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Short Note

# Bis( $\mu$ -iodo)-tetrakis(*O*-methyl *N*-phenylthiocarbamate)-tetraiodo-dibismuth

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**Abstract:** In order to investigate the coordination chemistry of *O*-alkyl *N*-aryl thiocarbamate ligands, BiI<sub>3</sub> was reacted with two equivalents of MeOC(=S)N(H)Ph in MeCN solution to afford the dinuclear title compound complexes  $[\{I_2Bi(\mu_2-I)_2BiI_2\}\{\kappa^1\text{-MeOC(=S)N(H)Ph}\}_4]$  **1**. Compound **1** was characterized by IR, UV and NMR spectroscopy, the formation of a dinuclear framework is ascertained by a single-crystal X-ray diffraction study performed at 100 K.

**Keywords:** bismuth triiodide; thiocarbamate; thione; crystal structure; hirshfeld analysis



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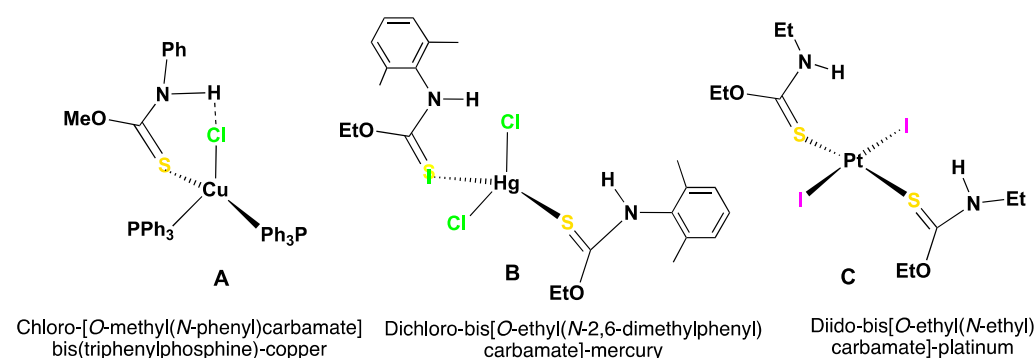
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## 1. Introduction

Thiocarbamates, also called thiocarbamides of general formula ROC(=S)N(H)R', play not only a role in organic chemistry as building blocks for further transformations, but found also application in various domains such biological and pharmacological activity or catalysis [1–5]. Furthermore, they have attracted the attention of coordination chemists, since the soft C=S thione function (according Pearson's HSAB principle) [6] readily coordinates to a wide range of transition metal complexes giving complexes with Cu(I), Ag(I), Au(I), Pd(II), Rh(III), etc. Some crystallographically characterized complexes ligated by *O*-alkyl *N*-aryl and *O*-alkyl *N*-alkyl thiocarbamates are presented in Scheme 1 [7–9].



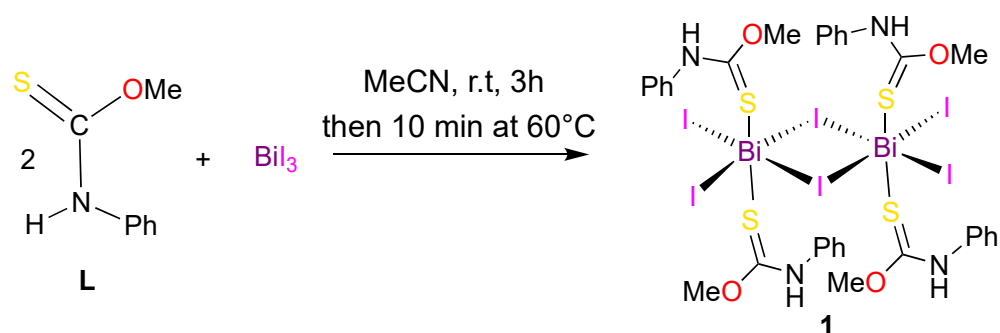
**Scheme 1.** Examples of some *O*-alkyl *N*-aryl(or alkyl) thiocarbamate complexes.

Surprisingly, despite the growing number of transition metal complexes bearing such type of thione ligands, there is a lack of *p* block metal complexes coordinated with *O*-alkyl *N*-aryl thiocarbamates. Since BiX<sub>3</sub> complexes with thione-type ligand are literature-known (see below) and may even display a biological activity [10–12], we reacted BiI<sub>3</sub> with *O*-methyl *N*-phenyl thiocarbamate and describe therein the crystal structure of the isolated

complex. This research is a continuation of our investigations on the coordination chemistry of thione-type ligand on diverse metal centers [13–16].

