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Short Note

Bis(μ-Iodo)-Tetrakis(*O*-Methyl *N*-Phenylthiocarbamate)-Tetraiodo-Dibismuth

Wafa Arar [1], Abderrahim Khatyr [2], Michael Knorr [2,*], Carsten Strohmann [3] and Annika Schmidt [3]

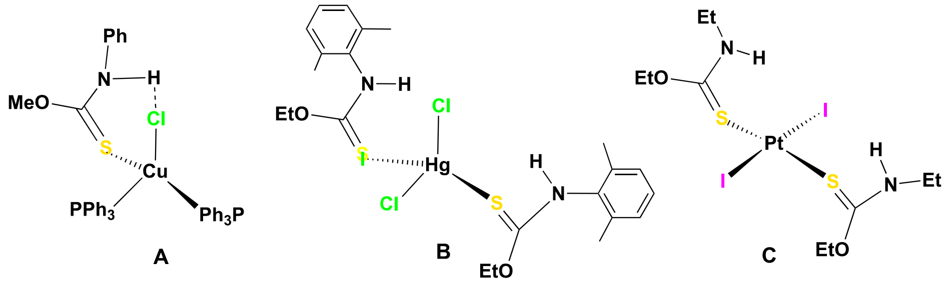
[1] Selective Organic- Heterocyclic Synthesis-Biological activity evaluation (LR17ESO01),Univesité de Tunis-El Manar 2092-Tunis,Tunisia; wafaarar22@gmail.com
[2] Institut UTINAM UMR 6213 CNRS, Université Bourgogne Franche-Comté, 16, Route de Gray, 25030 Besançon, France ;abderrahim.khatyr@univ-fcomte.fr
[3] Anorganische Chemie, Technische Universität Dortmund, Otto-Hahn Straße 6, 44227 Dortmund, Germany; carsten.strohmann@tu-dortmund.de, annika5.schmidt@tu-dortmund.de
* michael.knorr@univ- fcomte.fr; Tel. + [33] 3 81 66 62 70

Abstract: In order to investigate the coordination chemistry of *O*-alkyl *N*-aryl thiocarbamate ligands, BiI_3 has been reacted with two equivalents of MeOC(=S)N(H)Ph in MeCN solution to afford the dinuclear title compound complexes $[\{I_2Bi(\mu_2\text{-}I)_2BiI_2\}\{\kappa^1\text{-}MeOC(=S)N(H)Ph\}_4]$ **1**. Compound **1** has been characterized by IR, UV and NMR spectroscopy, the dinuclear framework has be ascertained by a single-crystal X-ray diffraction study performed at 100 K.

Keywords: Bismuth triiodide; thiocarbamate; thione; crystal structure; Hirshfeld analysis

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 Chart 1 [7–9].



Chloro-[*O*-methyl(*N*-phenyl)carbamate] bis(triphenylphosphine)-copper

Dichloro-bis[*O*-ethyl(*N*-2,6-dimethylphenyl) carbamate]-mercury

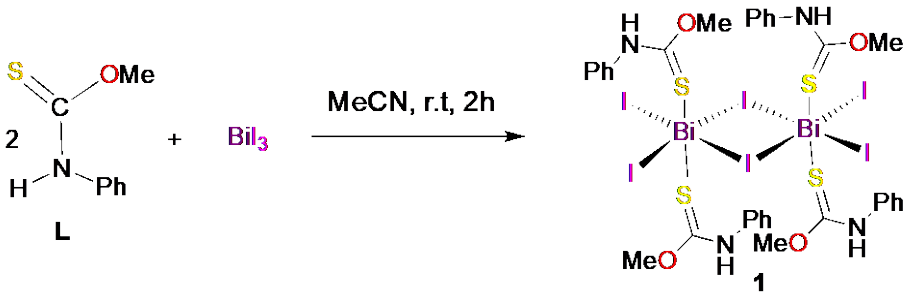
Diido-bis[*O*-ethyl(*N*-ethyl) carbamate]-platinum

Chart 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 thiocarbamate. Since BiX_3 complexes with thione-type ligand are literature-know (see below) and may even display a biological activity [10–12], we reacted BiI_3 with *O*-methyl *N*-phenyl thiocarbamate and describe therein the crystal structure of the isolated complex. This research makes part of our investigations on the coordination chemistry of thione-type ligand on diverse metal centers [13–16].

