Synthesis and crystal structure of the one-dimensional infinite chain bismuth(III) complexes \{Bi(NO₃)[S₂CN(C₄H₉)₂](CH₃OH)\}_∞ and \{Bi(NCS)[S₂CN(C₂H₅)₂]\}_∞

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Synthesis of two novel bismuth(III) complexes with dithiocarbamate. \{Bi(NO₃)[S₂CN(C₄H₉)₂](CH₃OH)\}_∞ (1) and \{Bi(NCS)[S₂CN(C₂H₅)₂]\}_∞ (2).

To date, a large number of transition-metal complexes with dithiocarbamate have been synthesized and structurally characterized including Ni(S₂CN(C₄H₉)₂), Cu[S₂CN(C₄H₉)₂], Zn[S₂CN(CH$_₂$Ph)$_₂$(2,2'-bipy)] and Fe[S₂CN(C₄H₉)₂](DMF). However, there are some reports on the synthesis and structure of bismuth(III) complexes with dithiocarbamate. As a continuation of our interest in sulfur-containing ligands, we report here the synthesis and structure of two novel bismuth(III) complexes with dithiocarbamate, \{Bi(NO₃)[S₂CN(C₄H₉)₂](CH₃OH)\}_∞ (1) and \{Bi(NCS)[S₂CN(C₂H₅)₂]\}_∞ (2).

Materials and Methods

Sodium dithiocarbamates were prepared as reported already. The elemental analyses were performed on a PE-2400-II elemental analyzer. IR spectra were recorded on a Nicolet-460 spectrophotometer as KBr discs. X-ray measurements were made on a Bruker Smart-1000 CCD diffractometer with graphite monochromated Mo-Kα (0.071073 nm) radiation.

Synthesis of complexes 1 and 2

For preparing the complex 1, aqueous solution of Bi(NO₃)$_₃$.5H₂O (2.0 mmol) and mannite (2.0 mmol) was added to a methanol-water solution of sodium N,N-dibutylidithiocarbamate (4.0 mmol). The mixture was stirred for 0.5 h at 30°C. The yellow solid was obtained by filtration. The product was recrystallized in acetonitrile to give yellow crystals (1.07 g), yield 77.4%, m.p. 253°C (decom). IR (KBr) ν: 3241, 2987, 2874, 1619, 1511, 1481, 1385, 1314, 1145, 1002, 692, 553, 459 cm⁻¹. Anal. calcd for C₁₈H₂₂BiN₃O₃S₅: C 31.88, H 7.3, N 5.90, S 28.44. Found: C 31.88, H 7.3, N 5.73, S 28.67.

For preparing the complex 2, aqueous solution of Bi(NO₃)$_₃$.5H₂O (2.0 mmol) and mannite (2.0 mmol) was added to a methanol-water solution of sodium dithioethanolaminocarbamate (4.0 mmol) and potassium thiocyanate (2.0 mmol). The mixture was stirred for 0.5 h at 30°C. The yellow solid was obtained by filtration. The product was recrystallized in acetonitrile to give yellow crystals (0.79 g), yield 70.6%, m.p. 301°C; IR (KBr) ν: 2980, 2875, 1855, 2086, 1623, 1521, 1475, 1383, 1139, 992, 895, 690, 544, 452 cm⁻¹. Anal. calcd for C₁₈H₂₂BiN₃S₅: C 23.44, H 3.58, N 7.46, S 28.44. Found: C 23.21, H 3.46, N 7.43, S 28.67.

Crystallographic measurements

The yellow crystals with dimensions 0.15 mm×0.10 mm×0.10 mm (1) or 0.10 mm×0.10 mm×0.08 mm (2) were mounted in a fiber. All measurements were made on a Bruker Smart-1000 CCD diffractometer with graphite monochromated Mo Kα (λ=0.071073 nm) radiation. The structures were solved by direct method and refinement Fourier map using SHELXL-97 program, and refined by full-
Table 1 — Crystallographic data of complexes 1 and 2

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<td>C₁₆H₁₀BiN₅O₂S₄</td>
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<td>b = 1.6142(3) nm</td>
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<td></td>
<td>c = 1.0333(4) nm</td>
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</tr>
<tr>
<td></td>
<td>α = 90.00(6) °</td>
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<td></td>
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<td></td>
<td>γ = 90.771(7) °</td>
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<td>R₁/σ(min)</td>
<td>8.18×10⁻³ - 8.71×10⁻³</td>
<td>9.78×10⁻³ - 6.13×10⁻³</td>
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</table>

matrix least-squares on F². All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located at calculated positions and refined isotropically. Crystallographic data of complexes 1 and 2 are given in Table 1.

