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Note

# Silver(I) complexes with heterocyclic thiones and tertiary phosphines as ligands. Part 4. Dinuclear complexes of silver(I) bromide: the crystal structure of bis[bromo-(pyrimidine-2-thione)(triphenylphosphine)silver(I)]

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## Abstract

Mixed-ligand complexes of the formula  $[Ag(PPh_3)(L)Br]_2$  were obtained by treatment of various heterocyclic thiones L  $\{L = pyridine-2-thione (py2SH), pyrimidine-2-thione (pymtH), benz-1,3-imidazoline-2-thione (bztztH), 1-methyl-1,3-imidazoline-2-thione (meimtH) and 5-methoxy-benz-1,3-imidazoline-2-thione (5MeObzimtH_2)} with equivalent quantities of silver(I) bromide and triphenylphosphine in dry acetone. The compounds were characterized by their IR, far-IR, UV-Vis and <sup>1</sup>H NMR spectroscopic data. The crystal structure of <math>[Ag(PPh_3)(pymtH)Br]_2$  was determined by single-crystal X-ray diffraction methods. The complex exhibits a planar  $Ag_2Br_2$  moiety in which each of the doubly bromine-bridged Ag(I) centres is further bonded to one phosphine P and one thione S atom. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Crystal structures; Heterocyclic thione complexes; Photolysis; Silver(I) bromide complexes; Triphenylphosphine complexes

#### 1. Introduction

A considerable amount of work has been performed on the synthesis and characterization of metal complexes containing heterocyclic thiones as ligands in the past two decades [1]. The chemical interest of these thiones is due to the fact that they are potentially ambidentate or multi-functional donors with either the exocyclic S or heterocyclic N (or S or O) atom available for coordination, whereas their biological interest arises from their structural analogy to thiolated nucleosides. In this context, our research has been focused for some time on coordination compounds of copper(I) with a large range of heterocyclic thiones containing triarylphosphines as bulky  $\pi$ -acceptor co-ligands, whereby particular emphasis has been placed on the determination of the factors causing variations of copper(I) geometry. In doing so, several synthetic routes have been applied that have led to an exciting variety of structures, ranging from mononuclear three- or four-coordinate species with trigonal planar and tetrahedral copper(I) respectively, to dimers with a pseudo-four-coordinated geometry [2].

In view of such extraordinary flexibility of the stereochemistry of copper(I) with soft ligands, we decided to extend our investigations to the related complexes of the other coinage metals, starting with the examination of any possible analogies when replacing copper(I) by silver(I). In our first attempt, monomeric complexes of the type  $[Ag(PPh_3)_2(L)Cl]$  were observed as a result of the reaction between the cubane-like  $[Ag(PPh_3)Cl]_4$  and several heterocyclic thiones [3]. This result contrasted

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with the corresponding reactions with copper(I), where binuclear complexes of the general formula [Cu(PPh<sub>3</sub>)(L)X]<sub>2</sub> were realized. More recently, two different types of monomeric complex,  $[Ag(PPh_3)_2(L)_2]$ - $NO_3$  and  $[Ag(PPh_3)_2(L)]$ , have been obtained on the reaction of AgNO<sub>3</sub> with several heterocyclic thiones and triphenylphosphine as ligands [4]. Since these unexpected results showed the thione-containing coordination compounds of the heavier coinage metals to be just as structurally diverse as their copper analogues, with the promise of further surprising results, we decided to continue our investigations in this very interesting field of research. Here we report the preparation and characterization of several silver(I) complexes obtained by interaction of heterocyclic thiones with silver(I) bromide in the presence of triphenylphosphine as a soft, bulky co-ligand. On the occasion of the fact that both terminal and bridging bonding modes were observed for bromo ligands in [Cu(PPh<sub>3</sub>)<sub>2</sub>(pymtH)Br] [5] or in [Cu(tmtp)(pymtH)Br]<sub>2</sub> [6] and [Cu(PPh<sub>3</sub>)(pymtH)Br]<sub>2</sub> respectively, the molecular structure [7] of [Ag(PPh<sub>3</sub>)(pymtH)Br]<sub>2</sub> has been determined by singlecrystal X-ray diffraction methods in order to discuss how, in this case, the bromine atom acts.

