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Silver(I) complexes with heterocyclic thiones and tertiary phosphines as ligands

Part 2. Mononuclear complexes of silver(I) nitrate. The crystal structures of $[Ag(PPh_3)_2(pytH)_2]NO_3$ and $[Ag(PPh_3)_2(pymtH)]NO_3$

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Abstract

The preparation and characterization of mononuclear silver(I) nitrate complexes with various heterocyclic thiones (pytH = pyridine-2-thione, pymtH = pyrimidine-2-thione, quin2tH = quinoline-2-thione, tzdtH = thiazolidine-2-thione, mbzimtH$_2$ = *N*-methyl-benzimidazoline-2-thione, pur6tH = purine-6-thione) and triphenylphosphine as ligands are described. The X-ray determination of the crystal structures of $[Ag(PPh_3)_2(pytH)_2]NO_3$ (I) and $[Ag(PPh_3)_2(pymtH)]NO_3$ (II) is also reported. Compound I crystallizes in the monoclinic system, space group $P2_1/c$, with $a = 12.588(3)$, $b = 18.234(5)$, $c = 18.527(5)$ Å, $\beta = 96.29(2)°$, $V = 4227$ Å^3 and $Z = 4$, while crystals of II are triclinic, space group $P\bar{1}$, with $a = 10.084(2)$, $b = 13.508(3)$, $c = 14.326(3)$ Å, $\alpha = 77.43(2)$, $\beta = 78.77(2)$, $\gamma = 79.14(2)°$, $V = 1846$ Å^3 and $Z = 2$. The coordination geometry about the silver atom is distorted tetrahedral in I, with one nitrate ion bridging two adjacent complex molecules via strong hydrogen bonds with the thione NH groups. The structure of II consists of almost trigonal-planar AgP_2S units and strongly distorted nitrate ions hydrogen bonded to the protonated nitrogen atoms of the heterocyclic thione ligands. The electronic factors imposing the above difference in coordinating behavior are investigated by means of semi-empirical molecular orbital considerations.

Keywords: Silver(I) complexes; Heterocyclic thione complexes; Triphenylphosphine complexes; Crystal structures; Semi-empirical molecular orbital considerations

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1. Introduction

In recent years a large number of reports concerned with the structural and kinetic features of silver(I)–phosphine complexes have been published [1]. Our interest in mixed ligand silver(I) complexes with heterocyclic thiones and triaryl-phosphines stems from our current research on coordination compounds of coinage metals with these ligands [2], which show an interesting and in some cases unpredictable structural variety both at the local chromophore and at the overall geometry level. We were especially interested in unravelling the factors causing variations on metal-site geometry, detailed investigation of which revealed that it depends primarily upon the steric demands of the ligands. Since the distortions away from the ideal tetrahedral geometry induced by the bulkiness of the thione ligands were found to be relatively small, attention has been drawn to the possible tuning of the geometries through the steric demands of the phosphine ligands. Indeed three-coordinate species were obtained, at least, with monovalent copper on substituting the medium-sized triphenyl-, tri-*p*- and tri-*m*-tolyl-phosphines with the more bulky tri-*o*-tolyl-phosphine. Recently we initiated a study on the result of replacing copper(I) by silver(I) in the course of which the reaction between the cubane-like $[Ag(PPh_3)Cl]_4$ and several heterocyclic thiones was observed to lead to mononuclear complexes of the type $[Ag(PPh_3)_2(L)Cl]$ [3]. This result contrasted with the corresponding reactions with monovalent copper where binuclear complexes of general formula $[Cu(PPh_3)(L)X]_2$ were realized. It was therefore interesting to continue the comparative investigation, and in the present paper we report on the reaction of silver(I) nitrate with triphenylphosphine and various heterocyclic thione ligands, as well as the structures of two specific compounds, $[Ag(PPh_3)_2(pytH)_2]NO_3$ and $[Ag(PPh_3)_2(pymtH)]NO_3$.

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2. Experimental

2.1. Materials and measurements

The solvents used were of reagent grade and were used without further purification. Triphenylphosphine (Merck) was used as obtained, while silver(I) nitrate (Merck) and the thiones (Aldrich) were recrystallized from hot ethanol.

IR, electronic and ^{1}H NMR spectra, molar conductivities, melting points, magnetic susceptibility measurements and elemental analyses for carbon, nitrogen and hydrogen were performed as described previously [4].

2.2. Preparative

The title complexes were prepared according to the following general procedure. A suspension of 0.5 mmol $AgNO_3$ in 30 ml chloroform was treated with a 30 ml solution of 1 mmol of PPh_3 in the same solvent and was heated until a clear colorless solution emerged. A 40 ml chloroform solution of 1 mmol of the appropriate thione was then added to the hot solution and the reaction mixture was stirred for 2 h at 40 °C. The clear solutions produced were filtered and allowed to evaporate slowly at room temperature. The microcrystalline substances deposited were identified by elemental analyses and by their IR and UV–Vis spectra.

2.3. Solution of the structures

Suitable crystals of the title complexes $[Ag(PPh_3)_2(pytH)_2]NO_3$ (**I**) and $[Ag(PPh_3)_2(pymtH)]NO_3$ (**II**) were obtained by slow evaporation of acetone solutions at room temperature. The complete crystal structures were determined from single-crystal X-ray diffraction data. Intensity data were collected at 170 K for **I** and at room temperature for **II** on a Siemens-P3 four circle diffractometer. All calculations were done using the SHELXTL PLUS program system. The structures were solved with Patterson [5] and refinements were carried out using the SHELXL93 program [6,7] on a DEC VAX cluster [5–7]. For **I** all hydrogen atoms were located from Fourier difference maps, while for **II** they were refined isotropically with $U = 1.2U(C)$ and only the bridging H(1A) atom was located from a Fourier difference map.

