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INORGANIC CHEMISTRY COMMUNICATIONS

Inorganic Chemistry Communications 11 (2008) 11-14

www.elsevier.com/locate/inoche

Cyclopentanone thiosemicarbazone (Hcptsc) induces a new bonding pattern in $(Ph_3P)Cu(\mu-Br)(\mu_3-S,N-Hcptsc)CuBr(PPh_3)$ dimer

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> Received 22 August 2007; accepted 2 October 2007 Available online 13 October 2007

Abstract

Reaction of cyclopentanone thiosemicarbazone (Hcptsc) with copper(I) bromide and Ph_3P in 1:1:1 molar ratio in acetonitrile has formed an asymmetric dimer, $[(Ph_3P)Cu(\mu-Br)(\mu_3-S,N-Hcptsc)CuBr(PPh_3)]$ (1), with a new { $Cu(\mu-Br)(\mu_3-S,N)Cu$ } bonding core in metal-thiosemicarbazone chemistry.

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Keywords: Cyclopentanone thiosemicarbazone; Copper; Triphenyl phosphine; Asymmetric dimer; Bridging mode

The chemistry of thiosemicarbazones with copper(I) is of current interest in view of their variable bonding modes, structures as well as their biological [1–7] and analytical applications [8]. In the literature, both halogen (Mode A) and sulfur bridging (Mode B) have been observed in the complexes of copper(I) halides (CuX) with thiosemicarbazones based on aldehydes (Structure I, $R^1 = Ph$, pyrrole, etc.; $R^2 = H$, Chart 1) [3–5]. The exhibition of these bridging modes revealed that there is small energy difference between these bridging modes (A, B), and the type of the halogen as well as the substituents at C² can determine the type of a mode in the complex.

Mode C has been observed only in $[Cu_2(\mu-I)_2(\mu-S-Hap-tsc)(PPh_3)_2]$ in which two iodine and one S atoms are bridging two copper atoms [9].

In this communication, the behaviour of a thiosemicarbazone in which C^2 carbon is a part of the ring (Structure II, Chart 1) is reported. In a typical reaction, cyclopentanone thiosemicarbazone (Hcptsc) with copper(I) bromide in the presence of PPh₃ in CH₃CN has yielded a compound of stoichiometry, Cu₂Br₂(PPh₃)₂(Hcptsc). X-ray crystallography has shown that it exists as a dimer, $[(Ph_3P)Cu(\mu-Br)-(\mu_3-S,N-Hcptsc)CuBr(PPh_3)](1)$, with a new $\{Cu(\mu-Br)(\mu_3-S,N)Cu\}$ coordination core (Mode D).

Reaction of CuBr (0.025 g, 0.174 mmol) with cyclopentanone thiosemicarbazone (0.027 g, 0.174 mmol) in the presence of Ph₃P (0.046 g, 0.174 mmol) in 20 mL acetonitrile in 1:1:1 molar ratio has formed a compound of stoichiometry Cu₂Br₂(PPh₃)₂(Hcptsc) (Scheme 1). Its IR spectrum showed the presence of v(N–H) bands at 3468, 3268 cm⁻¹ (due to $-N^{1}H_{2}$) and 3153 cm⁻¹ (due to $-N^{2}H_{-}$). Further, the most characteristic thioamide band due to v(C=S) appeared at 847 cm⁻¹ in the complex, which is at low enegy region vis-à-vis the free ligand (866 cm⁻¹). Thus IR shows that Hcptsc is coordinating to the metal center via S donor atom as a neutral ligand. A band due to v(P–C_{Ph}) at 1097 cm⁻¹ indicates the presence of Ph₃P.

The crystal structure of $Cu_2Br_2(PPh_3)_2(Hcptsc)$ has shown that this compound exists as a dimer $[(Ph_3P)Cu-(\mu-Br)(\mu_3-S,N-Hcptsc)CuBr(PPh_3)]$ (1), in which two copper atoms are differently coordinated. One copper atom is bonded to one terminal Br, one bridging Br, one P and one bridging S atoms, while the second copper atom is bonded to one bridging Br, one P, one N³ and one bridging S atoms. The ligand Hcptsc adopts N³, S-chelation-cum-S

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^{1387-7003/\$ -} see front matter @ 2007 Elsevier B.V. All rights reserved. doi:10.1016/j.inoche.2007.10.001



Scheme 1.