## 2. Experimental

## 2.1. Materials and instruments

Silver bromide (Aldrich) and triphenylphosphine (Fluka) were used as obtained, whereas the thiones (Merck or Aldrich) were recrystallized from hot ethanol prior to their use. All solvents used were of reagent grade. IR, UV, Vis and NMR spectra, conductivities, melting points and elemental analyses of carbon, nitrogen and hydrogen were performed as described previously [8]. The far-IR spectra were obtained from polyethylene discs of approximate composition 1:15

sample to polyethylene on a Perkin–Elmer Spectrum GX FT-IR system. The photolyses of non-gaseous solutions of the complexes and quantum yields measurements were carried out in 1 cm quartz cells using a high-pressure HBO 200W/4 Osram lamp; a 2 cm water filter and an 'Applied Photophysics' monochromator were applied. All the photochemical work was carried out in the dark.

#### 2.2. Preparation of the complexes

The complexes of the formula  $[Ag(PPh_3)(L)Br]_2$  were prepared according to the following general procedure. A solution of 0.5 mmol triphenylphosphine and 0.5 mmol of the appropriate thione in 50 ml of acetone was added to a suspension of 0.5 mmol of AgBr in 15 ml acetone and the mixture was moderately heated for 12 h. The resulting clear solution was allowed to cool and slow evaporation of the solvent at room temperature gave the microcrystalline solid, which was filtered off and dried in vacuo. All complexes prepared and their elemental analyses are given in Table 1.

#### 2.3. Collection and reduction of X-ray data

The unit cell and intensity data were collected on a Delft Instruments FAST diffractometer using the routines ENDEX, REFINE and MADONL in the MADNES software [9] and processed using ABSMAD [10]; detailed procedures are described in the literature [11]. Absence of crystal decay in the X-ray beam was confirmed by checking equivalent reflections at the beginning and end of data collection, which lasted about 8 h. The structure was solved with SIR92 [12] and refined with SHELX93 [13]. Details are given in Table 2. The silver, bromine, sulfur, phosphorus, nitrogen and carbon atoms were refined with anisotropic temperature factors. The hydrogen atoms were allowed to ride on their attached

Table 1										
Melting po	ints, ar	nalytical	data <sup>a</sup> a	and	electronic	spectral	data <sup>b</sup>	of the	complex	es

Complex		M.p. (°C)	Elemental analysis (%)			UV–Vis $\lambda_{\max}$ (log $\varepsilon$ )	
			C	Н	Ν	_	
1.	[Ag(PPh <sub>3</sub> )(py2SH)Br] <sub>2</sub>	132	50.02 (49.22)	3.87 (3.59)	2.58 (2.50)	327.5(3.90)-285.(4.52)-258(4.30)	
2.	[Ag(PPh <sub>3</sub> )(pymtH)Br] <sub>2</sub>	124	47.16 (46.92)	3.60 (3.58)	5.08 (4.97)	273(3.93)-266(3.97)-242.6(3.85)	
3.	$[Ag(PPh_3)(bzimtH_2)Br]_2$	141	50.04 (50.02)	3.54 (3.53)	4.53 (4.66)	309.0(3.93)-249.0(3.86)	
4.	[Ag(PPh <sub>3</sub> )(bztztH)Br] <sub>2</sub>	218	49.07 (48.64)	3.30 (3.26)	2.52 (2.27)	329.5(4.85)-244.5(4.48)	
5.	[Ag(PPh <sub>3</sub> )(meimtH)Br] <sub>2</sub>	133	47.06 (46.83)	3.76 (3.75)	4.81 (4.96)	285.5(3.99)-263.5(4.27)	
6.	$[Ag(PPh_3)(5MeObzimtH_2)Br]_2$	221	49.08 (49.55)	3.58 (3.68)	4.43 (4.44)	322(3.92)-251.5(3.87)	

<sup>a</sup> Calculated percentages follow the obtained values in parentheses.

<sup>b</sup> Maxima observed in  $\text{CHCl}_3$  (log  $\varepsilon$  values in parentheses).

Table 2 Crystal data and structure refinement

Empirical formula	C. H. Ag Br. N. P. S.
Formula weight	1124 4
Temperature (K)	293(2)
Wavelength (Å)	0 710 73
Crystal system	Monoclinic
Space group	$C^{2/c}$
Unit cell dimensions	02/0
a (Å)	27 284(3)
$b(\mathbf{A})$	9 219(2)
c (Å)	18.465(2)
$\beta$ (°)	108.44(2)
Volume (Å <sup>3</sup> )	4406.1(12)
Z	4
Density (calculated)	1.695
$(Mg m^{-3})$	
Absorption coefficient	2.906
$(mm^{-1})$	
F(000)	2224
Crystal size (mm)	$0.35 \times 0.21 \times 0.21$
$\theta$ range for data	2.33 to 25.04
collection (°)	
Index ranges	$-30 \le h \le 23$
	$-10 \le k \le 9$
	$-18 \le l \le 21$
Reflections collected	9013
Independent reflections	3359 ( $R_{\rm int} = 0.0537$ )
Observed reflections	2854
$[I > 2\sigma(I)]$	
Refinement method	Full-matrix least squares on $F^2$
Number of parameters	254
Goodness-of-fit on $F^2$ (S)	0.95
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.027, \ wR_2 = 0.063$
<i>R</i> indices (all data)	$R_1 = 0.033, wR_2 = 0.069$
Final weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0352P)^2]$ where $P = (F_o^2 + 2F_o^2)/3$
Residual diffraction max. $(e^{-} Å^{-3})$	0.41
Residual diffraction min. $(e^{-} Å^{-3})$	-0.40

