Communication

Synthesis of Catena-bis(µ-bromo)-(O-methyl-N-phenylthiocarbamate)-dicopper(I) and Its Reactivity towards PAr₃ (Ar = Ph, p-Tol)

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Abstract: In order to investigate the coordination chemistry of O-alkyl N-aryl thiocarbamate ligands toward coinage metals, CuBr was reacted with one equivalent of MeOC(=S)N(H)Ph L in MeCN solution to afford the 1D-polymeric title compound [[Cu(µ₂-Br)₂Cu(µ₂-MeOC(=S)N(H)Ph)₂]ₙ CP1. Compound 1 was characterized by IR spectroscopy and an elemental analysis. The formation of a polymeric 1D ribbon built upon µ₂-bridging bromido and thione ligands via the C=S bond was ascertained by a single-crystal X-ray diffraction study performed at 100 K. In the presence of PAr₃ (Ar = Ph, p-Tol), the polymer chain was broken to yield the mononuclear complexes [(Ar₃P)₂Cu(MeOC(=S)N(H)Ph)Br] C1 and C2.

Keywords: copper bromide; thiocarbamate; thione; crystal structure; hydrogen bonding; aryl phosphate

1. Introduction

Thiocarbamates, also called thiocarbamides, with the general formula ROC(=S)N(H)R’ play not only a role in organic chemistry as building blocks for further transformations but also in applications in various domains, such as biological and pharmacological activities or catalysis [1–5]. Furthermore, they have attracted the attention of coordination chemists, since the soft C=S thione function (according to Pearson’s HSAB principle) [6] readily coordinates to a wide range of transition metal complexes, forming complexes with Cu(I), Ag(I), Au(I), Hg(II), Ru(II), Rh(III), etc. [7–11]. Furthermore, they may act as potential ditopic ligands capable of coordinating to a metal center both via their soft C=S function or through the harder HNR₂ group as demonstrated by the crystal structure determination of the square-planar bis(O-methylphenylthiocarbamato)(triphenylphosphine)-palladium [11].

We have recently demonstrated that O-methyl-N-phenyl thiocarbamate can even be coordinated to p-block metal salts, such as Bi₃ [12]. Some representative examples of crystallographically characterized mono- and dinuclear complexes ligated by O-methyl-N-phenyl thiocarbamate are presented in Scheme 1 [7,8,12].

With the aim to investigate putative arene-C−H···π(quasi-chelate ring) interactions in copper(I) crystal structures, Tiekink et al. reported in 2014 on the synthesis of the complex [(Ph₃P)₂Cu(ROMe)₂(NH₂)] by the reaction of CuCl with L in the presence of two equivalents of PPh₃ [7], shown as complex A in Scheme 1. In a continuation of our investigations on the coordination chemistry of thione-type ligands on diverse metal centers [13–16], our group extended the preparation of this type of Cu(I) complex


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to CuBr and CuI, systematically analyzed by crystal structure determinations a wide series of complexes [(Ar₅P)₂Cu(ROC(S)N(H)Ph)X] (Ar = Ph, p-C₆H₄OMe; X = Br, I), and investigated the biological activity of these compounds featuring intramolecular N⋯H⋯Hal bonding, giving rise to six-membered cycles [17]. We also reported that the formation of [(Ar₅P)₂CuROC(S)N(H)Ph]I] is preceded in the initial phase of the reaction by the formation of monodimensional coordination polymers of type [Cu(μ₂-Br)₂Cu(μ₂-L)₂]₈ [17]. We now investigate in more detail the outcome of the reaction of CuBr with L, describing herein the synthesis and crystal structure of the resulting coordination polymer [(Cu(μ₂-Br)₂Cu)(μ₂-MeOC(S)N(H)Ph)]₈ CP1 and reporting on its reactivity towards PAr₅.

Scheme 1. Examples of some O-methyl N-arylthiocarbamate complexes.