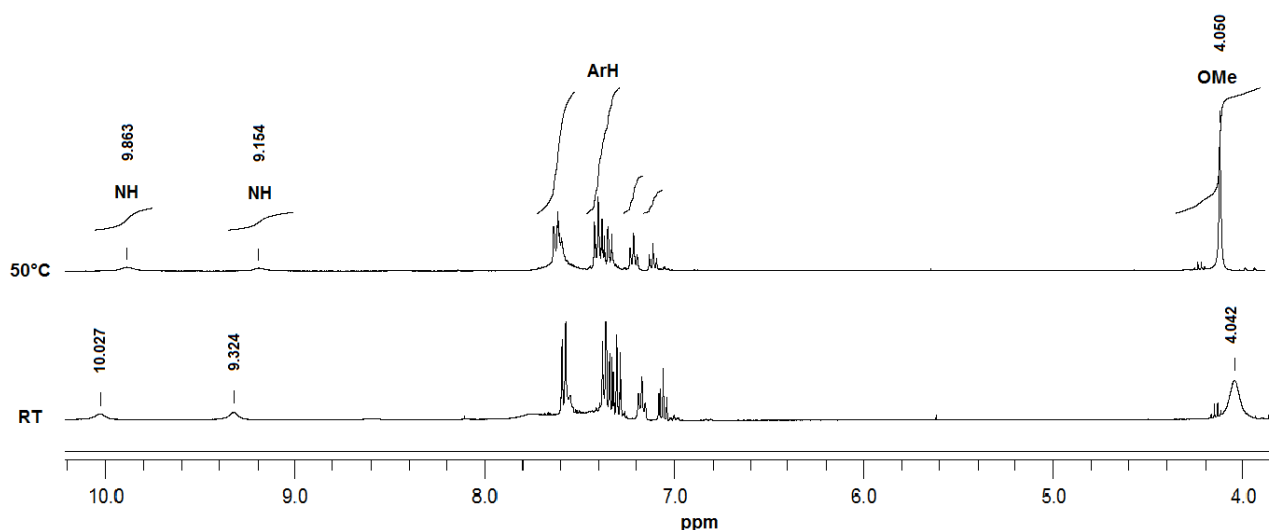
## 2. Results

The hitherto unknown complex  $[\text{I}_2\text{Bi}(\mu_2\text{-I})_2\text{BiI}_2]\{\kappa^1\text{-MeOC(=S)N(H)Ph}\}_4$  **1** was obtained by addition of two equivalents of *O*-methyl *N*-phenyl thiocarbamate **L** to a suspension of  $\text{BiI}_3$  in MeCN (Scheme 2). After stirring for 3 h followed by short heating to  $60^\circ\text{C}$ , a deep orange solution formed. Slow evaporation of the solvent yielded dark-orange air-stable crystals, whose IR-ATR spectrum confirmed the complexation of **L** on Bi(III). According to the elemental analysis, two **L** molecules are attached per  $\text{BiI}_3$  motif.