3. Results and discussion

3.1. General considerations

The reaction of $AgNO_3$ with PPh_3 and the appropriate thione ligand in 1:2:2 molar ratio in chloroform yielded mixed ligand complexes of the type $[Ag(PPh_3)_2(L)_2]NO_3$ (L = pytH, tzdtH, quin2tH, mbzimtH_2) and $[Ag(PPh_3)_2(L)]NO_3$ (L = pymtH, pur6tH), respectively.

Heterocyclic thione compounds exhibit thione–thiol tautomerism having both the thione sulfur and the heterocyclic nitrogen atoms potentially available for coordination [8]. In neutral solutions the thione form is the prevailing one and S-donation occurs almost exclusively although when more than one α-nitrogen heteroatom is present the ligands are potentially S,N-ambidentate. During investigations on copper(I) complexes with neutral thiones, this ambidentate character has not been observed and the exocyclic sulfur atom appears in all cases to be the only effective donor. The well-known tendency of the soft copper(I) to attach the soft base S is likely to be a plausible explanation for this behavior, far more so in the case of silver(I) with its $4d^{10}$ configuration.

All the prepared complexes are air stable microcrystalline solids insoluble in water and only slightly soluble in common organic solvents such as acetonitrile, chloroform, acetone and methanol. The elemental analyses confirm their stoicheiometry and their physical properties are in accordance with the proposed structures (Table 1). Room temperature magnetic measurements on several species confirm that the central metal ion is diamagnetic Ag(I). The molar conductance in acetonitrile solutions is in good agreement with those reported for 1:1 electrolytes [9], therefore confirming the composition of cationic $[Ag(PPh_3)_2(thione)_n]$ units and nitrate counteranions.

3.2. Spectroscopic studies

The IR spectra of the compounds, recorded in the range 4000–250 cm^{-1}, using KBr pellets, are mainly characterized by vibrational absorptions of coordinated thiones and reveal, apart from the strong phosphine bands, the usual four 'thioamide' bands [10] in the regions ~1510, 1320, 1000 and 750 cm^{-1}, suggesting, along with the absence of ν(SH) bands, that the ligands exist in the thione form. The NO_3 anion presents its N–O asymmetric stretching mode (ν_1) as a band with medium-to-strong intensity at ~1380 cm^{-1} and the out-of-plane deformation (ν_2) as a weak one at ~820 cm^{-1} indicating weak interactions with the central metal ions [11]. Nothing certain can be stated for the splitting of the N–O stretching band which could be used as evidence for the asymmetry of the NO_3 anion [11b] since it may coincide with the thioamide band in the region 1310–1320 cm^{-1}.

The UV–Vis spectra of the complexes in methanol and acetonitrile solutions are dominated by intraligand bands and consist of one intense sharp band in the region 215–225 nm and a rather broad one at 280–380 nm which are attributed to thione-originating intraligand bands while a rather strong sharp one observed in the region 250–260 nm corresponds to intraligand phosphine excitations. In several instances, e.g. in the quinoline-2-thione complex, vibronic coupling is present in the low energy band. Relevant UV–Vis data are reported in Table 1.

3.3. Crystal structure of I

Details regarding the crystal data collection and refinement for the complex are reported in Table 2.

Table 1
Some physical properties and analytical data of the complexes (calculated percentages follow obtained values in parentheses)

Compound	Yield (%)	%C	%H	%N	Solvent	Λ_m [a]	UV–Vis [b]		
$[Ag(PPh_3)_2(pytH)_2]NO_3$	65	59.80(60.25)	4.30(4.37)	4.15(4.58)	MeOH: 95	357(4.02)	273(4.50)		222(4.54)
					MeCN: 120	368(4.02)	285(4.52)		210(4.93)
$[Ag(PPh_3)_2(pymtH)]NO_3$	60	61.21(59.56)	4.17(4.24)	5.08(5.21)	MeOH: 101	348(3.43)	270 sh	258(4.36)	222(4.39)
					MeCN: 123	364(3.23)	282(4.26)	254(4.27)	211(4.57)
$[Ag(PPh_3)_2(pur6tH)]NO_3$	72	60.06(58.03)	4.10(4.27)	9.12(8.25)	MeOH: 95	328(4.19)		255(4.36)	220(4.56)
					MeCN: 115	331(4.14)		252(4.31)	213(4.60)
$[Ag(PPh_3)_2(tzdtH)_2]NO_3$	66	54.84(53.96)	4.22(4.52)	4.41(4.49)	MeOH: 103	269(4.47)		247(4.56)	215(4.78)
					MeCN: 132	273(4.55)		252(4.50)	210(4.71)
$[Ag(PPh_3)_2(quin2tH)_2]NO_3$	84	63.36(63.78)	4.49(4.36)	4.41(4.13)	MeOH: 94	382(3.99)	277(4.17)		216(4.38)
					MeCN: 117	379(3.83)	280(4.05)		214(4.85)
$[Ag(PPh_3)_2(mbzimtH_2)_2]NO_3$	70	61.73(61.05)	4.72(4.53)	7.05(6.84)	MeOH: 92	305(4.71)		247(4.66)	219(4.70)
					MeCN: 109	312(4.74)		253(4.53)	212(4.85)

[a] Data (mho cm^2 mol^{-1}) obtained in 10^{-3} M solutions in the solvents referred to in the table.