atoms with common isotropic temperature factors for methyl and non-methyl hydrogen atoms. An absorption correction was made with DIFABS [14].

#### 3. Results and discussion

All the complexes are solids soluble in chloroform, methanol, ethanol, acetone and acetonitrile. Their elemental analyses (given in Table 1) are in accordance with the proposed structures. Their solutions are nonconducting in acetone and chloroform. Room-temperature magnetic measurements confirm the diamagnetic nature of the compounds.

# 3.1. Spectroscopy

The UV–Vis spectra of the complexes in chloroform solutions are dominated by two main broad bands in the regions 240–260 and 290–320 nm, which can be attributed to intraligand transitions of the phosphine and thione ligands respectively.

The main feature of the solid-state infrared spectra of the compounds, recorded in the range 4000–250 cm<sup>-1</sup>, apart from the existence of strong phosphine bands, is the production of the usual four 'thioamide bands' at wavenumbers around 1510, 1320, 100 and 750 cm<sup>-1</sup> [15], as well as of the characteristic NH stretching vibrations observed in the 3050–3160 cm<sup>-1</sup> [16] region, suggesting, in combination with the lack of v(SH) bands at approximately 2500–2600 cm<sup>-1</sup> [17], the exclusive S-coordination mode of the thione ligands.

New bands in the far-IR spectra can be attributed to metal-ligand vibrations, provided that they are sufficiently distinct from those generated by the thione or phosphine ligands in the same region. In fact, a single band lying in the 217-228 cm<sup>-1</sup> region in most of the complexes under investigation can be positively assigned to v(AgS) stretching modes. This is a strong indication for the terminal bonding mode of the thione ligands; consequently, the bromine atoms may act as bridging ligands between the two metals forming an asymmetric Ag<sub>2</sub>Br<sub>2</sub> core. Further useful information supporting the above conclusion could be obtained from the halogen-sensitive bands, for which, as has already been well demonstrated [18], a good correlation exists between the v(AgBr) wavenumbers and the Ag–Br bond lengths. Given that the v(AgBr) band for  $[AgBr(PPh_3)_2]$  with an Ag–Br bond length of 2.568(1) Å lies at  $170 \text{ cm}^{-1}$  [18], whereas the corresponding value for the 'long' Ag-Br bond of 2.742(1) Å in  $[Ag_2Br_2(PPh_3)_4]$ .2CHCl<sub>3</sub> is decreased by 50 cm<sup>-1</sup>, two v(AgBr) bands assigned to the two inequivalent Ag-Br bonds, shifted near the 120 cm<sup>-1</sup> region and separated by less than  $50 \text{ cm}^{-1}$ , are expected for the complexes under investigation. However, even this region of the far-IR spectra is occupied, in most of the cases, by strong thione absorptions, making a definite location of these halogen-sensitive bands impossible.

The prevalence of the thione tautomer in the complexes is further confirmed by the <sup>1</sup>H NMR spectra of the compounds, which display, apart from the signals expected for the phosphine and thione ligands, a single resonance at  $\delta \approx 11-13$  ppm attributed to the NH proton.

#### 3.2. Photolysis

Room-temperature irradiation of the complexes at  $\lambda_{\text{exit}} = 270-310 \text{ nm}$  in non-degassed chloroform solutions causes decomposition into two photoproducts as

can be estimated according to the method of Coleman et al. [19]. In accordance with our earlier observations in analogous copper(I) mixed-ligand complexes, the decomposition occurs within seconds and can be checked by comparison of the intensities of the bands in the UV-spectra, since no evolution of new bands or significant shifts could be observed during the experiment. The constitution of the solid products, which in all cases deposit quickly, verified by means of elemental analyses and by their IR spectra, is in agreement with  $[Ag(L)_2Br]_{w}$ .