2. Results and Discussion

The hitherto unknown coordination polymer [(Cu(μ₂-Br)₂Cu)(μ₂-MeOC(S)N(H)Ph)]₈ CP1 was obtained by the addition of one equivalent of O-methyl N-phenyl thiocarbamate L to a solution of CuBr in MeCN (Scheme 2). After stirring for 20 min, the precipitation of a colorless microcrystalline material occurred, which upon heating for 5 min almost redissolved. Upon cooling, colorless crystals started to grow. According to the elemental analysis of this air-stable material, one L molecule is attached per CuBr motif. This polymeric material, whose characterization is described below, reacts straightforwardly upon the addition of two equivalents of PPh₃ per CuBr unit to form by the splitting of the μ₂-Br bridges of CP1 the mononuclear tetrahedral complex [(Ph₃P)₂Cu(MeOC(S)N(H)Ph)Br] C1 (Scheme 2). Since this complex has been recently fully characterized, we refer for its spectroscopic data to ref. [17]. In an analogous manner, CP1 reacts with tris(p-tolyl)phosphine PTOl₃-p to yield the derivative [(TOl₃P)₂Cu(MeOC(S)N(H)Ph)Br] C2 with over an 85% yield as an air-stable crystalline solid. Its ³¹P NMR spectrum in CDCl₃ shows a single broadened resonance at δ −6.34 with a Δδ of 0.92 ppm with respect to free PTOl₃ [18]. The ^1H NMR spectrum displays a strong singlet at δ 2.33 ppm, attributed to the six equivalent methyl groups of the p-tolyl rings. The characteristic signals of the thiocarbamate moiety at δ 4.06 and 10.54 ppm are assigned to -OCH and the NH group while the aromatic protons are observed as a multiplet between δ 7.03 and 7.39 ppm (Figure S2). In the proton-decoupled ^13C NMR spectrum, a single resonance at δ 21.4 ppm is seen for the six magnetically equivalent Me substituents. The C-atom of the ligated thione function resonates at δ 187.3 ppm (Figure S3). The ATR-IR spectrum features a broadened N-H vibration at 3160 cm⁻¹, indicative of an intramolecular N-H⋯Br interaction, as was crystallographically evidenced for C1 (Figure S4). Upon the treatment of CP1 with an excess of PPh₃, the dissociation of the coordinated thione ligand occurs, yielding finally, among other non-identified products, the cluster compounds [(PPh₃)₂Cu(μ₂-Br)₂CuPPh₃] and [Cu₄Br₄(PPh₃)₄], which are already known in the literature, as evidenced by X-ray diffraction [19].
intramolecular $N$-H···Br interaction. For the molecular compounds $[\text{Cu}(\mu_2\text{-Br})_2\text{Cu}(\mu_2\text{-PhC(=S)NH}_2)]_n$, in which the metal centers within the rhomboid clusters are separated by 2.857(3) and 2.7851(12) Å, respectively [23,24]. For the molecular compounds $[\text{Cu}(\mu_2\text{-Br})_2(\text{1-oxa-4,7-dithiaclononane})_2]$ (2.852(1) Å), $[\text{Cu}(\mu_2\text{-Br})_2(\text{dibenzo}[e,m][1,4,8,11]\text{dioxadithia-cyclotetradecine-S,S'})_2]$ (2.919(7) Å), and the supermolecular compound tetrakis(4,5-bis(methylsulfanyl)-1,3-dithiole-2-thione)-bis($\mu_2$-bromo) dicopper (2.893(1) Å), the Cu···Cu interaction lies in a similar range [16,25,26]. A further example is the thione-bridged dinuclear complex $[\text{Cu}_2\text{Br}_2(\mu^{-}\text{S-mimzSH})_2(\eta^1\text{-S-mimzSH})_2]$ (2.877(6) Å), obtained by the reaction of CuBr with 1-methyl-1,3-imidazoline-2-thione (mimzSH) in a 1:2 molar ratio [27].