2. Results

The hitherto unknown complex $[\{I_2Bi(\mu_2\text{-}I)_2BiI_2\}\{\kappa^1\text{-}MeOC(=S)N(H)Ph\}_4]$ **1** was obtained by addition 2 two equivalents of *O*-methyl *N*-phenyl thiocarbamate **L** to a suspension of BiI_3 in MeCN (Scheme 1). After stirring for several hours, 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 BiI_3 motif.



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

The ^{1}H-NMR recorded in *d*$_6$-actetone reveals a broad hump at δ 4.04 por the methoxy group, whereas the aryl signals are well resolved. Furthermore, two distinct N-H resonances are found at δ 9.32 and 10.03. A further indication of dynamic processes occurring in solution is provided by the ^{1}H NMR spectrum of **1** recorded at 323 K, in which the OMe resonance at δ 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.

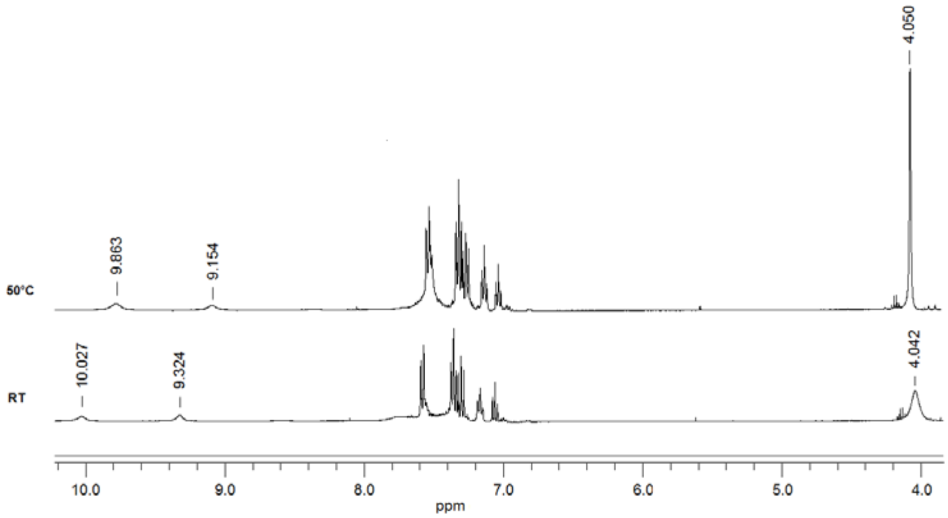


Figure 1. ^{1}H NMR spectra (400 MHz, acetone-d$_6$) of compound **1** at RT and 50°C.

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 $P\overline{1}$ by an X-ray diffraction study performed at 100 K. As shown in Fig. 2, a dinuclear species has been formed, in which the two crystallographically different coordinated Bi(III) centers are linked mutually through two μ^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

doi:10.20944/preprints202205.0129.v1

ligands with a mean Bi–I$_{\text{term}}$ 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$_{\text{bridg}}$ bond distance of 3.225(3) Å being far longer than the Bi–I$_{\text{term}}$ one.