bridging in complex 1. The unequal Cu-S {2.344(8), 2.426(9) Å} and equal Cu–Br $\{2.488(5) \text{ Å each}\}$ distances reveal that Cu₂SBr core is slightly distorted square planar. As expected, the bridging Cu–S distance $\{2.426(9) \text{ Å}\}$ is longer than the terminal Cu-S distance $\{2.344(2) \text{ Å}\}$ in bromo bridged dimer, $[Cu_2(\mu-Br)_2(\eta^1-S-Hbtsc)_2(Ph_3P)_2]$ (2) (Structure I, R = Ph, Hbtsc) [3], while the bridging Cu–S distance $\{2.344(8) \text{ Å}\}$ is same as in 2. The bridging Cu–Br distance is comparable with that $\{2.485(8) \text{ Å}\}$ in 2 [3] and terminal Cu–Br distance $\{2,450(5) \text{ Å}\}$ is shorter than $\{2.548(8) \text{ Å}\}$ in $[CuBr(\eta^{1}-S-Hpytsc)(Ph_{3}P)_{2}]$ (3) (Structure I, R = pyridine, Hpytsc) [3]. Also Cu(2)–N(3) distance $\{2.076(3) \text{ Å}\}$ is normal, and similar to the literature trends [10]. The terminal Cu–P distances {2.217(8), 2.210(8) Å} are close to $\{2.234(13) \text{ Å}\}$ in 2 [3]. The $Cu \cdots Cu$ separation in 1 {2.771(5) Å} is less than twice the van der Waals radius of the Cu atom $\{2.80 \text{ Å}\}$ [11] (see Fig. 1).

The bond angles around Cu(I), Cu(2), S and Br atoms $\{109.23(2)^\circ, 111.98(3)^\circ, 71.03(2)^\circ \text{ and } 67.68(15)^\circ, \text{ respectively}\}$ in central Cu(μ -Br)(μ -S,N)Cu core, reveal severe



Fig. 1. Structure of complex 1 with atomic numbering scheme. Selected bond lengths (Å) and angles (°): Cu(1)-P(1) 2.217(8), Cu(2)-P(2) 2.210, Cu(1)-S 2.426(9), Cu(2)-S 2.344(8), Cu(1)-Br(1) 2.450(5), Cu(1)-Br(2) 2.488(5), Cu(1)-Cu(2) 2.771(5), Cu(2)-N(3) 2.076(3), Cu(2)-Br(2) 2.488(5), and P(1)-Cu(1)-Br(1) 113.62(2), S-Cu(1)-Br(1) 96.23(2), P(1)-Cu(1)-Br(2) 111.94(2), S-Cu(1)-Br(2) 109.23(2), N(3)-Cu(2)-P(2) 126.62(8), N(2)-Cu(2)-S 117.33(3), N(3)-Cu(2)-Br(2) 102.22(8), S-Cu(2)-Br(2) 111.98(3), Cu(1)-Br(2)-Cu(2) 67.68(15), Cu(2)-S-Cu(1) 71.03(2), C(1)-S-Cu(2) 95.61(11).

angular adjustment for accommodation of unusual bridging pattern. The bond angles around each copper atom $\{Cu(I), Cu(2)\}$ indicate distorted tetrahedral geometry. The angles at bridged sulfur and bridged bromine atoms {Cu-S-Cu}, 71.03(2)°; Cu-Br-Cu, 67.68(15)° are much shorter relative to the angles observed in bridged sulfur and bromine dimers {Cu-S-Cu}, 77.80(2)° and Cu-Br-Cu, $74.22(2)^{\circ}$ [3]. From the packing diagram of 1, it can be seen that the hydrogen atoms of amino group are engaged in both the inter- and intra-molecular hydrogen bonding. One hydrogen atom of the amino group forms an intermolecular hydrogen bond $\{H-N^1-H\cdots Br(1),$ 2.53 Å} with the terminal bromine atom, while the second hydrogen atom of the amino group forms intramolecular hydrogen bond with the bridging Br atom $\{H-N^{1} H \cdots Br(2)$, 2.86 Å. Thus in this complex, various dimeric units are linked together by intermolecular hydrogen bonding and form a polymeric chain (see Fig. 2).