**Scheme 2.** Synthesis of the title compound **1**.

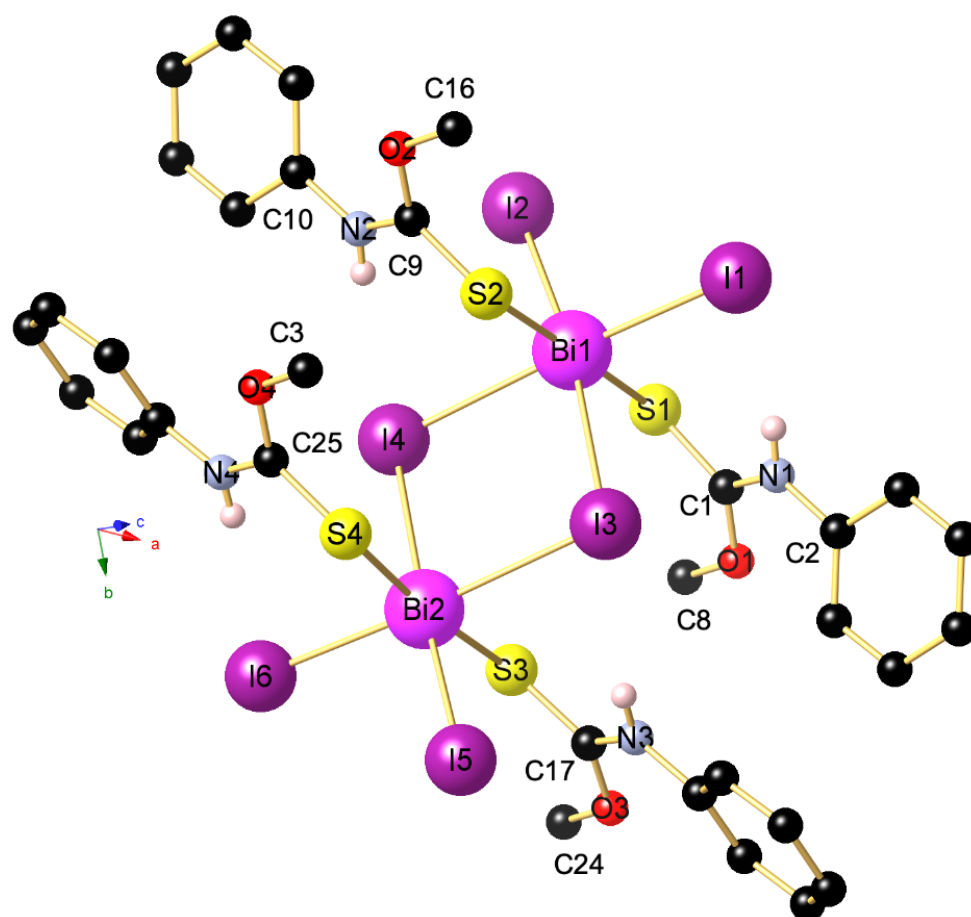
The  $^1\text{H-NMR}$  recorded in  $d_6$ -acetone reveals a broad hump at  $\delta$  4.04 for the methoxy group, whereas the aryl signals are well resolved. Furthermore, two distinct N-H resonances are found at  $\delta$  9.32 and 10.03. A further indication of dynamic processes occurring in solution is provided by the  $^1\text{H NMR}$  spectrum of **1** recorded at 323 K, in which the OMe resonance at  $\delta$  4.05 is considerably sharpened (Figure 1). There is also a noticeable high-field shift of the N-H signals. This dynamic behavior has not been investigated in more detail.



**Figure 1.**  $^1\text{H NMR}$  spectra (400 MHz, acetone- $d_6$ ) of compound **1** at RT and  $50^\circ\text{C}$ .

Since according to a literature survey, no Bi(III) complexes ligated by thiocarbamates have been crystallographically characterized yet, we examined the product crystallizing in the triclinic space group  $P\bar{1}$  by an X-ray diffraction study performed at 100 K. As shown in Figure 2, a dinuclear species has formed, in which the two crystallographically different coordinated Bi(III) centers are linked mutually through two  $\mu_2$ -bridging I3 and I4 iodido ligands. The Bi...Bi separation of 4.720 Å excludes any intermetallic interaction. The