This is in contrast with the recently described iodido analog $[\text{Cu}(\mu_2\text{-I})_2\text{Cu}(\mu_2\text{-MeOC(=S)N(H)Ph})_2]_n$ CP2, for which a much shorter Cu···Cu separation of only 2.6563(7) Å was evidenced [17]. The C=S bond is slightly elongated with respect to that of non-ligated MeOC(=S)N(H)Ph (1.711(5) vs. 1.6708(11) Å) [28].
Figure 1. Crystal structure of the 1D ribbon of [Cu(μ₂-Br)₂Cu(μ₂-L)]₂, CP1 running along the a axis. Selected bond lengths (Å) and angles (deg) of CP1: Cu···Cu 2.8649(10), Cu–Cu 2.8339(10), Br–Cu 2.4620(7), Cu–S 2.2966(12), Cu–S² 2.4157(12), S–C1 1.711(5), O–C1 1.313(5), O–C2 1.453(5), N–C1 1.335(5), N–C3 1.421(6); Cu²–Cu–Cu 171.28(5), S–Cu–Br 117.68(4), S–Cu–Br¹ 107.64(4), S–Cu–S 106.11(4), Br–Cu–Br¹ 109.12(3), Br–Cu–Cu¹ 54.83(2), Br–Cu–Cu² 130.17(3), Br¹–Cu–Cu² 120.12(3), S–Cu–Cu¹ 131.40(4), S–Cu–Cu² 51.13(3), S–Cu–Cu¹ 131.30(4), N–C1–S 121.7(3), C8–C3–N 115.3(4), and C7–C8–C3 120.4(3). Symmetry transformation used to generate equivalent atoms: \( t \): \( x \), \( y \), \( z \); \( t' \): \( x \), \( 1-y \), \( 2-z \); \( t'' \): \( 1-x \), \( 1-y \), \( 2-z \).

Noteworthy is also the occurrence of the secondary N–H···Br interaction of 2.62(6) Å (dN···Br 3.440(4) Å, indicated by the red dashed lines in Figure 1. This interaction is noticeably shorter and in consequence stronger than the weak intramolecular N–H···I contacts of 2.748 Å and 2.803 Å encountered for CP2 [17]. A similar systematic shortening of the intramolecular N–H···X bonding occurring in [(Ph₃P)₂Cu(MeOC(=S)N(H)Ph)X] (X = I, Br, Cl) and giving rise to six-member cycles has also been evidenced recently by us (see Scheme 1) [17]. Note that in the latter case, this intramolecular hydrogen bonding is even stronger for the molecular bromido complex C1 compared to CP1 (2.51(2) vs. 2.62(6)). Furthermore, a loose intramolecular S···H contact of 2.672 Å occurs between the sulfur atom and the H atom of the NH group.

In the packing, the ribbons of CP1 are aligned in a co-parallel arrangement and are running along the a axis (Figure 2). There are also weak supramolecular interchain contacts between Br and the H atom of C7 of the aryl cycle (C7–H7···Br 2.919 Å).

To check the phase purity of this material, a grounded sample has been analyzed by powder X-ray diffraction (PXRD). The experimental PXRD pattern matches well with the simulated ones, confirming the homogeneity of the phases. A comparison of the PXRD patterns of CP1 is illustrated in Figure 3.
Figure 2. Perspective view of the packing, showing several ribbons of CP1 running along the a axis in a parallel arrangement.

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Figure 3. Comparison of the experimental PXRD pattern of CP1 with the simulated one (blue).

3. Experimental Section

*Synthesis of CP1*—We added 1 eq. of O-methyl N-phenylthiocarbamate L (334 mg, 2 mmol) to a solution of CuBr (286 mg, 2 mmol) in 12 mL of acetonitrile. A colorless precipitation was immediately noticed. The mixture was stirred 20 min at room temperature and then shortly heated till almost all of the precipitates had redissolved. After 1 d, pale yellowish crystals of CP1 were formed and then collected by filtration. Yield: 79%. Anal. Calc. for C$_8$H$_9$BrCuNOS (M.W = 310.67 g·mol$^{-1}$). C, 33.09; H, 4.01; N, 4.29; S 9.81%. Found: C, 32.95; H, 4.00; N, 4.15; S 9.75. IR-ATR: 1026 (C–O), 1215 (C=S), 1440 $\nu$(C–N), 3199 $\nu$(N–H···Br), 3276 $\nu$(N–H) cm$^{-1}$.

*Synthesis of C1*—We added two equivalents of PPh$_3$ (52 mg, 0.2 mmol) to a suspension of CP1 (31 mg, 0.1 mmol) in 4 mL of MeCN, prepared as described above. The mixture
was then heated for 20 min to 60 °C till all of the product was dissolved. Upon cooling, C1 crystallized. The characterization data are identical to those described previously [18].