[b] Maxima observed in the solvents indicated (log ϵ values in parentheses).

Positional parameters for $[Ag(PPh_3)_2(pytH)_2]NO_3$ are given in Table 3. Bond lengths and angles around Ag(I) are listed in Table 4. A drawing of the complex with the labeling of the atoms is given in Fig. 1. The silver nucleus in the complex is tetracoordinated with a P_2S_2 ligand donor set. The deviation from perfect tetrahedral coordination is best illustrated by the P(1)–Ag–P(2) angle whose value is 118.0(1)° and can be accounted for by the steric hindrance induced by the two triphenylphosphines, consequently depressing the S(1)–Ag–S(2) angle to 99.5(1)°. The existence of strong hydrogen bonds between the nitrogen atoms of the pyridine ligands and the oxygen atoms of the nitrate anions also contributes to the angular distortions about the silver atom.

The Ag–P bond distances (Ag–P(1) = 2.463(1), Ag–P(2) = 2.503(1) Å) are comparable to those found in $[Ag(PPh_3)_2(pytH)Cl]$ [3] and agree well with the values 2.426(2)–2.504(7) Å found for a number of complexes containing silver atoms coordinated to two phosphorus atoms [12–15]. The Ag–S bond distances (Ag–S(1) = 2.632(1), Ag–S(2) = 2.602(1) Å), also somewhat longer than the sum (2.56 Å) of the corresponding tetrahedral radii, are within the expected ranges.

In the strictly planar nitrate ions one oxygen atom is connected to two different $[Ag(PPh_3)_2(pytH)_2]^+$ ions through strong hydrogen bonding contacts with two thione-nitrogen-bound hydrogen atoms (Table 4). These interactions provoke significant variations in the N–O bond lengths but not in the O–N–O angles of the nitrate groups. So, the N(3)–O(2) distance (1.288 Å) including the oxygen which participates in the hydrogen bridges is markedly longer than the other two N–O bond lengths (1.230 and 1.223 Å, respectively), whereas the bond angles are very close to the ideal value of 120°. Within the phosphine and thione ligands, distances and angles are quite normal.

3.4. *Crystal structure of II*

Parameters for the crystal data collection and refinement are given in Table 2.

Univalent coinage metals form complexes with coordination number 3 only when steric factors mitigate against the coordination of 4 ligands. Such steric requirements that favor tricoordinate copper(I) were realized, for example, by using the bulky tri-*o*-tolyl-phosphine, but triphenylphosphine, despite its cone angle of 145°, forms four-coordinate complexes of the type $[M(PPh_3)_2L_2]X$ or $[M(PPh_3)_2LX]$ even if bulky heterocyclic thiones L are acting as co-ligands [2a]. It can be assumed therefore that electronic factors additionally affect the ligation properties of the pyrimidine-2-thione ligand in the present complex.

Positional parameters for $[Ag(PPh_3)_2(pymtH)]NO_3$ are given in Table 5, and bond lengths and angles are listed in Table 6. The molecular structure is depicted in Fig. 2. In the nearly planar AgP_2S core the values of the angles are not far from the idealized value of 120°. Since the best rearrangement of the ligands around the silver seems to be strongly influenced by steric interactions, the largest angle (127.8(1)°) arises between the two bulky triphenylphosphine ligands.

The striking feature of this structure is the orientation of the thione molecule. Because of the participation of one nitrogen atom of the heterocycle in a weak Ag(I)···N interaction, there is a strong distortion of the Ag–S–C(4) angle which is very small (89.60°). This Ag(I)···N distance (2.748(3) Å) on the part of the non-protonated N atom of the heterocyclic

Table 2
Details of the X-ray diffraction studies for $[Ag(PPh_3)_2(pytH)_2]NO_3$ (I) and $[Ag(PPh_3)_2(pymtH)]NO_3$ (II)

Formula	$C_{46}H_{40}N_2P_2S_2Ag\cdot NO_3$	$C_{40}H_{34}N_2P_2SAg\cdot NO_3$
Formula weight	916.7	806.6
Temperature (K)	173 (2)	293 (2)
Wavelength (Å)	0.71073	0.71073
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	12.588(3)	10.084(2)
b (Å)	18.234(5)	13.508(3)
c (Å)	18.527(5)	14.326(3)
α (°)		77.43(2)
β (°)	96.29(2)	78.77(2)
γ (°)		79.14(2)
V (Å^3)	4227 (2)	1846.3 (7)
Z	4	2
Density (calc.) (g cm^{-3})	1.44	1.45
Absorption coefficient (mm^{-1})	0.695	0.731
$F(000)$	1880	824
Crystal dimensions (mm)	0.34×0.32×0.17	0.24×0.12×0.26
θ Range	2.17-27.06	2.08-27.06
Index ranges	$0\leq h\leq 16$ $0\leq k\leq 23$ $-23\leq l\leq 23$	$0\leq h\leq 12$ $-16\leq k\leq 17$ $-17\leq l\leq 18$
Reflections collected	9565	8570
Independent reflections	9278 ($R_{int}=0.0234$)	8109 ($R_{int}=0.0182$)
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	9278/0/674	8109/0/455
Goodness of fit on F^2	1.035	1.119
Final R indices ($I>2\sigma(I)$)	$R_1=0.0426$, $wR^2=0.0839$	$R_1=0.0526$, $wR^2=0.0915$
R indices (all data)	$R_1=0.0681$, $wR^2=0.0943$	$R_1=0.0742$, $wR^2=0.0981$
Max. and min. electron density in final difference map (e Å^{-3})	1.096 and −0.641	0.513 and −0.530