Table 3						
Selected	bond	distances	(Å)	and	angles	(°)

Ag(1) - P(1)	2.4390(7)	P(1)–C(11)	1.825(3)
Ag(1)-S(1)	2.5548(9)	N(1)-C(2)	1.322(4)
Ag(1)–Br(1) # 1 <sup>a</sup>	2.7350(6)	N(1)-C(1)	1.347(4)
Ag(1)-Br(1)	2.8241(5)	N(2)-C(4)	1.332(4)
$Br(1)-Ag(1) # 1^{a}$	2.7349(6)	N(2)–C(1)	1.357(4)
S(1)–C(1)	1.689(3)	C(2)–C(3)	1.366(5)
P(1)-C(5)	1.824(3)	C(2)–C(3)	1.366(5)
P(1)-C(17)	1.826(3)	C(3)–C(4)	1.343(5)
$P(1) = A \sigma(1) = S(1)$	118 03(3)	$C(5) = P(1) = A \sigma(1)$	114 88(9)
$P(1) = A g(1) = Br(1) \# 1^{a}$	110.00(3) 119.30(2)	C(17) = P(1) = A g(1)	117.00(9)
$S(1) = A\sigma(1) = Br(1) \# 1^{a}$	102 95(3)	$C(11) = P(1) = A\sigma(1)$	110 76(8)
P(1) = Ag(1) = Br(1)	110 33(2)	C(2)=N(1)=C(1)	117.7(3)
S(1) - Ag(1) - Br(1)	108.37(3)	C(4)-N(2)-C(1)	122.2(3)
$Br(1) \neq 1-Ag(1)-Br(1)^{a}$	95.17(2)	N(1)-C(1)-N(2)	118.6(3)
$Ag(1) # 1-Br(1)-Ag(1)^{4}$	<sup>a</sup> 84.83(2)	N(1)-C(1)-S(1)	120.4(2)
C(1)-S(1)-Ag(1)	111.77(11)	N(2)-C(1)-S(2)	120.9(2)
C(5)-P(1)-C(17)	102.96(13)	N(1)-C(2)-C(3)	125.9(3)
C(5)-P(1)-C(11)	104.63(13)	C(4)-C(3)-C(2)	115.7(3)
C(17)-P(1)-C(11)	104.34(13)	N(2)-C(4)-C(3)	120.7(4)
	( )		

<sup>a</sup> Atomic coordinates transposed by 3/2-x, 1/2-y, 1-z.



Fig. 1. A view of the complex with atom labels. Displacement ellipsoids are shown at the 50% probability level. Dashed lines denote N-H…Br hydrogen bonds.

## 3.3. Description of the structure

Bond lengths and valence angles are given in Table 3. The atomic arrangement in the complex is shown in Fig. 1. The basic structural unit of  $[Ag(PPh_3)(pymtH)Br]_2$  is a dimer, where the two monomers are related by inversion. The double bridging Br atoms generate a strictly planar  $Ag_2Br_2$  core in which each of the Ag atoms displays a distorted tetrahedral environment. The other two positions of each tetrahedron are occupied by one S atom from pymtH and one P atom from PPh<sub>3</sub>. The nitrogen-bonded hydrogen atoms of the two trans-positioned pymtH units participate in two short intramolecular hydrogen bonds  $[N \cdots Br = 3.301(3) \text{ Å}, H \cdots Br = 2.453(3) \text{ Å} and N-H-Br = 168.7(3)^\circ].$ 

The two Ag–P distances, both 2.4390(7) Å, are somewhat shorter than those found in other tetracoordinate silver(I) phosphine complexes, e.g.  $[Ag(PPh_3)_2(py2SH)-Cl]$  (2.482(1) and 2.476(1) Å) [3] and  $[Ag(PPh_3)_2-(boztH)_2]NO_3$  (2.480(1) and 2.514(2) Å) [20].

The Br–Ag–Br and Ag–Br–Ag angles (95.17(2) and 84.32(2)°) are remarkably similar to those found in other double-bromo-bridged species containing silver(I) in different environments, e.g. in  $[Ag_2(PPh)_3)_4Br_2]$  [18] and  $[Ag_2Br_4]^{2-}$  [21] with approximately tetrahedral and trigonal planar silver atoms respectively. Consequently, this arrangement in the  $Ag_2Br_2$  core can be hardly considered as a consequence of any steric repulsions between the terminal ligands, but can more easily attributed to the close Ag···Ag and Br···Br contacts within the  $Ag_2Br_2$  core. In general, the asymmetry in the molecule under investigation is greater than in  $[Ag_2(PPh)_3)_4Br_2]$ ·2CHCl<sub>3</sub> [18].

#### 4. Supplementary material

Supplementary data are available free of charge on request from the The Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk), quoting the deposition number CCDC 114092.

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