed. Yield 78%. m.p. 243°C (dec.). Anal. Calcd (%) for $C_{20}H_{36}N_8S_8Bi_2I_2$ (Mr=1316.81): C, 18.24; H, 2.76; N, 8.51. Found : C, 18.42; H, 2.38; N, 8.39. 1H NMR ($CDCl_3$) δ : 2.65 (m, 16H, $NHCH_2$), 2.48 (m, 16H, NCH_2), 2.08 (m, 4H, NH). IR (KBr) $\nu(cm^{-1})$: 3440, 2850, 1634, 1493, 1406, 1378, 1310, 1238, 1124, 1005, 987, 946, 887, 552, 476.

$[^nBu_2NCS_2]_2BiI_2$ (**2**)

The method of synthesis of the complex **2** was similar as described for **1**. The resulting solid was recrystallized from acetonitrile to give orange crystals. Yield 78%. m.p. 207°C (dec.). Anal. Calcd (%) for $C_{36}H_{72}N_4S_8Bi_2I_2$ (Mr=1489.27): C, 29.03; H, 4.87; N, 3.76. Found : C, 29.33; H, 4.56; N, 3.92. 1H NMR ($CDCl_3$) δ : 3.65 (t, 16H, $N-CH_2-$), 1.55-1.30 (m, 32H, $-CH_2-CH_2-$), 0.96 (t, 24H, $-CH_3$). IR (KBr) $\nu(cm^{-1})$: 3393, 2980, 2935, 2867, 2850, 1635, 1481, 1406, 1384, 1347, 1279, 1147, 1075, 998, 829, 559, 451.

$\{[O(CH_2CH_2)_2NCS_2]_2BiI_2\}_2$ (**3**)

The method of synthesis of the complex **3** was similar as described for **1**. The resulting solid was recrystallized from ethanol to give orange-red crystals. Yield 78%. m.p. 259°C (dec.). Anal. Calcd (%) for $C_{20}H_{32}N_4O_4S_8Bi_2I_2$ (Mr=1320.78): C, 18.19; H, 2.44; N, 4.24. Found : C, 18.36; H, 2.52; N, 4.20. 1H NMR ($CDCl_3$) δ : 3.67(t, 16H, $-CH_2-O-CH_2-$), 2.87 (t, 16H, $-CH_2-N-CH_2$). IR (KBr) $\nu(cm^{-1})$: 3441, 2909, 2852, 1632, 1485, 1424, 1384, 1300, 1265, 1128, 986, 539, 455.

$\{[(CH_2)_5NCS_2]_2BiI_2\}_2$ (**4**)

The method of synthesis of the complex **4** was similar as described for **1**. The resulting solid was recrystallized from ethanol to give orange crystals. Yield 78%. m.p. 267°C(dec.). Anal. Calcd (%) for $C_{24}H_{40}N_4S_8Bi_2I_2$ (Mr=1312.84): C, 21.96; H, 3.07; N, 4.27. Found : C, 21.78; H, 3.01; N, 4.43. 1H NMR ($CDCl_3$) δ : 1.67(t, 24H, $-CH_2-CH_2-CH_2-$), 2.24 (t, 16H, $-CH_2-N-CH_2$). IR (KBr) $\nu(cm^{-1})$: 3441, 2935, 2850, 1637, 1512, 1473, 1418, 1406, 1384, 1347, 1279, 1147, 1110, 989, 844, 559, 459.

$\{(Bz_2NCS_2)_2BiI_2\}_2$ (**5**)

The method of synthesis of the complex **5** was similar as described for **1**. The resulting solid was recrystallized from ethanol to give yellow crystals. Yield 73%. m.p. 195°C (dec.). Anal. Calcd (%) for $C_{60}H_{56}N_4S_8Bi_2I_2$ (Mr=1761.40) : C, 40.91; H, 3.20; N, 3.18. Found : C, 40.59; H, 3.46; N, 3.29. 1H NMR ($CDCl_3$) δ : 6.57-7.80 (m, 40H, Ph-H), 3.39 (s, 16H, NCH_2) IR (KBr) $\nu(cm^{-1})$: 3377, 2937, 2852, 1638, 1508, 1489, 1436, 1422, 1384, 1277, 1237, 1131, 1095, 1021, 999, 842, 556, 439.