$$wR^2=\frac{\Sigma[w(F_o^2-F_c^2)^2]}{\Sigma[w(F_o^2)^2]^{1/2}}.$$

$$R_1=\frac{\Sigma||F_o|-|F_c||}{\Sigma|F_o|}.$$

Condition of fit: $\frac{\Sigma[w(F_o^2-F_c^2)^2]}{(n-p)^{1/2}}$; n = number of reflections, p = total number of parameters.

ring is comparable with the values observed in complexes containing an Ag(I) center coordinated to tris(2-(diphenylphosphino)ethyl)amine [16].

The structural features within the triphenylphosphine and the pyrimidine-2-thione molecules in **II** are consistent with those commonly found in other complexes containing such molecules as ligands.

3.5. Computational considerations

The striking difference in coordination between two seemingly similar thiones was probed by a computational study in order to unravel any underlying electronic factor. First the thione form of each ligand was considered, since this tautomer is present in most coordination compounds at least with monovalent Group 11 metals, and its optimized molecular structure was obtained under the constraint of total ring planarity. The optimizations were carried out using the AM1 Hamiltonian [17] and a very tight SCF convergence criterion.

The hybridization of the thioketo carbon atom in both thione ligands is sp^2, therefore, the exocyclic sulfur atom participates in the bonding scheme with two orbitals suitable for σ and π bond formation thus allowing for two lone pairs. Indeed a Natural Bonding Orbital analysis [18] reveals $s^{1.23}p^{2.75}$ and $s^{1.26}p^{2.71}$ (or equivalently $sp^{2.24}$ and $sp^{2.15}$, respectively) hybridization for the thioketo carbon atoms in pytH and pymtH, respectively. For the nitrogen atoms to which a hydrogen is assumed to be bonded the corresponding computed values reveal a tendency for pyramidalization, since they are midway between sp^2 and sp^3, i.e. $sp^{2.57}$ for pytH and $sp^{2.55}$ for pymtH, while the pyridine-like nitrogen atom in the latter is clearly sp^2 (formally $sp^{1.98}$). In this respect, secondary contributions to the bonding of the two ligands resulting in different local structures within the chromophore cannot be attributed to the α-imido nitrogen heteroatom.

A major difference observed in the electronic structure of the two thiones is the nature of their frontier orbitals (Scheme 1). The HOMO of pytH (−8.46 eV) is a delocalized π MO and the next highest occupied molecular orbital (−8.54 eV) bears a $0.96p_y$ S contribution. The situation is altogether different in pymtH, where the HOMO (−8.67 eV) is predominantly p_y S (coefficient 0.95, in accordance with experimental findings of the UV–Vis spectra where the

Table 3
Atomic coordinates and isotropic temperature factors of $C_{46}H_{40}N_2P_2S_2Ag\cdot NO_3$