**Synthesis of C2**—We added two equivalents of PTol (608 mg, 2 mmol) in several portions to an in situ prepared suspension of CP1 (1 mmol). The mixture was then heated for 20 min to 60 °C till all product was dissolved. Upon cooling, C2 crystallized in form of colorless plates and was isolated with 82% yield. Anal. Calc. for C₈H₅CuBrNOP₃S (M.W. = 919.43 g·mol⁻¹): C, 65.32; H, 5.59; N, 1.52; S, 3.49%. Found C, 65.20; H, 5.53; N, 1.59; S, 3.42%. ¹H NMR: δ 2.33 (s, 18H, CH₃), 4.08 (s, 3H, OCH₃), 7.04 (d, 12H, PC₆H₄, ³JHH = 7.9 Hz), 7.15–7.39 (m, 17H, Ph and PC₆H₄, ³JHH = 7.9, ³JPH = 9.7 Hz), 10.54 (s, br, 1H, NH), ¹³C[¹H] NMR: δ 21.4 (CH₃Ar), 58.4 (CH₂O), 121.9 (CH, Ph, Cneta), 125.3 (CH, Ph, Cpara), 128.9 (CH, Ph, Cortho), 129.2 (d, CH, m-PC₆H₄), ³JCP = 9.2 Hz), 130.4 (d, Cq, CipsoPC₆H₄, ³JCP = 27.7 Hz), 133.9 (d, CH, o-PC₆H₄, ²JCP = 14.9 Hz), 137.2 (s, Cq, Cipso), 139.4 (Cq, p-PC₆H₄), 187.3 (Cq, C=S). ³¹P[¹H]: δ = −6.34. IR-ATR: 1093 ν(C=O), 1222 ν(C=S), 1444 ν(C=N), 3160, 3110 ν(N−H) cm⁻¹.

Crystal data for C₈H₅BrCuNOP₃S were as follows: M = 310.67 g·mol⁻¹, pale yellow crystals, crystal size 0.362 × 0.102 × 0.047 mm³, Triclinic, space group PT, a = 5.6823(2) Å, b = 7.6782(4) Å, c = 11.4019(5) Å, α = 97.689(2)°, β = 91.143(2)°, γ = 91.143(2)°, V = 492.58(4) Å³, Z = 2. Dcalc = 2.095 g/cm³, T = 100 K, R₁ = 0.0475, Rw = 0.0976 for 5163 reflections with I ≥ 2σ(I) and 2995 independent reflections. Largest diff. peak/hole e/Å⁻³ 1.04/−1.34. Data were collected on Bruker D8 Venture four-circle diffractometer equipped with a PHOTON II CPAD detector by Bruker AXS GmbH, using graphite-monochromated MoKα radiation λ = 0.71073 Å and were deposited at the Cambridge Crystallographic Data Centre as CCDC 2252606 (Supplementary Materials). The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/getstructures, accessed on 3 February 2023. The structure was solved by direct methods and refined by full-matrix least-squares calculation against F² (SHELXL, 2015) [29–31].

## 4. Conclusions

We have crystallographically evidenced that CuBr reacts like CuI with a stoichiometric amount of O-methyl-N-phenylthiocarbamate to yield a halide-bridged mono-dimensional coordination polymer. We are currently extending this facile preparation of polymeric materials to other O-alkyl N-arylsulfuricarboxamates, such as MeOC(=S)N(H)Cy, and are investigating the splitting of the polymer chain by other P and As donor ligands.

### Supplementary Materials

The following supporting information can be downloaded online: CIF file, Check-CIF report, and IR and NMR spectra.

### Author Contributions

W.A. and M.K. prepared the compounds; C.S., R.S. and L.V. collected the X-ray data and solved the structure; I.J., L.V. and M.K. designed the study and analyzed the data and M.K. wrote the paper. A.B.A., I.J. and M.K. contributed with the conceptualization. All authors have read and agreed to the published version of the manuscript.

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### Data Availability Statement

The X-ray data were deposited at the CCDC as stated in the paper.

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### Conflicts of Interest

The authors declare no conflict of interest.

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