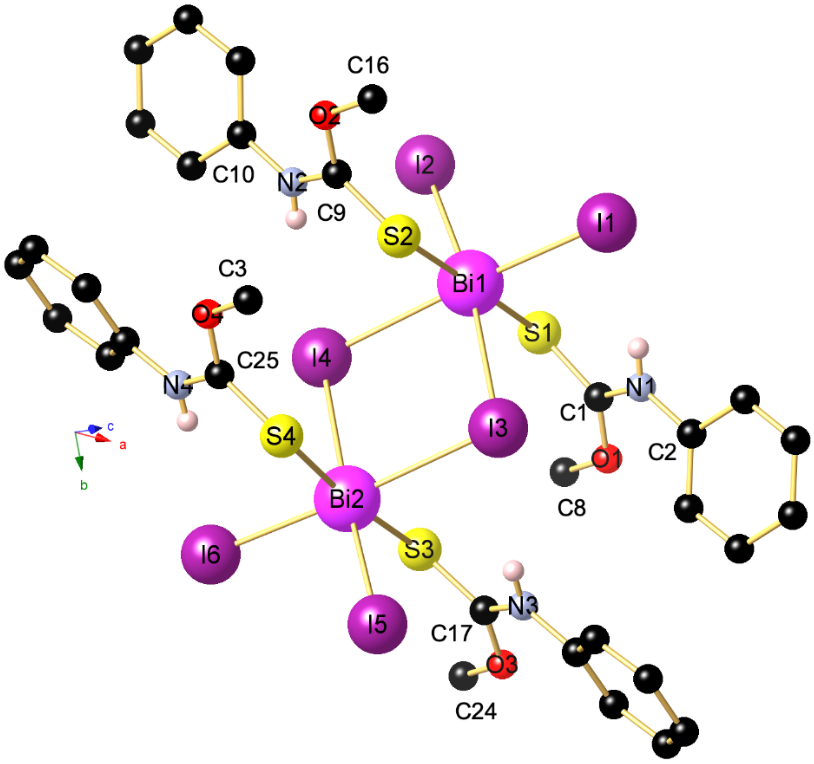


Figure 2. Molecular structure of **1**. Selected bond lengths (Å) and angles (deg) of **1.** Bi1–I1 2.9650(3), Bi1–I2 2.8848(3), Bi1–I3 3.2832(3), Bi1–I4 3.2010(3), Bi1–S1 2.8309(11), Bi1–S2 2.8733(12), Bi2–I3 3.2040(3), Bi2–I4 3.2512(3), Bi2–I5 2.8941(3), Bi2–I5 2.8941(3), Bi2–I6 2.9507(3), Bi2–S3 2.8952(11), 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 week interactions are present such as between atoms I1^{i}–H22 (3.081 Å), C14^{i}–H24A (2.757 Å), H5–H8B^{i} (2.293 Å) and I3^{i}–H29 (3.128 Å). Furthermore, as shown in Figure 3, loose intramolecular S···H and N···H contacts occur.

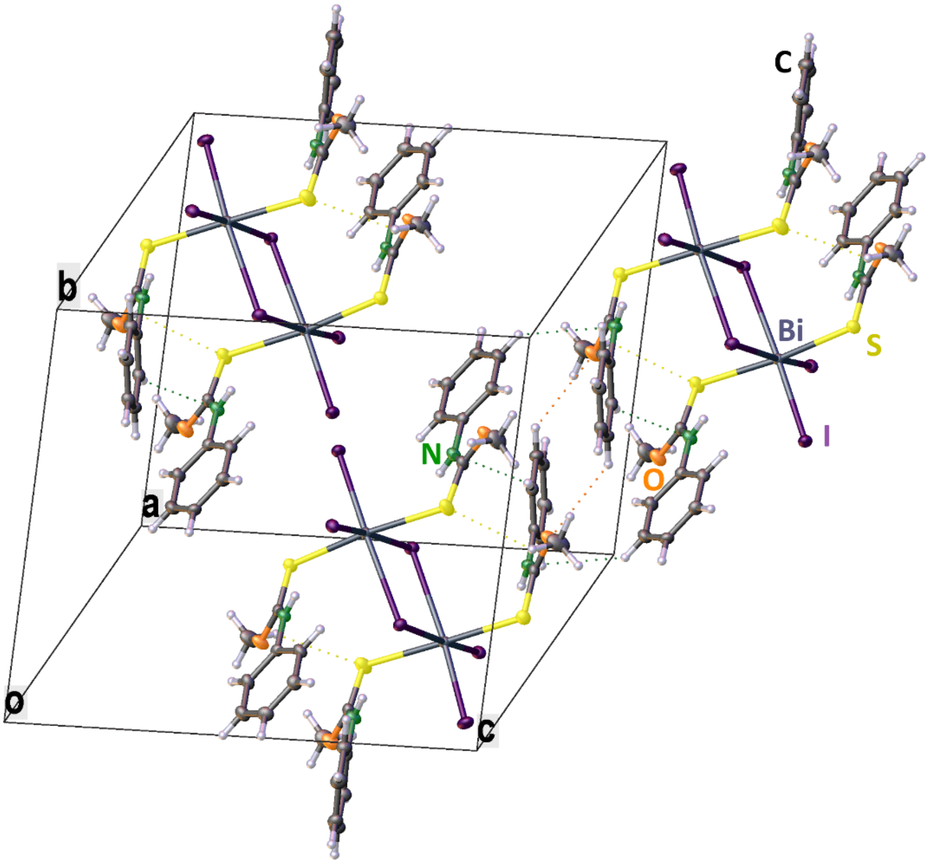


Figure 3. OLEX-generated view of the unit cell of **1** indicating several weak intra- and intermolecular interaction by dotted lines (S2···H32C 2.98094(15) Å, S3···H8A 3.05129 (15) Å and N3···H7 2.90335(11) Å).

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_{norm} in the range from –0.0743 to –1.2577 (arbitrary units). The corresponding fingerprints plots are presented in the Supporting Material.