$\{(Et_2NCS_2)_2BiI_2\}_2$ (**6**)

The method of synthesis of the complex **6** was similar as described for **1**. The resulting solid was recrystallized from methanol to give yellow crystals. Yield 69%. m.p. 218°C (dec.) Anal. Calcd (%) for $C_{20}H_{40}N_4S_8Bi_2I_2$ (Mr=1264.85): C, 18.99; H,

3.19; N, 4.43. Found : C, 18.58; H, 3.45; N, 4.72. $^1\text{H NMR}$ (CDCl_3) δ : 3.43 (q, 16H, N- CH_2 -). 1.04 (t, 24H, $-\text{CH}_3$). IR (KBr) $\nu(\text{cm}^{-1})$: 3426, 2976, 2863, 1637, 1508, 1492, 1421, 1383, 1353, 1272, 1199, 1143, 1095, 1069, 997, 829, 563, 441.

2.4 Crystallographic measurement

The single crystal having approximate dimensions of 0.13 mm \times 0.13 mm \times 0.12 mm was mounted in a glass capillary. All measurements were made on a Bruker Smart 1000 CCD diffractometer equipped with a graphite-monochromated Mo- $K\alpha$ (0.071073 nm) radiation at 298 (2) K by using the φ - ω scan technique. A total of 10661 reflections were collected in the range of $2.17^\circ < \theta < 25.03^\circ$ and 7148 were independent ($R_{\text{int}} = 0.0242$), of which 4663 reflections were observed ($I > 2\sigma(I)$). The structure was solved by direct methods and difference Fourier map with SHELXL-97 program [22], and refined by full-matrix least-squares on F^2 . All non-hydrogen atoms were refined anisotropically. Position of hydrogen atoms were calculated and refined isotropically.

Table 2 Crystallographic data of complex 1

Complex	1
Empirical formula	$\text{C}_{20}\text{H}_{36}\text{N}_8\text{S}_8\text{Bi}_2\text{I}_2$
Formula weight	1316.81
Temperature (K)	298 (2)K
Wavelength (\AA)	0.71073
Crystal system	Triclinic
Space group	$P-1$
a (\AA)	10.276 (3)
b (\AA)	10.281 (3)
c (\AA)	10.391 (3)
α ($^\circ$)	109.047 (4)
β ($^\circ$)	104.507 (4)
γ ($^\circ$)	98.770 (4)
Volume (\AA^3)	971.1 (5)
Z	1
Calculated density (Mg/m^3)	2.252
$F(000)$	612
Crystal size (mm)	0.13 \times 0.13 \times 0.12
Scan range θ ($^\circ$)	2.51 to 25.00
Limiting indices h	-12 to 12
k	-10 to 12
l	-12 to 12
Total/unique/ R_{int}	4663/3231/0.0524
Goodness-of-fit on F^2	1.055
R_1/wR_2	0.0744/0.1948

3. Results and discussion

3.1 IR spectra

The assignment of IR bands of these complexes have been made by comparison it with the IR spectra of relative sodium dithiocarbamate. A new absorption band appears at 439~476 cm^{-1} which was the characteristic vibrations of Bi-S bond formed [23].

The most significant IR bands in complexes **1~6** is shown in Table IV. It is well known that dithiocarbamate can potentially adopt two different resonance forms (I) and (II), the thioureido form (II) resulting from delocalization of the nitrogen lone-pair [24]. The band in the range 1473~1493 cm^{-1} is attributed to the $\nu(\text{C-N})$ stretching vibration [25], the important bands arising from $\nu(\text{CS}_2)_{\text{asym}}$ and $\nu(\text{CS}_2)_{\text{sym}}$ appear at 1124~1147 and 986~999 cm^{-1} , respectively, with the $\Delta\nu$ value ($\nu(\text{CS}_2)_{\text{asym}} - \nu(\text{CS}_2)_{\text{sym}}$) of 137~158 cm^{-1} , suggesting the dithiocarbamate ligands are coordinated to the Bi atom in a bidentate fashion[26-28], which suggests that resonance form (II) is also a major contributor.

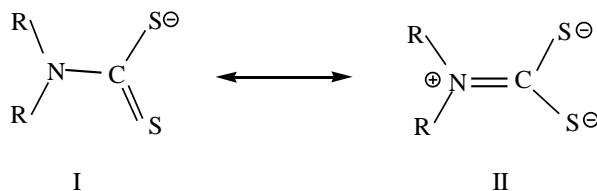


Table 3 Most significant IR band (cm^{-1}) of complexes 1~9

Complex	1	2	3	4	5	6
$\nu(\text{C-N})$	1493	1481	1485	1473	1489	1492
$\nu(\text{CS}_2)_{\text{asym}}$	1124	1147	1128	1147	1131	1143
$\nu(\text{CS}_2)_{\text{sym}}$	987	998	986	989	999	997
$\Delta\nu$	137	149	142	158	132	146