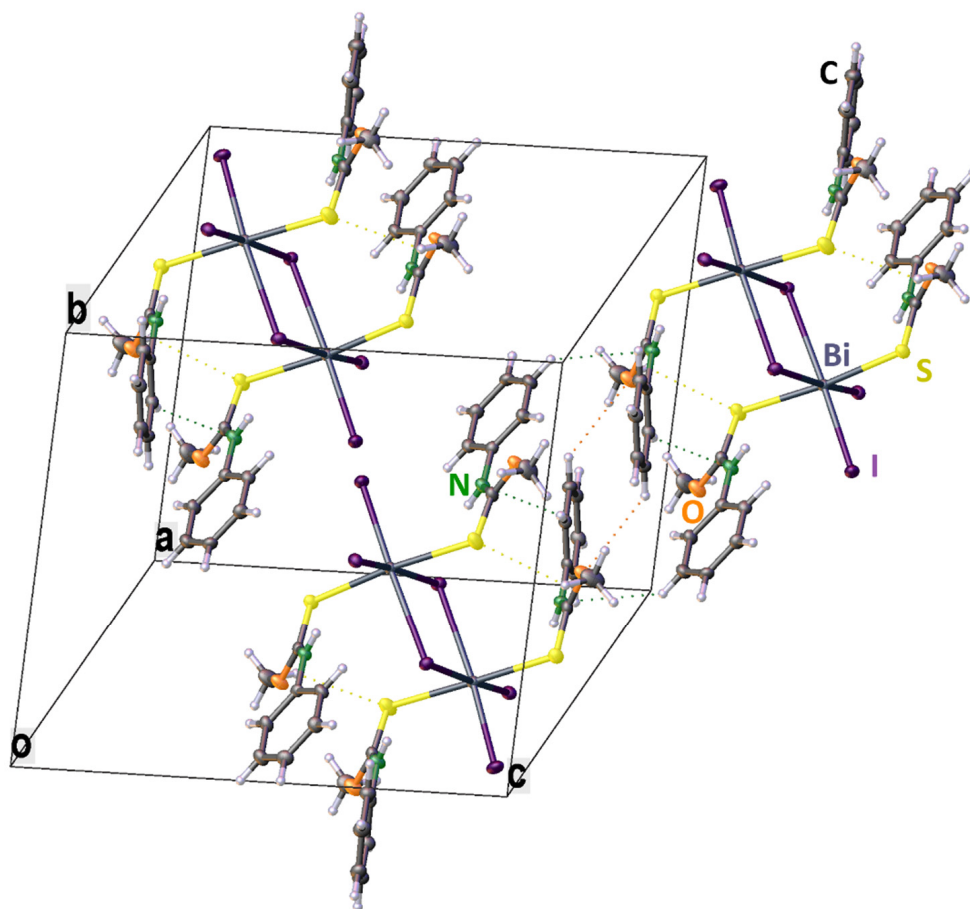
octahedral coordination sphere around each Bi atom is completed by two terminal iodide ligands with a mean Bi–I<sub>term</sub> distance of 2.924(3) Å and two *trans*-arranged thiocarbamate ligands. Each of the four L molecules is crystallographically different with Bi–S bond lengths varying from 2.8290(10) to 2.8952(11) Å. The mean C=S bond is slightly elongated with respect to that of non-ligated MeOC(=S)N(H)Ph (1.701(4) vs. 1.6708(11) Å) [17]. The two bridging I2 and I4 atoms are quite symmetrically bridging, the mean Bi–I<sub>bridg</sub> bond distance of 3.225(3) Å being far longer than the Bi–I<sub>term</sub> one.



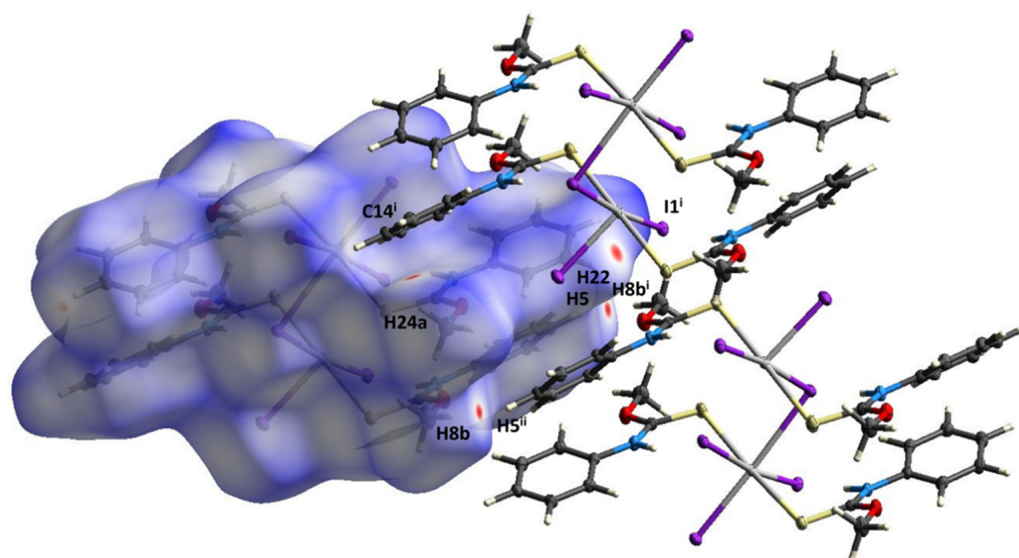
**Figure 2.** Molecular structure of **1**. Selected bond lengths (Å) and angles (deg) of **1**. Bi1–I1 2.9650(3), Bi1–I2 2.8848(3), Bi1–I3 3.2832(3), Bi1–I4 3.2010(3), Bi1–S1 2.8309(11), Bi1–S2 2.8733(12), Bi2–I3 3.2040(3), Bi2–I4 3.2512(3), Bi2–I5 2.8941(3), Bi2–I5 2.8941(3), Bi2–I6 2.9507(3), Bi2–S3 2.8952(11), Bi2–S4 2.8290(10), S1–C1 1.707(4), O1–C1 1.317(5), O1–C8 1.453(5), O2–C9 1.314(5), O3–C17 1.320(5), N1–C1 1.323(5), N1–C2 1.422(5); I1–Bi1–I3 88.884(8), I1–Bi1–I4 174.132(9), I2–Bi1–I1 99.236(9), I2–Bi1–I3 171.720(8), I2–Bi1–I4 85.776(9), I4–Bi1–I3 86.031(7), S1–Bi1–I1 91.54(2), S1–Bi1–I2 84.53(2), S1–Bi1–S2 178.91(3), S2–Bi1–I1 89.05(2), I3–Bi2–I4 86.520(7), I5–Bi2–I3 91.078(8), I5–Bi2–I6 95.627(9), S3–Bi2–I3 86.14(2), S4–Bi2–I3 90.37(2), O1–C1–S1 123.1(3), O1–C1–N1 115.3(3), N1–C1–S1 121.6(3), C3–C2–N1 115.9(3), C7–C2–N1 124.1(3), C7–C2–C3 120.0(3).