	x	*y*	*z*	U_{eq}
Ag(1)	0.28055(2)	0.06090(1)	0.22400(1)	0.0219(1)
P(1)	0.22391(7)	0.03903(5)	0.34526(5)	0.0192(3)
P(2)	0.47636(6)	0.07352(5)	0.21392(5)	0.0188(3)
S(1)	0.21055(7)	−0.04455(5)	0.13409(5)	0.0262(3)
S(2)	0.19601(7)	0.17332(5)	0.15271(5)	0.0314(3)
N(1)	0.0284(3)	−0.0787(2)	0.0566(2)	0.028(1)
N(2)	0.0110(3)	0.2339(2)	0.1736(2)	0.039(2)
C(1)	0.0776(3)	−0.0357(2)	0.1097(2)	0.032(1)
C(2)	0.0100(3)	0.0117(3)	0.1457(2)	0.046(2)
C(3)	−0.0974(4)	0.0165(3)	0.1217(3)	0.058(2)
C(4)	−0.1420(3)	−0.0267(3)	0.0639(3)	0.046(2)
C(5)	−0.0787(3)	−0.0739(2)	0.0321(3)	0.042(2)
C(6)	0.1116(3)	0.2191(2)	0.2035(2)	0.026(1)
C(7)	0.1375(3)	0.2444(2)	0.2747(2)	0.029(1)
C(8)	0.0642(4)	0.2812(2)	0.3105(2)	0.038(2)
C(9)	−0.0376(4)	0.2954(3)	0.2763(3)	0.047(2)
C(10)	−0.0617(4)	0.2716(3)	0.2077(3)	0.051(2)
C(11)	0.2529(3)	0.1154(2)	0.4076(2)	0.021(1)
C(12)	0.1857(3)	0.1374(2)	0.4581(2)	0.032(2)
C(13)	0.2103(3)	0.1983(2)	0.5011(2)	0.037(2)
C(14)	0.3007(3)	0.2383(2)	0.4945(2)	0.036(2)
C(15)	0.3682(3)	0.2177(2)	0.4437(2)	0.037(2)
C(16)	0.3444(3)	0.1569(2)	0.4010(2)	0.028(1)
C(17)	0.2885(3)	−0.0401(2)	0.3910(2)	0.025(1)
C(18)	0.3315(4)	−0.0399(3)	0.4627(2)	0.049(2)
C(19)	0.3782(5)	−0.1032(3)	0.4936(3)	0.075(3)
C(20)	0.3806(4)	−0.1667(3)	0.4536(3)	0.060(2)
C(21)	0.3393(3)	−0.1671(2)	0.3825(3)	0.039(2)
C(22)	0.2951(3)	−0.1045(2)	0.3508(2)	0.030(2)
C(23)	0.0826(3)	0.0217(2)	0.3505(2)	0.022(1)
C(24)	0.0438(3)	−0.0401(2)	0.3814(2)	0.041(2)
C(25)	−0.0660(3)	−0.0490(3)	0.3826(3)	0.051(2)
C(26)	−0.1353(3)	0.0026(2)	0.3542(3)	0.050(2)
C(27)	−0.0986(3)	0.0646(3)	0.3260(3)	0.062(2)
C(28)	0.0104(3)	0.0735(2)	0.3231(3)	0.051(2)
C(29)	0.5558(3)	−0.0061(2)	0.2456(2)	0.022(1)
C(30)	0.5418(3)	−0.0346(2)	0.3139(2)	0.030(1)
C(31)	0.6008(3)	−0.0951(2)	0.3407(2)	0.036(2)
C(32)	0.6719(3)	−0.1282(2)	0.3009(3)	0.040(2)
C(33)	0.6857(4)	−0.1015(2)	0.2329(3)	0.043(2)
C(34)	0.6286(3)	−0.0405(2)	0.2058(2)	0.031(2)
C(35)	0.5460(3)	0.1490(2)	0.2637(2)	0.022(1)
C(36)	0.5043(3)	0.2192(2)	0.2535(2)	0.032(2)
C(37)	0.5572(4)	0.2782(2)	0.2872(2)	0.040(2)
C(38)	0.6500(3)	0.2691(2)	0.3319(2)	0.035(2)
C(39)	0.6904(4)	0.2000(3)	0.3436(3)	0.054(2)
C(40)	0.6387(3)	0.1404(2)	0.3097(3)	0.044(2)
C(41)	0.5104(3)	0.0904(2)	0.1221(2)	0.022(1)
C(42)	0.4326(3)	0.0786(2)	0.0634(2)	0.025(1)
C(43)	0.4559(3)	0.0904(2)	−0.0070(2)	0.034(2)
C(44)	0.5569(4)	0.1129(2)	−0.0198(2)	0.039(2)
C(45)	0.6339(4)	0.1249(2)	0.0370(2)	0.038(2)
C(46)	0.6115(3)	0.1147(2)	0.1078(2)	0.031(2)
N(3)	0.0854(3)	0.7537(2)	−0.0001(2)	0.038(1)
O(1)	0.0935(3)	0.7609(2)	0.0662(2)	0.055(1)
O(2)	0.0828(2)	0.8120(2)	−0.0395(2)	0.047(1)
O(3)	0.0768(3)	0.6933(2)	−0.0290(2)	0.073(2)
H(1A)	0.0672(3)	−0.0103(7)	0.0359(2)	0.039(1)
H(2A)	−0.0038(4)	0.2227(3)	· 0.1292(3)	0.084(2)