Results and Discussion

IR spectra of complexes 1 and 2

The assignment of IR bands of the two complexes has been made by comparing the IR spectra of related complexes with those of sodium dithiocarbamates. A new absorption band appears at 459 and 452 cm⁻¹, which is characteristic vibration of Bi-S bond formed.

One obvious feature of the IR spectra is the similarity of the stretching bands arising from the dithiocarbamate groups. The relatively high value (1481 and 1475 cm⁻¹) for v(C-N) is similar to that reported for analogous tin complexes. It is suggested that the dithiocarbamate groups of two complexes are linked to Bi atom in a bidentate fashion.

In IR spectra, important bands arise from v(CS₂)asym and ν(CS₂)sym appearing at 1145, 1002 cm⁻¹ and 1139, 992 cm⁻¹, respectively. The Δv values[ν(CS₂)asym-ν(CS₂)sym] are 143 and 147 cm⁻¹, which are much smaller than the Δv for the R₂NCS₂R' and are larger than the Δv for the corresponding sodium dithiocarbamate, show that the dithiocarbamate groups are coordinated to Bi atom in an anisobidentate fashion.

In IR spectra of complex 1, the bands arising from NO₃⁻ appear at 1511 cm⁻¹ and 1314 cm⁻¹, respectively. The Δv value is close to 200 cm⁻¹. It shows that the NO₃⁻ group is coordinated to Bi atom in an anisobidentate fashion. In IR spectra of complex 2, the bands arise from thiocyanate group appearing at 2086 cm⁻¹, which are smaller than the νCN for the corresponding potassium thiocyanate, which shows that the thiocyanate group is coordinated to Bi atoms by N and S atoms.

Crystal structure of complexes 1 and 2

Complex 1

The molecular structure and perspective view showing the one-dimensional chain structure are shown in Figs 1 and 2, respectively. The selected bond lengths and angles are listed in Table 2.
The crystal consists of the complex 1 and uncoordinated methanol molecules. $\text{[Bi(NO}_3\text{)]_2\text{[S}_2\text{CN(C}_2\text{H}_5)_2\text{]}_2}$ possesses a polymeric structure, but this structure differs from that of the polymeric $\text{Bi(S}_2\text{CNET}_{3\text{H}}_{2})_2$ (Ref. 18). The coordination at the Bi atoms is distorted pentagonal bipyramidal configuration, surrounded axially by one oxygen atom of nitrile group, one sulfur atom of $N,N$-dibutylthiocarbamate group and equatorial by three sulfur atom of $N,N$-dibutylthiocarbamate groups, one oxygen atom of nitrate group and one oxygen atoms of nitrate group from an adjacent molecule.

From Fig. 2, it can be seen that, this complex has two different types of bismuth atoms [Bi(1) and Bi(2)], which are bridged by the oxygen atoms of nitrate groups, resulting in a novel one-dimensional chain polymeric structure.

The surrounding of Bi(1) in this complex, has two shorter Bi-S bonds [Bi(1)-S(2), 0.2630(5) nm; Bi(1)-S(3), 0.2595(5) nm] and two longer Bi-S bonds [Bi(1)-S(1), 0.2977(4) nm, Bi(1)-S(4) 0.2739(3) nm], and three long Bi-O bonds [Bi(1)-O(1), 0.2827(5) nm; Bi(1)-O(2), 0.2823(5) nm; Bi(1)-O(4), 0.2775(5) nm]. The two shorter Bi-S bonds indicate a strong S coordination while the other set corresponds to a weak interaction. It is noticeable that in all $N,N$-dibutylthiocarbamate ligands, the C-S bond associated with the strong Bi-S is significantly longer [S(2)-C(1) 0.1680(18) nm, S(3)-C(10) 0.1692(9) nm] than that [S(1)-C(1) 0.1669(19) nm, S(4)-C(10) 0.1675(9) nm] associated with the weaker Bi-S bond, showing clearly the localization double bonds.

In this complex, because the $N,N$-dibutylthiocarbamate ligands and nitrate group bond with Bi atom in bidinarte fashion by two sulfur atoms of $N,N$-dibutylthiocarbamate ligand and two oxygen atoms of nitrate group, the angles of oxygen atoms and sulfur atoms occupying equatorial place deviate from the standard pentagonal bipyramidal angle. For Bi(1) atom, due to the constraint of the chelate [the angle $\text{S(1)}$-Bi(1)-S(2) and O(1)-Bi(1)-O(2) are not 90° but only 65.80(16)° and 44.8(2)°], the S(2)(S(4)) and O(1) atoms cannot exactly occupy the corresponding two apical positions of the pentagonal bipyramid as the angle O(1)-Bi(1)-S(2) only being 163.99(12)° deviates from linear angle 180°. From this, the Bi(1) atom of complex 1 is distorted pentagonal bipyramidal configuration. From Table 2, we know that the Bi(2) atom of complex 1 has basically same coordinating structure as with Bi(1) atom and it is distorted pentagonal bipyramidal configuration too. But, distortions from true pentagonal bipyramidal symmetry are slightly less than that of Bi(1) atom.