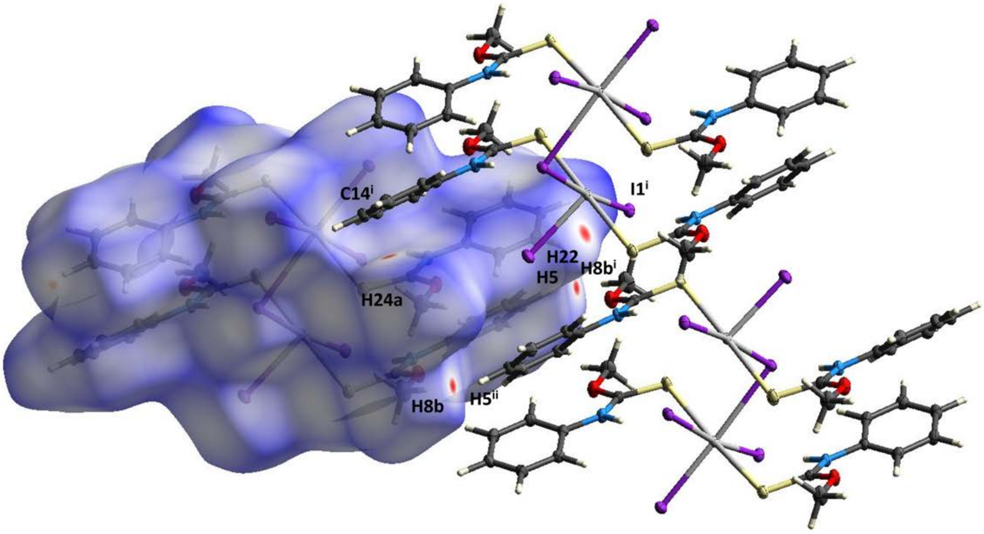


Figure 4. View of the Hirshfeld surface of compound **1** revealing some loose contacts in the crystal structure. Molecule *i* has been generated by the symmetry operation 1+*x*, +*y*, +*z* and molecule *ii* by the symmetry operation 1-*x*, 1-*y*, 2-*z*.

3. Discussion

A survey of the Cambridge Structural Database (CSD) reveals that in addition to several mononuclear tris(thione) complexes of type [X_3Bi(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(μ_2-X)$_2$BiX_2}(thione)$_4$] motif. One example is tetrakis(1-allyl-3-(2-pyridyl)-thiourea-S)-bis(μ_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(μ_2-Cl)$_2$BiCl_2}] core bearing four *trans*-arranged thione ligands is bis(μ_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 *trans*-[{I_2Bi(μ_2-I)$_2$BiI_2}(thione)$_4$] is bis(μ_2-iodo)-tetrakis(5-methoxy-1,3-dihydro-2*H*-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.

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^{-1}): 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 ν(C=S), 1483 ν(C–N), 1548 ν(N–H), 3281 ν(N–H bonded) cm^{-1}. ^{1}H NMR (acetone-d$_6$) at 298 K: δ 4.05 (*s*, br, 3H, OC$\underline{H_3}$), 7.04 -7.59 (*m*, 5 H, aryl-H), 9.32 and 10.03 (2s, br, 1H, N$\underline{H}$) ppm. UV-vis (acetone) [λ_{max} nm (ε M^{-1} cm^{-1})]: 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^{-1}, dark orange crystals, crystal size 0.15 × 0.113 × 0.073 mm^3, triclinic, space group $P\bar{1}$, a =12.8215(6) Å, b =13.5748(6) Å, c = 15.1534(8) Å,), α = 85.829° (2), β = 73.537(2) °, γ = 68.789(2)°,V = 2356.7(2) Å^3, Z = 2, D$_{calc}$ = 2.605 g/cm^3, T = 100 K, R_1 = 0.0286, Rw2 = 0.0470 for 104055 reflections with I > = 2σ (I) and 14441 independent reflections. Largest diff. peak/hole / e Å^{-3} 1.48/-1.51. Data were collected using graphite monochromated MoK$_\alpha$ radiation l = 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 [20–21]).

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 at: www.mdpi.com/xxx/s1, CIF file, Check-CIF report, UV-Vis spectrum and Hirshfeld fingerprint plot.

Author Contributions: A.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 analysed the data and M.K wrote the paper.

Funding: This research received no external funding

Data Availability Statement: The X-ray data are at CCDC as stated in the paper.

Acknowledgments: We thank Ms. Stéphanie Boullanger for recording the IR and NMR spectra.

Conflicts of Interest: The authors declare no conflict of interest

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