In ¹H NMR spectrum of **1**, the most characteristic N²H signal at δ 10.15 ppm is shifted to low field compared with the free ligand (δ 8.42 ppm) [12]. The signals due to N¹H₂ protons at δ 7.18, 6.41 ppm in the free ligand are obscured by PPh₃ in **1**. Ring protons appear at δ 2.16 (C^{3.6}H₂) and 1.60 ppm (C^{4,5}H₂), which are upfield relative to the free ligand (δ 2.40, 1.78 ppm, respectively). In ¹³C NMR, ring carbons C³, C⁴, C⁵ and C⁶ appear at δ 38.1, 25.4, 29.4 and 31.2 ppm, respectively, which are downfield compared with the free ligand { δ 33.2–27.7 ppm} [12]. The signals due



Fig. 2. Packing diagram of complex 1.

to the carbon atoms of the PPh₃ are clearly resolved and appear at δ 133.9 (*o*-C), 132.2 (*i*-C), 129.8 (*p*-C) and 128.5 ppm (*m*-C). Other signals due to C¹ and C² carbons could not be detected. The ³¹P NMR spectrum shows a single broad signal at δ –114.34 ppm with the upfield coordination shift { $\Delta\delta$ } of –1.19 ppm in **1**.

It is concluded from above that in the literature, complexes of cyclopentanone thiosemicarbazone (Hcptsc) with C^2 carbon being part of the ring have exhibited η^1 -S bonding in [CuI(Hcptsc)(Ph₃P)₂] [13], N³, S-chelation mode in [Hg(cptsc)Ph] [12] and [Tl(cptsc)Ph₂] [14]. Surprisingly, in complex 1, it has shown a new coordination core, Cu(μ -Br)(μ -S-Hcptsc)Cu, (mode D), not reported to date in metal-thiosemicarbazone chemistry. Also, complex 1 represents the first dimer formed by a ligand such as Hcptsc, in which C² is part of the ring. Another similar ligand, namely, isatin-3-thiosemicarbazone has formed only tetrahedral [15] and octahedral [16] mononuclear complexes.

Compound 1: M.p. 220–224 °C (melt), yield, 0.042 g, 50%. C, H, N, analysis for Cu₂Br₂H₄₂C₄₀N₃P₂S: C, 52.08; H, 4.13; N, 4.34. Found: C, 52.24; H, 4.10; N, 4.29%. Main IR peaks (KBr, cm⁻¹): v(N–H), 3468s, 3268s (–NH₂), 3153m (–NH); δ (NH₂) + v(C=N) + v(C–C), 1604s, 1546s; v(C=S) + v(C– N), 1068s, 1027s, 847m (thioamide moiety); v(P–C_{Ph}), 1097s. ¹H NMR data (δ , ppm; CDCl₃), 10.15 (s, N²H), 7.21–7.51(m, Ph), 2.16 (s, C^{3,6}H₂), 1.60 (s, C^{4,5}H₂). ¹³C NMR data (δ , ppm; CDCl₃), 25.4 (C⁴), 29.5 (C⁵), 31.2 (C⁶), 38.1 (C³), 128.5 (*m*-C, $J_{P-C} = 11.4$ Hz), 129.8 (*p*-C), 132.4 (*i*-C, $J_{P-C} = 41.6$ Hz), 133.9 (*o*-C, $J_{P-C} = 36.1$ Hz). ³¹P NMR data (δ , ppm; CDCl₃), -114.34 ppm, $\Delta\delta$ ($\delta_{complex} - \delta_{ligand}$) = -1.19 ppm.

Crystallographic data for **1**: $C_{42}H_{40}Br_2Cu_2N_3P_2S$, M = 967.67, triclinic, a = 8.6797(8) Å, b = 9.0973(9) Å, c = 14.2451(14) Å, $\alpha = 76.175(2)^{\circ}$, $\beta = 72.646(2)^{\circ}$, $\gamma = 64.567(2)^{\circ}$, V = 961.52(16) Å³, T = 293(2) K, space group $P\bar{1}$, $\rho_{calcd} = 1.671$ mg m⁻³, Z = 1, μ (Mo K α) = 3.357 mm⁻¹, 7553 reflections measured on a Bruker SMART CCD-1000 diffractometer, unique 6176 ($R_{int} = 0.0254$). The final R_1 0.0331 was for 5872 reflections [$I > 2.0\sigma(I)$] and wR_2 was 0.0869.

Acknowledgement

Financial support from CSIR {Scheme no. 01(1993)/05/ EMR II}, New Delhi is gratefully acknowledged.

Appendix A. Supplementary material

CCDC 657238 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2007.10.001.

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