Table 4
Main bond distances (Å) and angles (°) of $[Ag(PPh_3)_2(pytH)_2]NO_3$

Ag–P(1)	2.463(1)	P(1)–Ag–P(2)	118.0(1)
Ag–P(2)	2.503(1)	P(1)–Ag–S(1)	110.4(1)
Ag–S(1)	2.632(1)	P(2)–Ag–S(1)	106.5(1)
Ag–S(2)	2.602(1)	P(1)–Ag–S(2)	116.6(1)
P(1)–C(11)	1.821(3)	P(2)–Ag–S(2)	103.9(1)
P(1)–C(17)	1.819(3)	S(1)–Ag–S(2)	99.5(1)
P(1)–C(23)	1.820(3)	Ag–P(1)–C(17)	113.2(1)
P(2)–C(29)	1.823(3)	C(11)–P(1)–C(17)	105.3(1)
P(2)–C(35)	1.826(3)	Ag–P(1)–C(23)	117.3(1)
P(2)–C(41)	1.826(4)	C(11)–P(1)–C(23)	103.2(2)
S(1)–C(1)	1.693(4)	C(17)–P(1)–C(23)	103.2(2)
S(2)–C(6)	1.711(4)	Ag–P(1)–C(11)	113.4(1)
N(1)–C(1)	1.354(5)	Ag–P(2)–C(35)	117.0(1)
N(1)–C(5)	1.377(5)	C(29)–P(2)–C(35)	102.8(1)
C(1)–C(2)	1.429(6)	Ag–P(2)–C(41)	114.7(1)
C(2)–C(3)	1.379(6)	C(29)–P(2)–C(41)	104.9(2)
C(3)–C(4)	1.395(7)	C(35)–P(2)–C(41)	101.2(2)
C(4)–C(5)	1.352(6)	Ag–P(2)–C(29)	114.4(1)
N(2)–C(6)	1.352(5)	Ag–S(1)–C(1)	110.6(1)
N(2)–C(10)	1.356(6)	Ag–S(2)–C(6)	110.5(1)
C(6)–C(7)	1.402(5)	C(1)–N(1)–C(5)	123.8(3)
C(7)–C(8)	1.370(6)	C(6)–N(2)–C(10)	124.0(3)
C(8)–C(9)	1.390(6)	S(1)–C(1)–N(1)	119.9(3)
C(9)–C(10)	1.345(7)	S(1)–C(1)–C(2)	123.7(3)
N(3)–O(1)	1.230(4)	N(1)–C(1)–C(2)	116.2(3)
N(3)–O(2)	1.288(5)	C(1)–C(2)–C(3)	120.0(4)
N(3)–O(1)	1.223(5)	C(2)–C(3)–C(4)	120.7(5)
		C(3)–C(4)–C(5)	119.1(4)
Hydrogen bridges		N(1)–C(5)–C(4)	120.0(4)
O(1)···N(1)^{i}	3.039(4)	S(2)–C(6)–C(7)	125.7(3)
O(1)···H(1A)^{i}	2.54(4)	N(2)–C(6)–C(7)	115.5(3)
H(1A)–N(1)^{i}	0.81(4)	S(2)–C(6)–N(2)	118.8(3)
O(1)···H(1A)^{i}–N(1)^{i}	121(3)	C(6)–C(7)–C(8)	121.1(3)
		C(7)–C(8)–C(9)	120.5(4)
O(2)···N(1)^{i}	2.807(4)	C(8)–C(9)–C(10)	118.1(4)
O(2)···H(1A)^{i}	2.08(4)	N(2)–C(10)–C(9)	120.7(4)
O(2)···H(1A)^{i}–N(1)^{i}	148(4)	O(2)–N(3)–O(3)	120.0(3)
		O(1)–N(3)–O(2)	118.2(3)
O(2)···N(2)^{ii}	2.761(5)	O(2)–N(3)–O(3)	121.8(4)
O(2)···H(2A)^{ii}	2.03(5)		
H(2A)–N(2)	0.77(5)		
O(2)···H(2A)^{ii}–N(2)^{ii}	159(5)		
O(3)···N(2)^{ii}	3.083(5)		
O(3)···H(2A)^{ii}	2.51(5)		
O(2)···H(2A)^{ii}–N(2)^{ii}			

^{i} $x, 1-y, z$; ^{ii} $-x, 1-y, -z$.

lowest energy excitation is predicted to be mainly of n → π^* character) and the next HOMO with an energy of −8.85 eV is a π MO. Furthermore, in pymtH, the following occupied orbital is essentially the pyridine-like nitrogen heteroatom lone pair (energy −11.39 eV, coefficients: −0.37s, 0.32p_x, 0.56p_y). The LUMO and the next LUMO are, in both cases, π^* MOs extensively delocalized.

Extended Hückel computations taking into consideration the orbital stabilization and core–core repulsion energy terms [19] were performed on the $Ag(PH_3)_2{}^+$ fragment assuming Ag–P and P–H distances equal to 2.47 and 1.30 Å, respectively. Variation of the P–Ag–P angle revealed a minimum in total energy at 180°, in accordance with experimental data

Table 5
Atomic coordinates and isotropic temperature factors of $C_{40}H_{34}N_2P_2SAg \cdot NO_3$