In the packing, several secondary weak interactions are present such as between atoms I1<sup>i</sup>–H22 (3.081 Å), C14<sup>i</sup>–H24A (2.757 Å), H5–H8B<sup>i</sup> (2.293 Å) and I3<sup>i</sup>–H29 (3.128 Å). Furthermore, as shown in Figure 3, loose intramolecular S···H and N···H contacts occur.

These interactions have also been assessed by means of a Hirshfeld surface analysis using the *CrystalExplorer17* software (Figure 4) [18,19]. The Hirshfeld surface was mapped over  $d_{\text{norm}}$  in the range from  $-0.0743$  to  $-1.2577$  (arbitrary units). The corresponding fingerprints plots are presented in the Supporting Material.



**Figure 3.** OLEX-generated view of the unit cell of **1** indicating several weak intra- and intermolecular interactions by dotted lines ( $S2 \cdots H32C$  2.98094(15) Å,  $S3 \cdots H8A$  3.05129(15) Å and  $N3 \cdots H7$  2.90335(11) Å).



**Figure 4.** View of the Hirshfeld surface of compound **1** revealing some loose contacts in the crystal structure. Molecule *i* was generated by the symmetry operation  $1+x, +y, +z$  and molecule *ii* by the symmetry operation  $1-x, 1-y, 2-z$ .

### 3. Discussion

A survey of the Cambridge Structural Database (CSD) reveals that in addition to several mononuclear tris(thione) complexes of type  $[X_3Bi(\text{thione})_3]$  such as tris(2-benzylidenehydrazine-1-carbothioamide)-tribromo-bismuth (refcode QASQAG) or tris(1,3-diazinane-2-thione)-triiodo-bismuth (refcode BOSDAR) [12], there are some other examples of dinuclear complexes with a  $[(X_2Bi(\mu_2-X)_2BiX_2)(\text{thione})_4]$  motif. One example is tetrakis(1-allyl-3-(2-pyridyl)-thiourea-S)-bis( $\mu_2$ -chloro)-tetrachloro-dibismuth bismuth (refcode ALPBIA), but in this compound the thione ligands on each  $BiCl_3$  unit are *cis*-arranged and not in *trans*-position as in compound **1** [20]. An example for a complex with a  $[(Cl_2Bi(\mu_2-Cl)_2BiCl_2)]$  core bearing four *trans*-arranged thione ligands is bis( $\mu_2$ -chloro)-tetrachloro-tetrakis(2-[1-(3-ethylpyrazin-2-yl)ethylidene]-N-methylhydrazine-1-carbothioamide)-di-bismuth (refcode KOTNAL). However, the only representative of a iodido complex  $[-25]trans-[I_2Bi(\mu_2-I)_2BiI_2](\text{thione})_4$  is bis( $\mu_2$ -iodo)-tetrakis(5-methoxy-1,3-dihydro-2H-benzimidazole-2-thione)-tetraiodo-di-bismuth (refcode MADZAW), recently described by the research group of Ozturk et al. [10]. Maybe the fluxional behavior revealed by NMR spectroscopy is due to a *trans-cis* isomerization occurring in solution, involving dissociation and re-coordination of L (facilitated by the polar solvent acetone). Alternatively, the four O-alkyl N-aryl thiocarbamate ligands may adopt somewhat different arrangements at ambient temperature due to N-H... contacts and are getting more equivalent on the NMR time-scale when rising the temperature. Formation of weak hydrogen bonding between the N-H groups of L and the O=C function of acetone used as solvent may also be taken in account.