3.2 UV-vis spectra

The electronic absorption spectral data of these new mixed bismuth(III) dithiolate complexes are listed in Table III and tentative assignments of the important characteristic bands have been made with the help of earlier publications [29, 30]. In all the bismuth complexes, the $\pi-\pi^*$ intramolecular charge transfer transitions are due to dithiocarbamate moiety overlap and exhibit the most intense broad band at 221~285 nm. The second band appears as a shoulder (304~308 nm) and is assigned to the $\pi-\pi^*$ transition in the $\text{N}::\text{C}::\text{S}$ (dithiocarbamate) group. The third band of low intensity at 345~363 nm is attributed to $n-\pi^*$ or charge transfer transition due to the dithiocarbamate moiety, exhibiting a hypsochromic shift by

12~21 nm when compared with the corresponding band of salts of dithiocarbamate acid [31]. This suggests that sulphur atoms of dithiocarbamate groups coordinate to bismuth atom.

Table 4 The UV spectra data (λ_{max} in nm) of complexes 1~9

Complex	1	2	3	4	5	6
Band I	224	222	223	226	223	221
Band II	306	308	307	306	304	305
Band III	348	363	345	353	355	360

3.3 ^1H NMR spectra

^1H NMR spectra of the six complex show that the chemical shifts of the protons on methylene connected directly with nitrogen appears at δ 3.15~3.65 ppm. They shift downfields δ 0.4~0.9 as compared with that of the salts of appropriate acid. It is shown that the coordinated dithiocarbamate group is more electronegative than in case of no coordination [31].

3.4 Structure of $\{[\text{NH}(\text{CH}_2\text{CH}_2)_2\text{NCS}_2]_2\text{BiI}\}_2$ (1)

The molecular structure of complex **1** is shown in FIGURE 1 along with the numbering scheme. This complex is dimeric structure and the $\text{Bi}(\text{NHC}_4\text{H}_8\text{NCS}_2)_2$ units are linked by iodine bridges. The two dithiocarbamate ligands are strongly coordinated through their negatively charged sulfur atoms. The C–S bond associated with the strong Bi–S (2.6615(4)Å) is longer (1.7435(14)Å) than that (1.731(14)Å) associated with the weak Bi–S(2.772(4)Å) bond [32], showing clearly the localisation of the double bond.

The N(2)-C(6)-S(4) angles (123.3(11)°) are considerably larger than the N(2)-C(6)-S(3) angles (120.4(11)°). The N(2)-C(6) bond distance (1.294(19) Å) indicates the presence of a partial double bond and supports the contribution of the thioureide form to the dithiocarbamate ligand as indicated by an earlier study based on IR data [33, 34]. The electronic effect of the iodine atom does not influence the C-N bond distances in this present complex.

Of the two Bi-I bonds, one is shorter (3.2777(15) Å) than the other (3.3139(16) Å). The Bi-I bond distances are normal, as observed in the diethyl analogue [35] and the other parameters of the dithiocarbamate ligands are normal.

As shown in FIGURE 1, the structure of $[\text{Bi}(\text{NHC}_4\text{H}_8\text{NCS}_2)_2\text{I}]_2$ consists of a binuclear centrosymmetric neutral complex in which four sulphur atoms from two ligand molecules and two iodine atoms coordinate to each bismuth atom, the resulting coordination being distorted octahedron. Two iodine atoms, related by a centre of symmetry, are bridging, so that the two octahedra share an edge. Each of central Bi atoms is surrounded equatorially by I(1), S(1), S(2), S(4) and axially by

S(3), I(1)#1 (-x, -y+1, -z+1). In complex, two $\text{NHC}_4\text{H}_8\text{NCS}_2$ ligands bond to Bi atom in bidentate fashion. The bond angles formed by three sulfur atoms and one iodine atom occupying equatorial place, and the sum of these angle is 357.13° , which shows that these atoms are approximately co-planar. Furthermore, due to the constraint of the chelate, the angle S(3)-Bi(1)-S(4) is not 90° but only $64.65(11)^\circ$, the S(3) atom can not exactly occupy the corresponding trans axial position of the octahedron bipyramid, the angle S(3)-Bi(1)-I(1)#1 being axial place is $175.16(10)^\circ$, which deviates from linear angle 180° . These data indicate that each Bi atom has a distorted octahedron bipyramidal coordination geometry.