	x	y	z	U_{eq}
Ag(1)	0.12095(3)	0.27223(3)	0.23073(2)	0.0392(1)
S(1)	−0.10257(11)	0.21110(9)	0.32515(8)	0.0534(5)
P(1)	0.16102(10)	0.44445(7)	0.23615(7)	0.0395(4)
P(2)	0.25960(9)	0.15162(7)	0.13190(7)	0.0357(4)
N(1)	−0.1001(4)	0.1305(3)	0.5105(3)	0.055(2)
N(2)	0.1089(3)	0.1676(3)	0.4187(2)	0.051(2)
C(1)	−0.0436(6)	0.0962(4)	0.5904(3)	0.073(3)
C(2)	0.0904(7)	0.0963(4)	0.5870(4)	0.082(3)
C(3)	0.1645(5)	0.1330(4)	0.4982(4)	0.068(2)
C(4)	−0.0265(4)	0.1664(3)	0.4243(3)	0.043(2)
C(5)	0.1839(4)	0.5317(3)	0.1191(3)	0.043(2)
C(6)	0.0722(5)	0.5677(3)	0.0699(3)	0.061(2)
C(7)	0.0906(6)	0.6253(4)	−0.0224(4)	0.072(3)
C(8)	0.2157(6)	0.6472(4)	−0.0678(4)	0.074(3)
C(9)	0.3258(6)	0.6140(4)	−0.0203(3)	0.072(2)
C(10)	0.3110(5)	0.5556(3)	0.0728(3)	0.056(2)
C(11)	0.3147(4)	0.4409(3)	0.2868(3)	0.044(2)
C(12)	0.4027(4)	0.3486(4)	0.3002(3)	0.059(2)
C(13)	0.5195(5)	0.3410(5)	0.3394(4)	0.080(3)
C(14)	0.5477(6)	0.4242(6)	0.3670(4)	0.085(3)
C(15)	0.4613(6)	0.5166(5)	0.3555(3)	0.075(3)
C(16)	0.3456(5)	0.5252(3)	0.3146(3)	0.057(2)
C(17)	0.0225(4)	0.5120(3)	0.3114(3)	0.045(2)
C(18)	−0.0472(4)	0.4536(4)	0.3895(3)	0.057(2)
C(19)	−0.1530(5)	0.4977(5)	0.4512(4)	0.077(3)
C(20)	−0.1924(5)	0.5999(5)	0.4346(4)	0.082(3)
C(21)	−0.1271(7)	0.6599(4)	0.3577(5)	0.100(3)
C(22)	−0.0180(6)	0.6161(4)	0.2964(4)	0.083(3)
C(23)	0.2025(4)	0.0301(3)	0.1377(3)	0.040(2)
C(24)	0.2879(5)	−0.0637(3)	0.1497(3)	0.059(2)
C(25)	0.2409(6)	−0.1530(4)	0.1465(4)	0.079(3)
C(26)	0.1089(7)	−0.1492(4)	0.1317(4)	0.079(3)
C(27)	0.0231(6)	−0.0570(4)	0.1222(4)	0.077(3)
C(28)	0.0683(4)	0.0315(4)	0.1262(3)	0.058(2)
C(29)	0.2937(3)	0.2032(3)	0.0030(3)	0.037(2)
C(39)	0.3152(4)	0.1424(3)	−0.0672(3)	0.048(2)
C(31)	0.3469(5)	0.1852(4)	−0.1643(3)	0.061(2)
C(32)	0.3562(5)	0.2866(4)	−0.1920(3)	0.069(2)
C(33)	0.3349(5)	0.3486(4)	−0.1238(3)	0.068(2)
C(34)	0.3021(4)	0.3072(3)	−0.0266(3)	0.054(2)
C(35)	0.4273(4)	0.1166(3)	0.1687(3)	0.040(2)
C(36)	0.5472(4)	0.1301(3)	0.1041(3)	0.049(2)
C(37)	0.6712(4)	0.1113(3)	0.1366(4)	0.063(2)
C(38)	0.6787(5)	0.0793(4)	0.2334(4)	0.069(3)
C(39)	0.5609(6)	0.0649(4)	0.2980(4)	0.069(3)
C(40)	0.4340(5)	0.0825(3)	0.2669(3)	0.055(2)
N(3)	−0.4400(5)	0.1675(4)	0.5724(3)	0.076(2)
O(1)	−0.3634(4)	0.1072(3)	0.5232(3)	0.088(2)
O(2)	−0.5636(4)	0.1789(3)	0.5804(3)	0.110(2)
O(3)	−0.3840(5)	0.2145(5)	0.6124(4)	0.144(3)
H(1A)	−0.1866(4)	0.1305(3)	0.5129(3)	0.047(1)

Table 6
Main bond distances (Å) and angles (°) of $[Ag(PPh_3)_2(pymtH)]NO_3$

Ag–S(1)	2.573(1)	S(1)–Ag–P(1)	118.7(1)
Ag–P(1)	2.455(1)	S(1)–Ag–P(2)	113.2(1)
Ag–P(2)	2.447(1)	P(1)–Ag–P(2)	127.8(1)
P(1)–C(5)	1.830(4)	C(11)–P(1)–C(17)	105.5(2)
P(1)–C(11)	1.823(4)	Ag–P(1)–C(11)	112.2(1)
P(1)–C(17)	1.819(4)	C(5)–P(1)–C(11)	104.6(2)
P(2)–C(23)	1.820(4)	Ag–P(1)–C(17)	112.7(1)
P(2)–C(29)	1.816(4)	C(5)–P(1)–C(17)	105.3(2)
P(2)–C(35)	1.816(4)	C(29)–P(2)–C(35)	104.6(2)
S(1)–C(4)	1.687(4)	Ag–P(2)–C(23)	118.9(1)
N(1)–C(1)	1.332(7)	Ag–P(2)–C(29)	115.1(1)
N(1)–C(4)	1.353(5)	C(23)–P(2)–C(29)	103.8(2)
N(2)–C(3)	1.322(6)	Ag–P(2)–C(35)	108.1(1)
N(2)–C(4)	1.355(5)	C(23)–P(2)–C(35)	105.0(2)
C(1)–C(2)	1.342(9)	Ag–S(1)–C(4)	89.6(1)
C(2)–C(3)	1.385(7)	S(1)–C(4)–N(2)	120.3(3)
N(3)–O(1)	1.247(6)	N(1)–C(4)–N(2)	119.2(4)
N(3)–O(2)	1.213(7)	S(1)–C(4)–N(1)	120.6(3)
N(3)–O(3)	1.212(9)	C(1)–N(1)–C(4)	122.0(5)
		C(3)–N(2)–C(4)	118.5(3)
		N(1)–C(1)–C(2)	120.1(5)
Hydrogen bridges		C(1)–C(2)–C(3)	117.2(5)
O(1)···N(1)	2.699(6)	N(2)–C(3)–C(2)	123.0(5)
O(1)···H(1A)	1.86(4)		
H(1A)–N(1)	0.85(4)	O(1)–N(3)–O(2)	122.4(6)
O(1)···H(1A)–N(1)	171(4)	O(1)–N(3)–O(3)	116.3(5)
		O(2)–N(3)–O(3)	121.3(5)
O(3)···N(1)	3.079(6)		
O(3)···H(1A)	2.46(4)		
O(3)···H(1A)–N(1)	130(4)		

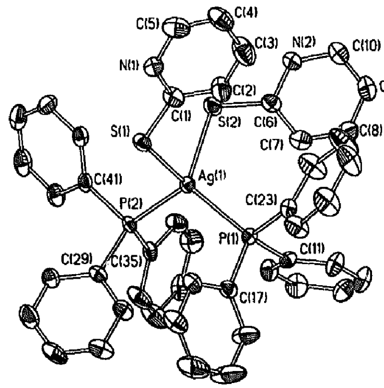


Fig. 1. ORTEP drawing with 50% thermal probability ellipsoids for the cationic unit of compound **I**.