### 4. Experimental

To a slurry of  $BiI_3$  (294.8 mg, 0.5 mmol) in 10 mL of acetonitrile, O-methyl N-phenylthiocarbamate L (167.2 mg, 1 mmol) was added in several portions. The reaction was first stirred at room temperature for 3h, and then heated to 60 °C for 10 min. After reaching ambient temperature, the solvent was allowed to evaporate partially. After 2 days, dark orange crystals of **1** were formed and then collected by filtration. Yield: 79%. Anal. Calc. for  $C_{32}H_{36}Bi_2I_6N_4O_4S_4$  (M.W = 1848.3 g.mol<sup>-1</sup>): C, 20.79; H, 1.96; N, 3.03; S, 6.93%. Found: C, 20.73; H, 1.94; N, 2.99; S, 6.89%. IR-ATR: 1230  $\nu$ (C=S), 1483  $\nu$ (C-N), 1548  $\nu$ (N-H), 3281  $\nu$ (N-H bonded) cm<sup>-1</sup>. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>) at 298 K:  $\delta$  4.05 (s, br, 3H, OCH<sub>3</sub>), 7.04–7.59 (m, 5H, aryl-H), 9.32 and 10.03 (2s, br, 1H, NH) ppm. UV-vis (acetone) [ $\lambda_{max}$  nm ( $\epsilon$  M<sup>-1</sup> cm<sup>-1</sup>): 247 (30100), 275 (25900), 375 (4100), 465 (3500).

Crystal data for  $C_{32}H_{36}Bi_2I_6N_4O_4S_4$ , M = 1848.25 g.mol<sup>-1</sup>, dark orange crystals, crystal size 0.15 × 0.113 × 0.073 mm<sup>3</sup>, triclinic, space group  $P\bar{1}$ ,  $a = 12.8215(6)$  Å,  $b = 13.5748(6)$  Å,  $c = 15.1534(8)$  Å,  $\alpha = 85.829^\circ$  (2),  $\beta = 73.537(2)^\circ$ ,  $\gamma = 68.789(2)^\circ$ ,  $V = 2356.7(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_{calc} = 2.605$  g/cm<sup>3</sup>,  $T = 100$  K,  $R_1 = 0.0286$ ,  $Rw_2 = 0.0470$  for 104,055 reflections with  $I \geq 2\sigma(I)$  and 14,441 independent reflections. Largest diff. peak/hole/e Å<sup>-3</sup> 1.48/-1.51. Data were collected using graphite-monochromated MoK $\alpha$  radiation  $\lambda = 0.71073$  Å and have been deposited at the Cambridge Crystallographic Data Centre as CCDC 2165826. (Supplementary Materials). The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk/getstructures>. The structure was solved by direct methods and refined by full-matrix least-squares against  $F^2$  (SHELXL,2015 [21,22]).

### 5. Conclusions

We have crystallographically evidenced that not only transition metals, but also p-block salts such as  $BiI_3$ , can constitute interesting targets for the coordination of thiocarbamate ligands via their thione function.

**Supplementary Materials:** The following supporting information can be downloaded, CIF file, Check-CIF report, UV-Vis spectrum and Hirshfeld fingerprint plot.

**Author Contributions:** W.A. prepared the compound; C.S. and A.S. collected the X-ray data and solved the structure; A.K. and M.K. designed the study and analyzed the data and M.K. wrote the paper. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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