In addition to the iodine bridges, the molecules are held together by strong interaction among S(1)-S(4)#2 (-x+1,-y+1,-z+1), S(4)-S(1)#2 (-x+1,-y+1,-z+1) and S(4)-S(41)#2 (-x+1,-y+1,-z+1), of the neighbouring molecules. In fact this dithiocarbamate moiety may be considered as functioning both as a dithiocarbamate bridge and as a chelating ligand since the S(1)-S(4)#2 $3.461(5) \text{ \AA}$, S(4)-S(1)#2 $3.461(5) \text{ \AA}$ and S(4)-S(4)#2 $3.340(8) \text{ \AA}$ are within the sum of the estimated van der Waal's radii. A representation of the scheme is shown in Fig 1.3, where the S-S interaction have been highlighted. These interactions appear to reinforce the dithiocarbamate bridges in the formation of the polymeric structure.

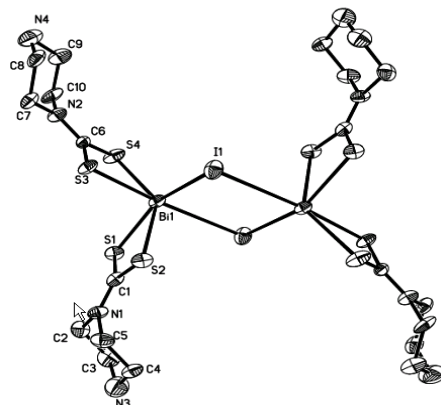


Figure. 1 Molecular structure of complex 1

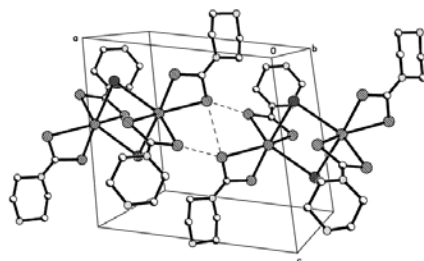


Figure. 2 Projection of the cell of complex 1

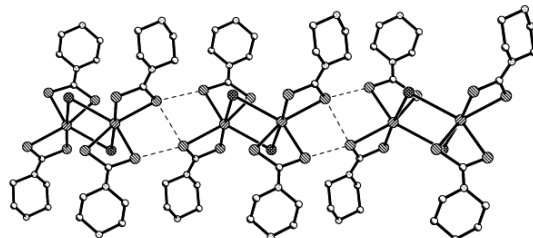


Figure. 3 One-dimensional chain network of complex 1

Table 5 Selected Bond Lengths (Å) and Bond Angles (°) for complex 1

Bi (1)-S (1)	2.661 (4)	Bi (1)-S (3)	2.662 (4)
Bi (1)-S (2)	2.696 (4)	Bi (1)-S (4)	2.848 (4)
Bi (1)-I (1)	3.2777 (15)	N (1)-C (1)	1.31 (2)
Bi (1)-I (1)#1	3.3139 (16)	N (2)-C (6)	1.294 (19)
I (1)#1-Bi (1)	3.3139 (16)	S (1)-C (1)	1.744 (14)
S (2)-C (1)	1.732 (14)	S (3)-C (6)	1.743 (14)
S (4)-C (6)	1.730 (15)	S (1)-S (4)#2	3.461 (5)
S(4)-S(4)#2	3.340 (8)	S (4)-S (1)#2	3.461 (5)
S (1)-Bi (1)-S (3)	94.99 (15)	S (1)-Bi (1)-S (2)	67.42 (12)
S (3)-Bi (1)-S (2)	88.45 (14)	S (1)-Bi (1)-S (4)	84.85 (14)
S (3)-Bi (1)-S (4)	64.65 (11)	S (2)-Bi (1)-S (4)	139.76 (16)
S (1)-Bi (1)-I (1)	148.61 (9)	S (3)-Bi (1)-I (1)	87.02 (10)
S (2)-Bi (1)-I (1)	81.36 (9)	S (4)-Bi (1)-I (1)	123.49 (10)
S (1)-Bi (1)-I (1)#1	89.85 (11)	S (3)-Bi (1)-I (1)#1	175.16 (10)
S (2)-Bi (1)-I (1)#1	93.17 (11)	S (4)-Bi (1)-I (1)#1	116.21 (9)
I (1)-Bi (1)-I (1)#1	88.70 (4)		

Symmetry transformations used to generate equivalent atoms: #1 -x, -y+1, -z+1, #2 -x+1, -y+1, -z+1

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 285308 for complex 1. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1233-336-033; e-mail: deposit @ ccdc. cam. ac. uk).

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