[20]. At this conformation both the orbital stabilization and the one electron energy terms acquire their minimum values as does the ionicity of the Ag–P bonds considered in terms of both the net charge resident at Ag and the total overlap population between Ag and P orbitals. On bending the P–Ag–P angle, the occupied levels rise continuously in energy, the HOMO chages from $d_{x^2-y^2}$ to d_{xy}, the Ag–P overlap decreases subsequently leading to a more electrophilic metal center. In all cases the LUMO of the system is an in-plane π^* orbital with contribution from the P atoms, except in the case where the fragment is linear and the LUMO is a degenerate orbital pure metal p in character.

Finally the approach of the thiones to $Ag(PH_3)_2^+$ in a way facilitating either a planar three-coordinate or a tetrahedral four-coordinate cationic chromophore was studied. The AM1 optimized molecular structures were used for the ligands in

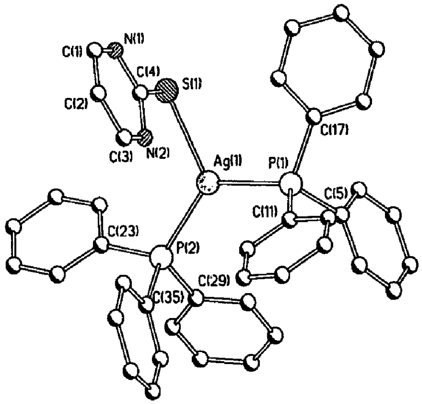
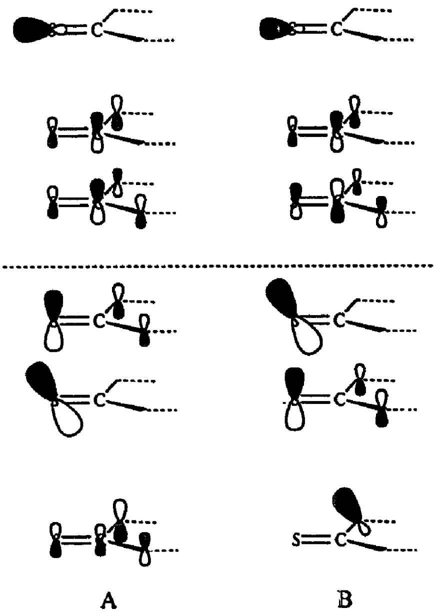
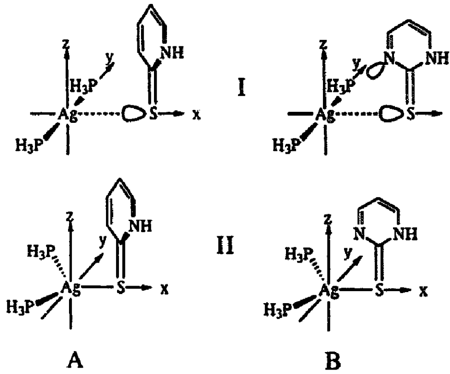


Fig. 2. ORTEP drawing with 50% thermal probability ellipsoids for the cationic unit of compound II.



Scheme 1. Frontier MOs of pyridine-2-thione (A) and pyrimidine-2-thione (B). Orbital partitioning in the coordinating region of the ligands drawn to scale, while orbital energies are not. The horizontal dashed line separates occupied from virtual levels.



Scheme 2. Initial (I) and final (II) stages of the approach of a single pyridine-2-thione (A) or pyrimidine-2-thione (B) ligand to Ag(PH$_3$)$_2$$^+$ aiming at the formation of a three-coordinate complex.

order to keep approximations to local geometries and interactions to a minimum. The possible interactions of ligand HOMOs with the LUMO of metal-containing fragment, leading to the trigonal planar complex, are depicted in Scheme 2. The approach of both ligands imposes substantial charge accumulation on silver even at a distance of 4 Å, therefore a rehybridization of the cationic fragment is essential along with an appropriate interaction to produce adequate π back-bonding. The computed metal–imino-nitrogen heteroatom interaction is antibonding for both ligands, while the metal–pyridine-like nitrogen interaction in the case of pymtH, is small but bonding in nature. Furthermore, the HOMO of the metal fragment, which eventually becomes a d$_{xy}$ orbital (vide supra) is capable of π back-donation in the case of pymtH but not for pytH, since the low-lying π^* MOs are in the former case directly interacting, while in the latter they are orthogonal to it, owing to the relative orientation of the heterocyclic rings of the thiones (coinciding with the xz and xy plane, respectively). The approach, therefore, of pyrimidine-2-thione is facilitated in a mode leading to a final trigonal planar complex.

Considering the approach of two thione ligands to the cationic Ag(PH$_3$)$_2$$^+$ unit, the general observation of charge accumulation on silver at an early stage of the approach is also true, therefore explaining to some extent the geometric rearrangement away from the desired linear coordination of the free cation.

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