Complex 2

The molecular structure and perspective view showing the one-dimensional chain structure are shown in Figs 3 and 4, respectively. The selected bond lengths and angles are listed in Table 3. In this complex, each bismuth atom adopts a distorted pentagonal bipyramidal geometry and the bridging thiocyanate groups link three Bi atoms to form double one-dimensional chain polymer (Fig. 4).

$\text{[Bi(NCS)]_2[S}_2\text{CN(C}_2\text{H}_5)_2\text{]}_2$ possesses an unequivocally polymeric structure. But, this structure differs from the complex 1. Each Bi atom is rendered seven-coordinate through coordination of the S atom of thiocyanate group from an adjacent molecule. The Bi atom is rendered a distorted pentagonal bipyramidal geometry surrounded axially by one nitrogen atom, one sulfur atom and equatorially by five sulfur atoms of the $N,N$-diethylthiocarbamate ligands and thiocyanate group.

In the structures of complex 2, the Bi-S and Bi-N bond lengths were Bi(1)-S(1), 0.2810(3) nm; Bi(1)-S(2), 0.2645(3) nm; Bi(1)-S(3), 0.2648(4) nm; Bi(1)-S(4), 0.2739(3) nm; Bi(1)-N(3), 0.2643(10) nm; Bi(1)-S(5A), 0.3319(2) nm; Bi(1)-S(5B), 0.3262(2) nm, respectively. The Bi-S bond lengths were almost equal to the bond distance in complex $\text{[Bi(SC}_6\text{F}_{5})_2\text{]}_2$ but longer than that of $\text{Bi(SC}_6\text{H}_{2}(2,4,6-f\text{-Bu})_2\text{]}_2$. So,
the Bi atom in complex 2 could be considered seven-coordinate within a pentagonal bipyramidal environment.

In complex 2, the N(1)-C(1) and N(2)-C(6) were 0.138(12) nm and 0.1339(14) nm, S(1)-C(1), S(2)-C(1), S(3)-C(6) and S(4)-C(6) were 0.1683(11), 0.1705(10), 0.1721(11) and 0.1714(12) nm, respectively. So, in complex 2, all these bond lengths of C-N and S-C were between the 'single' and 'double' bond.

Distortions from true pentagonal bipyramidal symmetry are reflected in the interatomic angles. In complex 2, the sum of equatorial angles [S(1)-Bi(1)-S(2) 65.58(9), S(2)-Bi(1)-S(4) 81.98(10), S(5B)-Bi(1)-S(4) 74.7(2), S(5B)-Bi(1)-S(5A) 71.8(2)], S(5A)-Bi(1)-S(1) 72.5(3)] is equal to 366.56°, which shows that these atoms are not co-planar. The N(3) atom occupies approximately one apical position of the pentagonal bipyramid. Conversely, due to the constraint of the chelate, the angle [S(3)-Bi(1)-S(4)] is not 90° but only 67.05(9). Thus, S(3) atom cannot exactly occupy the corresponding trans axial position of the pentagonal bipyramid. The angle N(3)-Bi(1)-S(3) only being 151.2(3), deviates from linear angle 180°. These data indicate that the Bi atom of this complex is of distorted pentagonal bipyramid configuration.

As shown in Fig. 4, complex 2 consists of a linear polymeric array of molecules in which the bismuth atoms are bridged by Bi-NCS-Bi contacts, and the dithioethylcarbamate groups are outside the molecular chain. In complex 2, each thiocynate group coordinates to three central Bi atoms, and all of them are rendered seven-coordinate in distorted pentagonal bipyramid geometries. Meanwhile, the thiocynate group is close to a line with the angle of N(3)-C(1)-S(3) 177.2(11). Thus, the SCN groups and Bi atoms form a trapeziform six-membered ring. This type of bismuth complex has not been reported so far.

**Table 3** — Selected bond lengths (nm) and bond angles (°) of complex 2

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<td>Bi(1)-S(5A)</td>
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<td>S(1)-C(1)</td>
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<td>S(3)-C(6)</td>
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<td>N(3)-Bi(1)-S(2)</td>
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<td>N(3)-Bi(1)-S(3)</td>
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**Acknowledgement**

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References